action constants obtained in this paper are compared with those obtained earlier.

Reaction constants for the dissociation of series of acids have been found to increase with the alcohol concentration in mixed water–alcohol solvents.[5b] The reaction constants reported in Table III are in agreement with this finding. The apparent exception, reported earlier,[5b] involving the reaction constants for the second pK's of benzenephosphonic acids was based on an erroneous ρ-value in 50% ethanol; the corrected value is given in Table III.

Acknowledgment.—The authors wish to thank Mrs. Barbara Stanley for performing the analyses necessary for this research.

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[Contribution from the Cryogenic Laboratory and the Department of Chemistry, The Ohio State University]

Pressure–Volume–Temperature Relationships of Liquid Normal Deuterium[1]

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Compressibility factors of liquid normal deuterium have been determined at pressures up to 100 atm. and at temperatures between the triple and critical points of D_2. Isochores, derived from the experimental isotherms, are linear and their slopes are a linear function of the density throughout the range investigated. $(\partial P/\partial T)_V = -14.1 + (665/V)$, where the pressure is in atmospheres, the temperature is in degrees absolute, and volume is in cc. per mole.

Introduction

The compressibility of liquid deuterium at 19.71, 20.31 and 20.97°K. has been determined by Bartholomé[2] at pressures up to 100 atm. However, the P–V–T properties of liquid deuterium in the temperature region between the boiling point of hydrogen and the critical point of deuterium have not previously been investigated. As part of this Laboratory's program of study of the thermal and physical properties of the isotopes of hydrogen, the data of state for liquid normal deuterium have been determined in this temperature range at pressures up to 100 atm.

Apparatus

The apparatus used in this research was the same as that employed in the earlier investigation on the compressibility of liquid hydrogen.[3] It consists of a high pressure copper

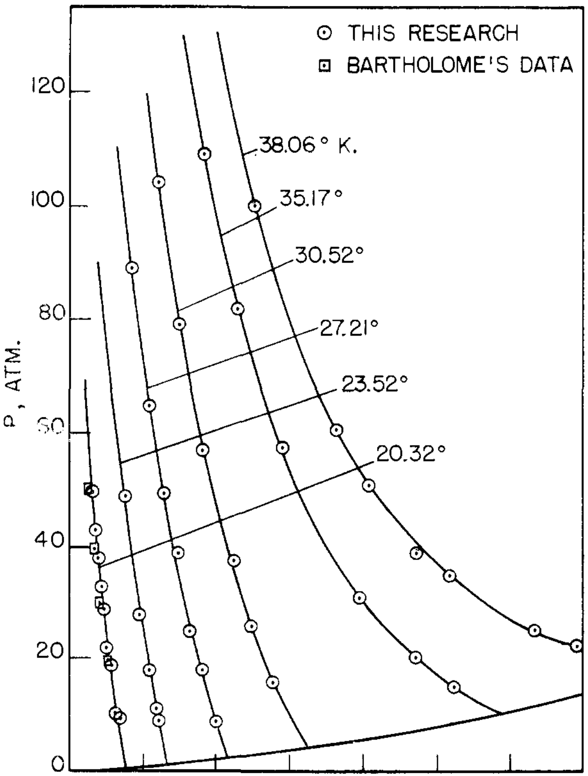

Fig. 1.—P vs. V for liquid D_2.

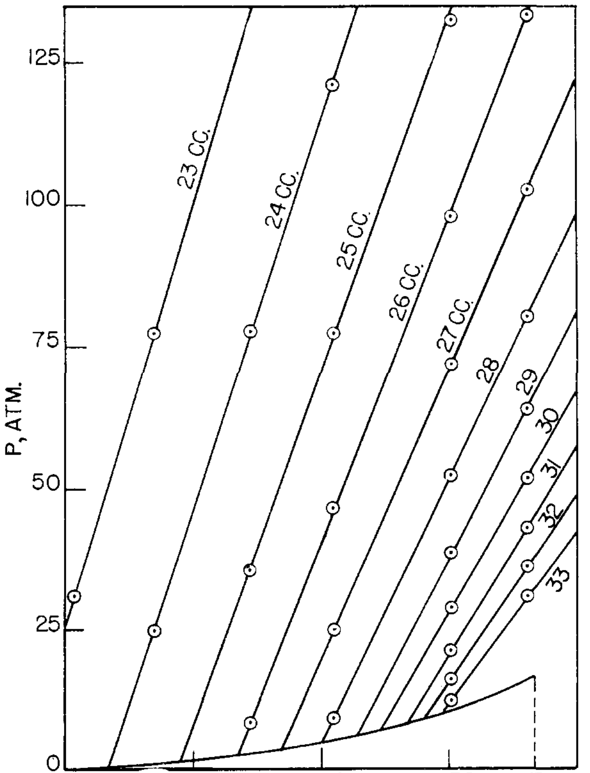

Fig. 2.—Isochores replotted from Fig. 1.

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[1] This work was done under the auspices of the Atomic Energy Commission.

[2] E. Bartholomé, *Z. physik. Chem.*, [B] **33**, 387 (1936).

[3] H. L. Johnston, W. E. Keller and A. S. Friedman, This Journal, **76**, 1482 (1954).

pipet of known volume surrounded by a bath of liquid or gaseous hydrogen under pressure. The temperature of the condensed deuterium is controlled by regulating the pressure on the hydrogen in the surrounding refrigerant container. The refrigerant container is surrounded by a copper vacuum vessel into which exchange gas can be introduced when required. The entire apparatus is suspended in a glass dewar (containing liquid nitrogen) which is enclosed in a brass cryostat having lucite windows.

TABLE I

DATA OF STATE FOR COMPRESSED LIQUID DEUTERIUM

P, atm.	*V*, cm.^{3}/mole	*PV/RT*
	$T = 20.33$°K.	
49.7762	22.688	0.67697
42.7241	22.795	.58380
33.2957	22.950	.45806
26.9584	23.059	.37263
19.3776	23.197	.26945
9.8326	23.381	.13781
	$T = 20.31$°K.	
36.8192	22.896	0.50584
29.3704	23.010	.40551
22.4228	23.143	.31138
16.6505	23.255	.23234
9.3726	23.396	.13158
	$T = 23.52$°K.	
49.0194	23.479	0.59634
39.0874	23.681	.47961
27.7939	23.914	.34439
18.3431	24.143	.22946
11.4385	24.333	.14422
8.6513	24.406	.10940
	$T = 27.21$°K.	
89.1436	23.719	0.94699
65.2593	24.224	.70802
49.4051	24.629	.54497
38.8324	24.950	.43393
26.5458	25.297	.30076
17.5746	25.636	.20179
9.2917	25.982	.10812
	$T = 30.52$°K.	
103.9240	24.367	1.01116
79.4150	24.972	0.79188
56.8661	25.672	.56022
36.8482	26.448	.38914
26.1743	26.952	.28169
16.1517	27.570	.17781
8.5591	28.121	.09611
	$T = 35.17$°K.	
108.7648	25.675	0.96764
81.9331	26.620	.75576
57.4881	27.810	.55398
30.8601	29.854	.31924
20.0473	31.362	.21786
14.7502	32.401	.16560
	$T = 38.06$°K.	
101.0915	27.045	0.87543
60.4571	29.247	.56617
38.8989	31.391	.39098
	$T = 38.06$°K.	
50.7367	30.141	0.48966
34.2905	32.332	.35500
25.2669	34.650	.28033
22.6234	35.698	.25859

The temperature is determined with a standard copper–constantan thermocouple. The pressure of the vapor over the liquid deuterium is measured with an oscillating-piston type dead-weight gage, and the number of moles is obtained by expanding the deuterium into a series of low pressure tanks thermostated at 25°.

Experimental

The experimental procedure is the same as that described for hydrogen.[3] The deuterium was prepared by the Stewart Oxygen Co. Mass spectrometer analyses, carried out in this Laboratory, yielded the composition 99.8 atomic % D, 0.2 atomic % H. The deuterium was further freed from traces of condensable impurities by passing it, at high pressures, through a copper coil submerged in liquid nitrogen. Conversion of the deuterium to the ortho modification was negligible since the duration of the runs was always less than about eight hours and the system was free from any known para–ortho conversion catalyst.

Results

Eight sets of runs were made at temperatures from 20.32 to 38.06°K. These included two sets of runs, each, at the lowest and highest temperatures to verify the consistency of the experimental procedure. The data are shown in Table I.

In Fig. 1, the pressure in atmospheres is plotted against the molar volume in cc./mole for the six isotherms. The curves terminate at the saturated vapor pressure curve.[4] Bartholomé's data at the boiling point of hydrogen are plotted as squares in the graph. A plot of pressure *vs.* temperature at constant volume is shown in Fig. 2. The isochores are linear in this region and hence can be expressed by equations of the form

$$P = A_{(\mathrm{v})} + B_{(\mathrm{v})}T \qquad (1)$$

It is also of interest to note that, just as in the case for hydrogen,[2] the slopes of the isochores $B_{(\mathrm{V})}$ vary linearly with the density. The slopes of the isochores of Fig. 2 can be expressed by the equation

$$B_{(\mathrm{v})} = \left(\frac{\partial P}{\partial T}\right)_V = -14.1 + \frac{665}{V} \qquad (2)$$

where the pressure is in atmospheres, the temperature is in degrees absolute, and the volume in cc./mole.

Table II compares the slopes of the isochores of Fig. 2 with those tabulated by equation 2 above.

TABLE II

V, cc./ mole	*B*(v), Fig. 2	*B*(v), Eq. 2.	*V*, cc./ mole	*B*(v), Fig. 2	*B*(v), Eq. 2.
23	14.7	14.8	29	8.7	8.8
24	13.8	13.6	30	7.8	8.0
25	12.5	12.5	31	7.4	7.4
26	11.5	11.4	32	6.6	6.7
27	10.3	10.5	33	6.2	6.0
28	9.5	9.6			

Acknowledgment.—We are grateful for the assistance given by Mr. S. Ruven Smith, of this Laboratory, who analyzed the deuterium on the mass spectrograph.

COLUMBUS, OHIO

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(4) A. S. Friedman, D. White and H. L. Johnston, THIS JOURNAL, **73**, 1310 (1951).