# Aqueous nonelectrolyte solutions. Part XV. The deuterium sulfide – deuterium oxide system and the deuterium sulfide p-hydrate

# Colin W. Clarke and David N. Glew

**Abstract:** The univariant  $(l_1 l_2 g)$  saturation vapor pressure of liquid deuterium oxide (phase  $l_1$ ) with liquid deuterium sulfide (phase  $l_2$ ) in equilibrium with a gas phase (g) has been measured in a stirred titanium reaction vessel at 19 temperatures from 33.003 to 18.905°C and at total pressures from 2.4500 to 1.7428 MPa. The univariant (hl<sub>1</sub>g) saturation vapor pressure of deuterium sulfide p-hydrate (phase h) in equilibrium with liquid deuterium oxide and a gas phase has been measured at 58 temperatures from 30.666 to 2.798°C and at pressures from 2.2959 to 0.11629 MPa. The maximum temperature for deuterium sulfide D-hydrate with a gas phase, the invariant quadruple point  $Q(hl_1l_2g)$ , has been determined from the cut of the  $(h_1g)$  and the  $(l_1l_2g)$  curves at temperature 30.770°C with standard error 0.0043°C and at pressure 2.3263 MPa with standard error 0.00018 MPa. The univariant (s<sub>1</sub>l<sub>1</sub>g) equilibrium of D-ice (phase s<sub>1</sub>) with liquid deuterium oxide and a gas phase containing deuterium sulfide has been measured at 11 temperatures from 3.8061 to 3.4540°C and at pressures between 0.00242 and 0.10542 MPa. The lowest temperature for stability of deuterium sulfide D-hydrate with liquid deuterium oxide, the invariant quadruple point  $Q(hs_1l_1g)$ , has been determined directly at 3.3917°C with standard error 0.0009°C and at pressure 0.12364 MPa with standard error 0.000011 MPa. This quadruple point  $Q(h_{1}l_{1}g)$  has also been defined by the cut of the  $(h_{1}g)$  and the  $(s_{1}l_{1}g)$  curves at temperature 3.3912°C with standard error 0.0006°C and at pressure 0.12363 MPa with standard error 0.000002 MPa. The deuterium sulfide - deuterium oxide gas mixture, represented by a Redlich-Kwong equation of state, has been used to evaluate the fugacities and compositions of the gaseous and liquid deuterium oxide phases for all equilibria. Raoult's law using fugacities has been used to evaluate the saturation mole fraction of deuterium oxide in liquid deuterium sulfide and the Henry's law constant for deuterium oxide solubility in liquid deuterium sulfide between 33.003 and 18.905°C. Data for the  $(l_1 l_2 g)$  and  $(s_1 l_1 g)$  equilibria have been accurately represented by simple twoparameter equations. Data for the (hl<sub>1</sub>g) equilibrium have required a model with seven significant parameters for proper representation betweem 30.666 and 2.798°C.

*Key words*: deuterium sulfide – deuterium oxide system, clathrate D-hydrate of deuterium sulfide, deuterium sulfide D-hydrate stability, freezing of deuterium oxide – deuterium sulfide, phase equilibria of deuterium sulfide – deuterium oxide.

Résumé : Opérant dans une cuve réactionnelle de titane sous agitation, à 19 températures allant de 33,003 à 18,905°C et à des pressions totales allant de 2,4500 à 1,7428 MPa, on a mesuré la tension de vapeur de saturation à une variable  $(1_11_2g)$  de l'oxyde de deutérium liquide (phase  $1_1$ ) avec du sulfure de deutérium liquide (phase  $1_2$ ) en équilibre avec une phase gazeuse (g). Opérant à 58 températures allant de 30,666 à 2,798°C et à des pressions allant de 2,2959 à 0,11629 MPa, on a aussi mesuré la tension de vapeur de saturation à une variable (h1<sub>1</sub>g) du D-hydrate de sulfure de deutérium (phase h) en équilibre avec de l'oxyde de deutérium liquide et une phase gazeuse. En se basant sur le point de jonction des courbes (h1<sub>1</sub>g) et (1<sub>1</sub>1<sub>2</sub>g) à une température de 30,770°C avec une erreur-type de 0,0043°C et à une pression de 2,3263 MPa avec une erreur-type de 0,00018 MPa, on a déterminé la température maximale du D-hydrate du sulfure de deutérium, le point quadruple invariant  $Q(h1_11_2g)$ . Opérant à 11 températures allant de 3,8061 à  $3,4540^{\circ}$ C et à des pressions allant de 0,00242 à 0,10542 MPa, on a mesure l'équilibre à une variable (s<sub>1</sub>1<sub>1</sub>g) de la glace-D (phase s<sub>1</sub>) avec de l'oxyde de deutérium liquide et une phase gazeuse contenant du sulfure de deutérium. Opérant à 3,3917°C avec une erreur-type de 0,0009°C et à une pression de 0,12364 MPa avec une erreur-type de 0,000011 MPa, on a déterminé directement la température minimale pour la stabilité du D-hydrate de sulfure de deutérium avec de l'oxyde deutérium liquide, le point quadruple invariant  $Q(hs_1 1_1g)$ . Ce point quadruple,  $Q(hs_1 1_1g)$ , a aussi été défini par le point de rencontre des courbes ( $h_{1,g}$ ) et ( $s_1 l_{1,g}$ ) à la température de 3,3912°C avec une erreurtype de 0,0006°C et à une pression de 0,12363 MPa avec une erreur type de 0,000002 MPa. On a utilisé le mélange gazeux sulfure de deutérium - oxyde de deutérium représenté par l'équation d'état de Redlich-Kwong pour évaluer les fugacités et les compositions des phases gazeuses et liquides de l'oxyde de deutérium de tous les équilibres. On a fait appel à la loi de Raoult utilisant des fugacités pour évaluer la fraction molaire de saturation de l'oxyde deutérium dans

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le sulfure de deutérium liquide et on a utilisé la constante de la loi de Henry pour évaluer la solubilité de l'oxyde de deutérium dans le sulfure de deutérium liquide entre 33,003 et 18,905°C. On peut donner une représentation graphique correcte des données des équilibres  $(1_11_2g)$  et  $(s_11_1g)$  en faisant appel à des équations simples à deux paramètres. Pour donner une représentation adéquate des données pour l'équilibre  $(h1_1g)$  entre 30,666 et 2,798°C, on doit faire appel à un modèle à sept paramètres significatifs.

*Mots clés* : système sulfure de deutérium – oxyde de deutérium, clathrate du D-hydrate de sulfure de deutérium, stabilité du D-hydrate du sulfure de deutérium, congélation de l'oxyde de deutérium – sulfure de deutérium, équilibre de phase du sulfure de deutérium – oxyde de deutérium.

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# Introduction

As part of a continuing study (1, 2) of the structural and thermodynamic properties of aqueous nonelectrolyte solutions and of their solid clathrate hydrate solutions, it became of interest to compare the thermodynamic properties of nonelectrolyte solutions in deuterium oxide with their solid clathrate D-hydrate solutions. The properties of aqueous hydrogen sulfide solutions (3, 4) and of the hydrogen sulfide gas hydrate (5-7) were well known, but the properties of deuterium sulfide solutions in deuterium oxide and of the deuterium sulfide D-hydrate had not been reported in the literature. Due to the importance in Canada of the hydrogen sulfide - water dual temperature exchange process (8, 9) for the initial extraction of deuterium oxide from water, it was desirable to know the equilibrium properties of deuterium sulfide with deuterium oxide and of deuterium sulfide D-hydrate.

The present experimental study, performed between 1963 and 1966, defines part of the deuterium sulfide – deuterium oxide system up to 33°C and the conditions for formation of deuterium sulfide D-hydrate with liquid deuterium oxide.

# Experimental

#### **Materials**

Deuterium oxide was 99.75% pure with 0.25 wt.% protium oxide as supplied by Atomic Energy of Canada Limited: a complete isotopic analysis of this deuterium oxide has been reported earlier (10). Deuterium sulfide was prepared by the reaction of deuterium oxide with CP grade aluminum sulfide as described previously (11, 12).

#### Apparatus

The deuterium oxide – deuterium sulfide system was studied in a continuously stirred titanium pressure vessel, which was suspended in an enclosed and insulated water thermostat bath. The vessel was constructed of titanium to resist corrosion and was stirred continuously by an impellor operated by magnetic induction. All metal fittings, valves, and tubing used to connect the titanium vessel to the pressure gauge and to the vacuum filling system were of type-316 stainless steel, which was completely resistant to corrosion by wet deuterium sulfide.

#### Titanium pressure vessel

The titanium pressure vessel, shown in Fig. 1, was axially symmetric and 360 mm high, and was constructed from three machined titanium bodies, which were aligned vertically on top of each other by two pairs of flanges F1 and F2. The upper motor body was 90 mm high with a lower flange F1, the middle shaft body was 170 mm high with an upper flange F1 and a lower flange F2, and the lower impellor body was 100 mm high with an upper flange F2. Each pair of flanges was drawn together by six hexagonal nuts on 9.5 mm lug-bolts and was sealed by compression of an enclosed 1.6 mm thick gasket of polytetrafluoroethylene.

The central stirrer shaft, 336 mm long, 6.35 mm o.d., was of type-316 stainless steel and carried the rotor of the induction motor at its upper end and a two-blade titanium impellor at its lower end. The bearing at the bottom of the stirrer shaft was polytetrafluoroethylene and at the top a nylon sleeve. The induction rotor, 51 mm high  $\times$  32 mm o.d., was protected from corrosion by an epoxy resin coating that had been baked to enhance its chemical resistance. The upper motor body was 41.5 mm o.d. and carried the external stator of the induction motor (not shown) and enclosed the internal rotor with a clearance of 1.6 mm. The underside of the upper flange pair F1 was supported 14 mm above the insulated top cover of the thermostat tank (not shown) and was about 36 mm above the level of the thermostat water. The lower 220 mm of the titanium vessel, comprised of the shaft body, the lower flange pair F2, and the impellor body, was immersed in the thermostat water. The shaft body was 15.9 mm o.d. and enclosed the drive shaft with a radial clearance of 1.6 mm.

The lower impellor body was 63.5 mm o.d. and enclosed a stirred internal cell space, 80 mm high  $\times$  50.8 mm i.d., this provided a maximum cell volume of ~158 cm<sup>3</sup> of which 90 cm<sup>3</sup> was occupied by deuterium oxide. A titanium thermowell, 6.35 mm o.d., containing a 10-junction copperconstantan thermocouple, was located 5 mm from the cell wall and extended 64 mm from the top of the cell to 16 mm above the bottom. The lower end of the drive shaft was reduced to 4.76 mm o.d. and was threaded enabling two nuts to fix the position of the upper collar, 14 mm high  $\times$  9.5 mm o.d., 4.77 mm i.d., of the impellor. The titanium impellor was composed of two vertically aligned, symmetrically opposed blades, 42 mm  $\times$  6 mm  $\times$  1.6 mm, welded along the upper collar. The impellor was located centrally within the cell and its blades swept out a cylinder, >30 mm high  $\times$ 16 mm o.d., within the stirred liquid sample.

#### **Temperature measurement**

The original experimental temperatures were measured on the International Practical Temperature Scale of 1948 (IPTS-48), and these have been converted to the International Temperature Scale of 1990 (ITS-90), using the approximate differences given in Table 4 of Goldberg and Weir (13). This





conversion has a root mean squared bias of less than 0.0003°C in the range zero to 40°C, of slightly smaller magnitude than the accuracy of our most precise measurements. All temperatures and equations are based on the units degree Celsius (ITS-90), with  $(t^{\circ}C + 273.15) = T$  K.

Temperatures were measured on the (IPTS-48) scale using a standardized 25 ohm platinum resistance thermometer with a Leeds and Northrup G-2 Mueller bridge, nanovolt amplifier, and galvonometer (11). Resistances were measured to within  $1 \times 10^{-5}$  ohm, corresponding to about 0.0001°C. The resistance at the triple point of water was checked regularly using Jarrett triple-point cells, by Trans-Sonics Incorporated, maintained in an insulated ice-packed chest (14). The thermostat temperature was controlled to within 0.001°C and was measured with the platinum resistance thermometer mounted in a cavity in a submerged stainless-steel block located within the rapidly recirculating water of the thermostat bath. The temperature difference between the titanium thermowell and the stainless-steel block was measured by a 10-junction copper-constantan thermocouple with the offbalance signal detected by a nanovolt amplifier and galvonometer. With this arrangement the temperature of the stirred liquid sample within the reaction cell could be readily determined with a precision of 0.0005°C.

#### **Pressure measurement**

The top of the motor body of the titanium vessel was connected via Swagelok fittings to small-bore high-pressure tubing, 1.6 mm i.d., 6.35 mm o.d., and high-pressure bonnet bar stock valves to (*i*) the quartz pressure gauge, (*ii*) the deuterium sulfide storage cylinder, and (*iii*) the high-vacuum system. For pressure measurements with the titanium vessel above  $25^{\circ}$ C the high-pressure tubing was heated electrically to about  $40^{\circ}$ C using a thermally and electrically insulated external winding of a flat, 3.2 mm in width nichrome heating ribbon: the motor body and the high-pressure valves were heated by infra-red lamps.

Pressure was measured using fused quartz spiral precision Bourdon gauges manufactured by Texas Instruments Incorporated, which were completely resistant to corrosion. The temperature of the compartment containing the capsule of the quartz spiral was controlled at 35°C, and the gauge was capable of measuring absolute pressure with an accuracy of 0.020% at low pressure and 0.030% at high pressures (11): the precision of pressure measurement was better by a factor of two. An electrical output from the quartz gauge was recorded continuously to follow the attainment of equilibrium. All pressures have been corrected to the standard acceleration due to gravity, 9.80665 m s<sup>-2</sup>.

Over the wide range of pressure exhibited by the deuterium sulfide D-hydrate, pressure was measured using three different capsules containing quartz spirals of different sensitivity: (*i*) the 16 psi capsule was used for pressures between 0.1163 and 0.1980 MPa, (*ii*) the 200 psi capsule between 0.1323 and 1.4449 MPa, and (*iii*) the 500 psi capsule between 1.1510 and 2.2959 MPa. The saturation pressure of the binary mixture of liquid deuterium sulfide and liquid deuterium oxide was measured using the 500 psi capsule. The pressure of the deuterium sulfide solutions in deuterium oxide with D-ice was measured using the 16 psi capsule.

#### **Experimental method**

Late in 1963 the 200 psi gauge was used for our initial measurements of the pressure. Approximately 90 cm<sup>3</sup> deuterium oxide liquid  $(l_1)$  was placed in the titanium cell and, with continuous stirring, was thoroughly degassed using the vacuum system. The thermostat was set at about 5°C, and deuterium sulfide from its storage cylinder was admitted to give a gas (g) pressure of about 100 psig in the cell. Rapid formation of solid deuterium sulfide D-hydrate (h) ensued as shown by a steady drop in pressure. After about 16 h, when it was evident that the three-phase (hl1g) equilibrium had been attained, data sets of 14-37 pairs of pressure-temperature measurements were made over periods of 2-5 days: the determinations reported are the means of these data sets. The thermostat temperature was then raised by about 1°C and the measurement procedure repeated. In 1965, when the pressure exceeded 1.4449 MPa the 200 psi gauge was replaced by the 500 psi gauge. Temperature was increased incrementally, with further additions of deuterium sulfide to maintain the D-hydrate phase at higher pressures, up to the temperature of the quadruple point  $Q(hl_1l_2g)$ , about 30.77°C, above which the solid deuterium sulfide D-hydrate (h) became unstable and decomposed into its two liquid

Temperature	P(1)	l <sub>1</sub> l <sub>2</sub> g)	Difference	Error on calculated	
(°C)	Observed (MPa)	Calculated (MPa)	(%)	pressure(%)	
33.003	2.4500	2.4501	-0.003	0.010	
32.984	2.4494	2.4490	0.017	0.010	
31.981	2.3924	2.3929	-0.019	0.009	
31.503	2.3656	2.3664	-0.035	0.008	
30.983	2.3380	2.3379	0.003	0.008	
30.505	2.3123	2.3119	0.017	0.007	
29.959	2.2831	2.2825	0.028	0.007	
28.930	2.2274	2.2277	-0.016	0.006	
27.916	2.1746	2.1747	-0.005	0.006	
27.850	2.1708	2.1712	-0.019	0.006	
26.853	2.1210	2.1201	0.041	0.006	
25.862	2.0702	2.0701	0.006	0.006	
24.877	2.0208	2.0212	-0.022	0.006	
23.874	1.9730	1.9724	0.031	0.007	
22.859	1.9242	1.9237	0.022	0.008	
21.881	1.8772	1.8778	-0.031	0.009	
20.887	1.8310	1.8318	-0.043	0.010	
19.866	1.7860	1.7855	0.024	0.011	
18.905	1.7428	1.7427	0.004	0.012	

Table 1. Vapor pressure of mixed liquids deuterium oxide and deuterium sulfide.

components, liquid deuterium oxide  $(l_1)$  and liquid deuterium sulfide  $(l_2)$ .

At higher temperatures, where the three-phase (l<sub>1</sub>l<sub>2</sub>g) system was stable, total equilibrium pressures were determined for the stirred, mutually saturated, partially miscible liquids. Measurements began at highest temperatures ~33°C, and data sets of exactly 18 equilibrium pressure-temperature measurements were collected for each temperature at intervals of 2-3 days. The temperature was decreased and the process repeated. In this manner the equilibrium pressure was most rapidly attained by the removal of super-saturation from the two liquid phases: attainment of equilibrium from lower temperatures and from undersaturated conditions required up to 7 days. The (l<sub>1</sub>l<sub>2</sub>g) equilibrium was also measured with continuous stirring below the quadruple point in the metastable region down to 18.9°C: below this temperature the stirred, two-liquid system spontaneously reformed the stable deuterium sulfide D-hydrate. Three high temperatures were finally remeasured for the  $(l_1 l_2 g)$  system to check the hysteresis and reproducibility of the 500 psi gauge. Equilibrium total pressures for the mutually saturated deuterium oxide and deuterium sulfide liquids are listed in Table 1.

In 1966, to define the  $(h_{1}g)$  system at lower temperatures with better accuracy, the 16 psi gauge was used (11), the stirred reactor temperature was reduced to 7.961°C, and some deuterium sulfide was removed so that excess solid Dhydrate did not impede the stirrer. Again data sets of exactly 18 equilibrium pressure–temperature measurements were collected at each temperature over periods of 3–4 days: the mean values are reported. The temperature was decreased and the process repeated down to 2.798°C. The seven measurements listed between 3.383 and 2.798°C are metastable relative to freezing of D-ice. Table 2 lists the equilibrium pressures for deuterium sulfide D-hydrate.

The pressure and temperature of the invariant lower quadruple point  $Q(hs_1l_1g)$  were determined directly from

equilibrium measurements of the  $(hs_1l_1g)$  system with the thermostat temperature controlled so that (*i*) the stirred D-hydrate (h) was neither forming nor decomposing, as shown by a constant observed pressure and (*ii*) the stirred D-ice ( $s_1$ ) was neither freezing nor melting, as shown by a zero signal from the 10-junction thermocouple. To confirm equilibrium conditions the impressed thermostat temperature was bracketed, with decreasing temperature differences, slightly above and slightly below the temperature of the stirred reactor at the quadruple point for a period of 15 days.

In our final study in 1966 the  $(s_1l_1g)$  system was measured at preselected total pressures of deuterium sulfide. The equilibrium temperature for the  $(s_1l_1g)$  system was measured directly for a period of 2 days, by bracketing the thermostat temperature to equal the thermowell temperature, so that the D-ice  $(s_1)$  was in equilibrium (neither freezing nor melting) with the stirred deuterium oxide  $(l_1)$  saturated with deuterium sulfide (g) at the pre-defined total pressure. Table 3 lists the total pressures and temperatures found for the  $(s_1l_1g)$  equilibrium.

All pressures and temperatures listed as determinations for the various equilibria are the mean values of the sets of repeated single measurements. All regression equations have been evaluated using the method of least squares (15). Standard error, abbreviated to SE, is to be understood to mean the statistical estimate of the standard error.

# **Results and discussion**

## **Equation of state**

Following our earlier work (11, 12) gas-phase imperfections have been represented by the Redlich–Kwong equation of state (16), using the extension to mixtures by Spear et al. (17). The  $a_{22}$  and  $b_{22}$  parameters used for deuterium sulfide vapor are those derived from the high temperature (h.t.) measurements from -30 to +30°C (11): the  $a_{11}$  and  $b_{11}$  for

Table 2. Pressure of deuterium sulfide D-hydrate with deuterium oxide liquid.

Temperature		P(	hl <sub>1</sub> g)	Difference	Error on calculated	
(°C)	Gauge	$w^{1/2}$	Observed (MPa)	Calculated (MPa)	(%)	pressure (%)
30.666	500	0.4	2.2959	2.2953	0.027	0.021
30.462	500	0.4	2.2338	2.2348	-0.046	0.018
29.940	500	0.4	2.0903	2.0902	0.003	0.013
29.883	500	0.4	2.0763	2.0752	0.053	0.013
29.375	500	0.4	1.9476	1.9472	0.017	0.011
28 945	500	0.4	1 8461	1 8469	-0.043	0.011
28.932	500	0.4	1 8431	1 8440	-0.048	0.011
28.378	500	0.4	1 7244	1 7245	-0.002	0.011
27 967	500	0.4	1.6425	1 6419	0.002	0.010
27.967	500	0.4	1 6408	1 6419	-0.065	0.010
27.957	500	0.4	1 6400	1 6399	0.003	0.010
26.985	500	0.4	1.4638	1 4640	_0.003	0.008
26.969	200	0.5	1.4030	1 4446	0.021	0.000
26.805	200	0.5	1.4449	1.4440	0.021	0.007
20.045	200	0.5	1.4400	1 2800	-0.002	0.007
25.075	200	0.3	1.2903	1.2899	0.051	0.005
25.855	500	0.4	1.2802	1.2870	-0.003	0.003
23.000	200	0.4	1.1702	1.1701	0.003	0.004
24.079	200	0.3	1.1540	1.1540	0.017	0.003
24.802	200	0.2	1.1510	1.1524	-0.120	0.009
23.997	200	0.5	1.0482	1.0481	0.011	0.005
23.003	200	0.5	0.9411	0.9410	0.005	0.007
21.961	200	0.5	0.8419	0.8417	0.017	0.008
20.980	200	0.5	0.7585	0.7585	-0.005	0.009
19.9/1	200	0.5	0.6821	0.6821	0.001	0.010
18.981	200	0.5	0.6149	0.6150	-0.012	0.010
17.972	200	0.5	0.5537	0.5538	-0.017	0.010
16.972	200	0.5	0.4991	0.4993	-0.033	0.010
15.968	200	0.5	0.4500	0.4502	-0.029	0.010
14.987	200	0.5	0.4070	0.4069	0.012	0.010
13.963	200	0.5	0.3664	0.3664	-0.003	0.010
13.383	200	0.5	0.3452	0.3452	-0.004	0.010
12.975	200	0.5	0.3311	0.3311	0.012	0.010
12.381	200	0.5	0.3116	0.3115	0.021	0.010
11.980	200	0.5	0.2990	0.2990	0.010	0.010
11.379	200	0.282	0.2813	0.2811	0.063	0.012
10.983	200	0.162	0.2703	0.2700	0.115	0.015
9.977	200	0.078	0.2438	0.2435	0.136	0.024
9.144	200	0.054	0.2238	0.2236	0.117	0.033
7.998	200	0.04	0.19899	0.19874	0.129	0.044
7.997	200	0.04	0.19907	0.19872	0.180	0.044
7.961	16	1	0.19798	0.19798	-0.002	0.008
6.993	200	0.04	0.17952	0.17922	0.167	0.044
6.974	16	1	0.17883	0.17887	-0.022	0.007
5.936	200	0.04	0.16111	0.16071	0.246	0.044
5.895	16	1	0.16002	0.16003	-0.007	0.007
5.068	200	0.04	0.14728	0.14694	0.229	0.044
5.014	16	1	0.14610	0.14612	-0.016	0.007
4.032	200	0.04	0.13231	0.13206	0.191	0.044
3.987	16	1	0.13148	0.13145	0.024	0.006
3.485	16	1	0.12481	0.12482	-0.003	0.005
3.392	16	1	0.12364	0.12363	0.007	0.004
3.383	16	1	0.12353	0.12351	0.009	0.004
3.284	16	1	0.12227	0.12226	0.004	0.004
3.190	16	1	0.12109	0.12109	0.004	0.005
3.097	16	1	0.11994	0.11994	0.000	0.005
2.998	16	1	0.11872	0.11873	-0.003	0.005
2.895	16	1	0.11746	0.11748	-0.019	0.006
2.798	16	1	0.11629	0.11632	-0.021	0.007

$P(s_1l_1g)$ (MPa)	t(s	1 <sup>1</sup> 1g)	Difference	Error on calculated	
	Observed (°C)	Calculated (°C)	(°C)	temperature (°C)	
0.00066		3.8125	_	0.00047	
0.00242	3.8061	3.8064	-0.00029	0.00047	
0.00563	3.7967	3.7954	0.00132	0.00045	
0.01552	3.7614	3.7615	-0.00018	0.00040	
0.02836	3.7160	3.7176	-0.00157	0.00035	
0.04150	3.6741	3.6725	0.00158	0.00031	
0.05402	3.6291	3.6297	-0.00062	0.00029	
0.06655	3.5866	3.5867	-0.00015	0.00029	
0.08341	3.5285	3.5290	-0.00045	0.00033	
0.08408	3.5264	3.5267	-0.00026	0.00033	
0.09313	3.4953	3.4957	-0.00034	0.00037	
0.10542	3.4540	3.4536	0.00039	0.00042	
0.12364	3.3917	3.3912	0.00055	0.00052	

Table 3. Freezing point of deuterium oxide solutions of deuterium sulfide.

deuterium oxide vapor are those derived for the solubility measurements (12).

# Method of evaluating compositions of aqueous and gaseous phases

The iterative process used to evaluate the intensive properties of the liquid deuterium oxide solution and of the binary gaseous phase at equilibrium with deuterium sulfide is similar in principle but different in method from that briefly outlined for the solubility (12). Modern values (*i*) for  $p_1^{\circ}$ , the saturation vapor pressure of deuterium oxide, are from Hill and MacMillan (18) and (*ii*) for  $V_1^{11}$ , the molar volume of liquid deuterium oxide, are from Kell (19), evaluated with proper allowance for the difference of the IPTS-48 and the IPTS-68 scales of temperature.

Consider the equilibrium evaporation at a total pressure P and temperature T of 1 g molar mass of deuterium oxide from its liquid solution with mole fraction  $x_1^{11}$  deuterium oxide into its binary gas phase with mole fraction  $y_1$  deuterium oxide as formally represented by the reaction equation:

[1] 
$$D_2O(l_1) \rightleftharpoons D_2O(g)$$
  
 $P, x_1^{11} P, y_1$   
 $G_1^{11}(P, x_1^{11}) G_1^g(P, y_1)$ 

The molar Gibbs energy for deuterium oxide in the liquid and in the gas phases are defined as  $G_1^{11}(P, x_1^{11})$  and  $G_1^g(P, y_1)$ , respectively. For the system in thermodynamic equilibrium at constant *T* and *P* the molar Gibbs energy of deuterium oxide is the same in both the liquid and the gas phases so that

[2] 
$$G_1^{11}(P, x_1^{11}) = G_1^{g}(P, y_1)$$

For the equilibrium evaporation of pure deuterium oxide with  $x_1^{11} = 1$ ,  $y_1 = 1$ , and  $P = p_1^{\circ}$ , eq. [2] yields the relations:

[3] 
$$G_1^{11}(p_1^{\circ}, 1) = G_1^{*11} = G_1^{g}(p_1^{\circ}, 1)$$
  
=  $G_1^{\circ g} + RT \ln f_1^{\circ}$ 

where  $G_1^{*11}$  is the molar Gibbs energy of pure liquid deuterium oxide at its saturation vapor pressure  $p_1^{\circ}$ , and where  $f_1^{\circ}$  is its saturation fugacity, and  $G_1^{\circ g}$  is the standard molar Gibbs energy of gaseous deuterium oxide at unit pressure.

For pure liquid deuterium oxide at a total pressure  $P(>p_1^\circ)$  the molar Gibbs energy  $G_1^{11}(P, 1)$  is

[4] 
$$G_1^{11}(P, 1) = G_1^{*11} + (P - p_1^{\circ})V_1^{11}$$
  
=  $G_1^{*11} + RT \ln f_1$ (Poynting)

where  $f_1(\text{Poynting}) = \exp((P - p_1^\circ)V_1^{11}/RT)$  is the Poynting pressure coefficient, and  $V_1^{11}$  is the molar volume of the liquid.

For dilute solutions of deuterium sulfide in deuterium oxide with mole fraction  $x_1^{11}$  of deuterium oxide at pressure *P* the molar Gibbs energy for deuterium oxide is taken as

[5] 
$$G_1^{11}(P, x_1^{11}) = G_1^{11}(P, 1) + RT \ln x_1^{11}$$

where the liquid is assumed to obey Raoult's law. The sum of eqs. [3]–[5] gives

[6a] 
$$G_1^{11}(P, x_1^{11}) = G_1^{\circ g} + RT \ln f_1^{\circ}$$

+*RT* ln  $f_1$  (Poynting) + *RT* ln  $x_1^{11}$ 

[6b] 
$$G_1^{11}(P, x_1^{11}) = G_1^{\circ g} + RT \ln [f_1^{\circ} \cdot f_1(\text{Poynting}) \cdot x_1^{11}]$$

expressing the molar Gibbs energy of deuterium oxide  $G_1^{11}(P, x_1^{11})$  at *P* and  $x_1^{11}$  in eq. [6*a*] in terms of the molar Gibbs energy for the pure liquid at its saturation vapor pressure with fugacity  $f_1^{\circ}$ , plus the Poynting molar Gibbs energy change with activity coefficient  $f_1$ (Poynting), plus the Raoult-law molar Gibbs energy change with activity coefficient  $x_1^{11}$ . Alternately eq. [6*b*] expresses the same molar Gibbs energy in terms of the fugacity product within the square brackets.

The Redlich–Kwong equation of state for gas mixtures (12, 16, 17) provides an independent expression for the fugacity  $f_1$  of deuterium oxide at mole fraction  $y_1$  in a gas mixture with deuterium sulfide at total pressure *P*. Under

Table 4. Properties of gas and liquid phases in the  $(l_1l_2g)$  equilibrium.

Temperature	$f_2^{\circ}$	$f_2$	$f_1$	<i>y</i> <sub>1</sub>	$x_2^{11}$	$x_3^{11}$	$x_1^{12}$
(°C)	(MPa)	(MPa)	(MPa)	$(\times 10^{3})$	$(\times 10^{3})$	$(\times 10^{6})$	(× 10 <sup>3</sup> )
33.003	2.0306	2.0039	0.00435	4.11	28.85	4.1	13.1
32.984	2.0298	2.0034	0.00435	4.10	28.85	4.1	13.0
31.981	1.9883	1.9626	0.00410	3.90	28.90	4.1	12.9
31.503	1.9687	1.9434	0.00399	3.81	28.92	4.0	12.8
30.983	1.9475	1.9234	0.00387	3.71	28.96	4.0	12.3
30.505	1.9281	1.9049	0.00376	3.62	28.99	4.0	12.1
29.959	1.9061	1.8837	0.00364	3.52	29.03	4.0	11.8
28.930	1.8652	1.8433	0.00342	3.34	29.09	3.9	11.8
27.916	1.8253	1.8047	0.00322	3.17	29.16	3.9	11.3
27.850	1.8228	1.8020	0.00321	3.16	29.16	3.9	11.4
26.853	1.7842	1.7653	0.00302	3.01	29.26	3.8	10.6
25.862	1.7463	1.7280	0.00284	2.86	29.33	3.8	10.5
24.877	1.7092	1.6914	0.00267	2.72	29.42	3.7	10.4
23.874	1.6719	1.6558	0.00251	2.58	29.53	3.7	9.6
22.859	1.6346	1.6193	0.00236	2.45	29.63	3.6	9.3
21.881	1.5992	1.5842	0.00221	2.33	29.72	3.6	9.4
20.887	1.5638	1.5494	0.00208	2.21	29.84	3.5	9.2
19.866	1.5279	1.5152	0.00195	2.10	29.98	3.5	8.3
18.905	1.4945	1.4824	0.00183	1.99	30.10	3.4	8.1

these conditions the molar Gibbs energy for deuterium oxide in the gas phase  $G_1^{g}(P, y_1)$  is given by

[7] 
$$G_1^{g}(P, y_1) = G_1^{og} + RT \ln f_1$$

Returning to the equilibrium of the binary aqueous phase with the binary gaseous phase, eqs. [6b] and [7] are substituted into eq. [2] to obtain the equilibrium relationship

[8] 
$$f_1 = [f_1 \circ f_1 (\text{Poynting}) \cdot x_1^{11}]$$

where the fugacity  $f_1$  of deuterium oxide from the Redlich– Kwong equation is equal to the saturation fugacity  $f_1^{\circ}$  of the pure liquid corrected for the effects of pressure and of solution mole fraction. The equilibrium values for  $f_1$  and  $x_1^{11}$  are obtained by successive approximations to evaluate eq. [8] as follows.

As a first approximation the gas-phase mole fraction of deuterium oxide  $y_1'$  at total pressure *P* is taken as

[9] 
$$y_1' = p_1^{\circ}/P$$

with  $p_1^{\circ}$  evaluated from the equation of Hill and MacMillan (18). This  $y_1'$  is used at *P* and *T* in the Redlich–Kwong (R–K) equation for gas mixtures (12, 16, 17) to obtain *V'* the molar volume of the gas mixture, and thence to evaluate the first approximations  $f_1'$  and  $f_2'$  for the R–K fugacities of deuterium oxide and of deuterium sulfide, respectively. This  $f_2'$  is used with the Henry's law solubility constant (12) and its Poynting correction to evaluate  $x_2^{11'}$ , the mole fraction of undissociated deuterium sulfide dissolved in deuterium oxide.

The Poynting correction for the deuterium sulfide solute is  $f_2(\text{Poynting}) = \exp((P - p_1^\circ)V_2^{11}/RT)$ , where  $V_2^{11}$  is the partial molar volume of deuterium sulfide in deuterium oxide. Values of  $V_2^{11}$  for deuterium sulfide are estimated from the measurements for hydrogen sulfide in water by Barbero et al. (20). The  $x_2^{11'}$  is used with the ionization constant for deuterium sulfide in deuterium oxide (12) to evaluate  $x_3^{11'}$ , the dissolved mole fraction of the deuterium sulfide anion. In the first approximation  $x_1^{11'}$ , the solution mole fraction of deuterium oxide, is given by  $(1 - x_2^{11'} - 2x_3^{11'}) = x_1^{11'}$ . The fugacity of deuterium oxide evaluated for the

The fugacity of deuterium oxide evaluated for the compressed solution using eq. [6b] is  $[f_1 \circ f_1(\text{Poynting}) \cdot x_1^{11'}]$ , which is greater than the fugacity  $f_1'$  evaluated from the Redlich–Kwong equation using  $y_1'$ . The reason that the R–K fugacity  $f_1'$  is too small is because our first approximation of  $y_1'$ , using partial pressures, is too small: thus, in our second approximation we multiply  $y_1'$  by a converging factor greater than unity.

In the second approximation the gas-phase mole fraction of deuterium oxide  $y_1''$  at total pressure *P* is taken as

[10] 
$$y_1'' = y_1' [f_1 \circ f_1 (\text{Poynting}) \cdot x_1'''] / f_1'$$

giving the second sequence of approximations,  $y_1'' \rightarrow V'' \rightarrow f_1'', f_2'' \rightarrow x_2^{11''}, x_3^{11''} \rightarrow x_1^{11''} \rightarrow y_1''[f_1^{\circ} f_1^{\circ}]$ (Poynting): $x_1^{11''}]/f_1'' = y_1$  (3rd approximation), and so on. The approximations converge rapidly to give equilibrium values after six cycles of iteration, satisfying eq. [8] within the limits of single precision arithmetic.

#### Liquid $D_2O$ – liquid $D_2S$ – gas $(l_1l_2g)$ equilibrium

Table 1 presents 19 determinations of  $P(l_1l_2g)$ , the saturation vapor pressure of the partially miscible liquids deuterium oxide and deuterium sulfide between 33.003 and 18.905°C, together with calculated values from the best (21) representative equation

[11]  $\ln P(l_1 l_2 g) = 7.95368 - 2160.7 / T$ 

with  $P(l_1l_2g)$  in MPa and absolute temperature *T* in Kelvin. The percentage differences between observed and calculated pressures, shown in the fourth column, indicate a SE of 0.025% on a single determination: this precision properly

Table 5. Properties of gas and aqueous phases in the  $(hl_1g)$  equilibrium.

30.666       1.8946       0.00380       3.65       28.74       4.0         30.462       1.8527       0.00375       3.62       28.25       3.9         29.940       1.7539       0.00364       3.55       27.11       3.8         29.883       1.7441       0.00363       3.54       27.00       3.8         29.375       1.6530       0.00352       3.49       25.05       3.6         28.945       1.5796       0.00334       3.46       25.05       3.6         28.378       1.4899       0.00324       3.41       23.23       3.4         27.967       1.4271       0.00324       3.41       23.20       3.4         27.957       1.4265       0.00333       3.38       21.33       3.3         26.845       1.2744       0.00303       3.38       21.30       3.2         25.873       1.1539       0.00285       3.39       19.80       3.1         25.869       1.2744       0.00303       3.38       21.30       3.2         25.873       1.1539       0.00285       3.39       19.80       3.1         25.800       1.0564       0.00271       3.40       18.54       2.9	Temperature (°C)	$f_2$ (MPa)	$f_1$ (MPa)	$y_1 (\times 10^3)$	$x_2^{11} (\times 10^3)$	$x_3^{11} (\times 10^6)$
30.462       1.8527       0.00375       3.62       28.25       3.9         29.940       1.7539       0.00364       3.55       27.11       3.8         29.883       1.7441       0.00352       3.49       25.93       3.7         28.945       1.5796       0.00343       3.46       25.02       3.6         28.932       1.5774       0.00343       3.46       25.02       3.6         28.937       1.4284       0.00324       3.41       23.23       3.4         27.967       1.4284       0.00323       3.41       23.20       3.4         27.957       1.4265       0.00323       3.41       23.20       3.4         26.885       1.2911       0.00305       3.39       21.53       3.3         26.885       1.2911       0.00303       3.38       21.30       3.2         25.853       1.1539       0.00285       3.39       19.80       3.1         25.853       1.1539       0.00285       3.39       19.85       2.9         24.862       1.0466       0.00271       3.40       18.54       2.9         24.862       1.0466       0.00268       3.41       18.33       2.9	30.666	1.8946	0.00380	3.65	28.74	4.0
29.940         1.7539         0.00364         3.55         27.11         3.8           29.883         1.7441         0.00363         3.54         27.00         3.8           29.375         1.6530         0.00352         3.49         25.93         3.7           28.945         1.5796         0.00343         3.46         25.05         3.6           28.378         1.4899         0.00324         3.41         23.23         3.4           27.967         1.4271         0.00324         3.41         23.20         3.4           26.985         1.2911         0.00305         3.39         21.53         3.3           26.869         1.2764         0.00303         3.38         21.35         3.2           25.873         1.1539         0.00285         3.39         19.80         3.1           25.873         1.1506         0.00285         3.39         19.75         3.1           25.000         1.0664         0.00271         3.40         18.38         2.9           24.879         1.0436         0.00268         3.41         18.33         2.9           23.003         0.8651         0.00224         3.52         1.48         2.5	30.462	1.8527	0.00375	3.62	28.25	3.9
29.883       1.7441       0.00363       3.54       27.00       3.8         29.375       1.6530       0.00352       3.49       25.93       3.7         28.945       1.5796       0.00343       3.46       25.05       3.6         28.932       1.5774       0.00343       3.46       25.02       3.6         28.378       1.4899       0.00324       3.41       23.23       3.4         27.967       1.4284       0.00323       3.41       23.20       3.4         27.967       1.4265       0.00303       3.38       21.33       3.3         26.869       1.2710       0.00303       3.38       21.33       3.2         26.869       1.2764       0.00303       3.38       21.33       3.1         25.873       1.1539       0.00285       3.39       19.80       3.1         25.853       1.1506       0.00271       3.40       18.54       2.9         24.879       1.0438       0.00268       3.41       18.33       2.9         24.862       1.0406       0.00224       3.52       14.82       2.5         20.980       0.7074       0.00211       3.57       13.80       2.4	29.940	1.7539	0.00364	3.55	27.11	3.8
29.375       1.6530       0.00352       3.49       25.93       3.7         28.945       1.5796       0.00343       3.46       25.02       3.6         28.378       1.4899       0.00322       3.42       23.97       3.5         27.967       1.4284       0.00324       3.41       23.23       3.4         27.957       1.4265       0.00323       3.41       23.20       3.4         26.985       1.2911       0.00305       3.39       21.53       3.3         26.845       1.2730       0.00303       3.38       21.35       3.2         25.873       1.1539       0.00285       3.39       19.80       3.1         25.000       1.0564       0.00271       3.40       18.54       2.9         24.879       1.0438       0.00269       3.41       18.33       2.9         24.879       1.0436       0.00264       3.43       17.21       2.8         23.003       0.8651       0.00239       3.47       15.99       2.6         21.961       0.7800       0.0024       3.52       14.82       2.5         20.800       0.7074       0.00113       3.77       13.80       2.2	29.883	1.7441	0.00363	3.54	27.00	3.8
28.945       1.5796       0.00343       3.46       25.05       3.6         28.932       1.5774       0.00343       3.46       25.02       3.6         28.378       1.4899       0.00324       3.41       23.23       3.4         27.967       1.4284       0.00324       3.41       23.21       3.4         27.957       1.4265       0.00323       3.41       23.20       3.4         26.895       1.2911       0.00305       3.39       21.53       3.3         26.869       1.2764       0.00303       3.38       21.30       3.2         25.873       1.1506       0.00285       3.39       19.80       3.1         25.873       1.1506       0.00285       3.39       19.80       3.1         25.873       1.1506       0.00285       3.39       19.80       3.1         25.000       1.0564       0.00271       3.40       18.38       2.9         24.862       1.0406       0.00268       3.41       18.33       2.9         23.997       0.9555       0.00224       3.52       14.82       2.5         20.980       0.7074       0.00211       3.57       13.80       2.4	29.375	1.6530	0.00352	3.49	25.93	3.7
28.9321.57740.003433.4625.023.628.3781.48990.003223.4223.973.527.9671.42840.003243.4123.233.427.9571.42650.003233.4123.203.426.8891.29110.003053.3921.533.226.8451.27300.003033.3821.353.226.8451.27300.003033.3821.303.225.8731.15390.002853.3919.753.125.8531.15060.002853.3919.753.125.0001.05640.002713.4018.542.924.8621.04060.002683.4118.382.923.9970.95550.002243.5214.822.520.9800.70740.002113.5713.802.419.9710.64010.001983.6412.832.221.9610.78000.001243.5214.822.519.9710.64010.001983.6412.832.218.9810.58020.001633.7111.952.117.9720.52500.001743.7811.122.015.9680.43030.001533.959.6401.814.9870.39050.001434.048.9981.612.3750.31970.001204.307.4961.513.8630.32270.001633.95	28.945	1.5796	0.00343	3.46	25.05	3.6
28.3781.4899 $0.00332$ $3.42$ $23.97$ $3.5$ 27.9671.4284 $0.00324$ $3.41$ $23.23$ $3.4$ 27.9671.4271 $0.00324$ $3.41$ $23.20$ $3.4$ 26.9851.2911 $0.00305$ $3.39$ $21.53$ $3.3$ 26.8691.2764 $0.00303$ $3.38$ $21.35$ $3.2$ 25.8731.1539 $0.00285$ $3.39$ $19.80$ $3.1$ 25.8731.1539 $0.00285$ $3.39$ $19.80$ $3.1$ 25.8621.0046 $0.00285$ $3.39$ $19.75$ $3.1$ 25.0001.0564 $0.00269$ $3.40$ $18.38$ $2.9$ 24.8791.0438 $0.00269$ $3.40$ $18.38$ $2.9$ 24.8621.0406 $0.00248$ $3.41$ $18.33$ $2.9$ 23.997 $0.9555$ $0.00224$ $3.43$ $17.21$ $2.8$ 23.003 $0.8651$ $0.00211$ $3.57$ $13.80$ $2.4$ 19.971 $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ 18.981 $0.5802$ $0.00163$ $3.87$ $10.35$ $1.9$ 15.968 $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ 14.987 $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ 13.363 $0.3227$ $0.00133$ $3.95$ $9.640$ $1.8$ 14.987 $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ 13.963 $0.3227$ $0.00129$ $4.20$ $8.038$ <td>28.932</td> <td>1.5774</td> <td>0.00343</td> <td>3.46</td> <td>25.02</td> <td>3.6</td>	28.932	1.5774	0.00343	3.46	25.02	3.6
27.9671.42840.003243.4123.233.427.9671.42710.003243.4123.213.427.9571.42650.003233.4123.203.426.9851.29110.003053.3921.533.326.8691.27640.003033.3821.353.226.8451.27300.003033.3821.353.225.8731.15390.002853.3919.803.125.0001.05640.002713.4018.542.924.8791.04380.002693.4018.382.924.8621.04060.002543.4317.212.823.0970.95550.002543.4317.212.823.0030.86510.002393.4715.992.621.9610.78000.002243.5214.822.520.9800.70740.002113.5713.802.419.9710.64010.001983.6412.832.218.9810.58020.001863.7111.952.117.9720.52500.001743.7811.122.016.9720.47530.001633.8710.351.913.9630.35270.001434.048.9981.713.9630.35270.001254.247.8131.612.3810.30130.001254.247.8131.612.3810.30130.001254.24	28 378	1 4899	0.00332	3 42	23.97	3.5
27.967 $1.4271$ $0.00324$ $3.41$ $23.21$ $3.4$ 27.957 $1.4265$ $0.00323$ $3.41$ $23.20$ $3.4$ 26.985 $1.2911$ $0.00305$ $3.39$ $21.53$ $3.3$ 26.869 $1.2764$ $0.00303$ $3.38$ $21.35$ $3.2$ 26.845 $1.2730$ $0.00303$ $3.38$ $21.30$ $3.2$ 25.873 $1.1539$ $0.00285$ $3.39$ $19.80$ $3.1$ 25.800 $1.0564$ $0.00271$ $3.40$ $18.54$ $2.9$ 24.879 $1.0438$ $0.00269$ $3.40$ $18.38$ $2.9$ 24.862 $1.0406$ $0.00236$ $3.41$ $18.33$ $2.9$ 23.907 $0.9555$ $0.00254$ $3.43$ $17.21$ $2.8$ 23.003 $0.8651$ $0.00239$ $3.47$ $15.99$ $2.6$ 21.961 $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ 20.980 $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ 19.971 $0.6401$ $0.00188$ $3.64$ $12.83$ $2.2$ 18.981 $0.5802$ $0.00163$ $3.87$ $10.35$ $1.9$ 15.968 $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ 14.987 $0.3005$ $0.00143$ $4.04$ $8.998$ $1.7$ 13.963 $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ 12.381 $0.3013$ $0.00125$ $4.24$ $7.813$ $1.6$ 12.775 $0.3197$ $0.00125$ $4.$	27.967	1.4284	0.00324	3.41	23.23	3.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	27 967	1 4271	0.00324	3 41	23.21	3.4
26.985 $1.2911$ $0.00305$ $3.39$ $21.53$ $3.3$ $26.869$ $1.2764$ $0.00303$ $3.38$ $21.35$ $3.2$ $26.845$ $1.2730$ $0.00303$ $3.38$ $21.35$ $3.2$ $25.873$ $1.1539$ $0.00285$ $3.39$ $19.80$ $3.1$ $25.853$ $1.1506$ $0.00285$ $3.39$ $19.75$ $3.1$ $25.873$ $1.1506$ $0.00285$ $3.39$ $19.75$ $3.1$ $25.873$ $1.0438$ $0.00269$ $3.40$ $18.54$ $2.9$ $24.879$ $1.0438$ $0.00269$ $3.40$ $18.38$ $2.9$ $23.997$ $0.9555$ $0.00254$ $3.43$ $17.21$ $2.8$ $23.003$ $0.8651$ $0.00239$ $3.47$ $15.99$ $2.6$ $21.961$ $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ $20.980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.977$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.977$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.985$ <t< td=""><td>27.957</td><td>1.4265</td><td>0.00323</td><td>3.41</td><td>23.20</td><td>3.4</td></t<>	27.957	1.4265	0.00323	3.41	23.20	3.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	26 985	1 2911	0.00305	3 39	21.53	33
26.845 $1.2730$ $0.00303$ $3.38$ $21.30$ $3.2$ $25.873$ $1.1539$ $0.00285$ $3.39$ $19.80$ $3.1$ $25.853$ $1.1506$ $0.00285$ $3.39$ $19.75$ $3.1$ $25.000$ $1.0564$ $0.00271$ $3.40$ $18.54$ $2.9$ $24.879$ $1.0438$ $0.00269$ $3.40$ $18.38$ $2.9$ $24.862$ $1.0406$ $0.00268$ $3.41$ $18.33$ $2.9$ $23.997$ $0.9555$ $0.00254$ $3.43$ $17.21$ $2.8$ $23.003$ $0.8651$ $0.00224$ $3.52$ $14.82$ $2.5$ $20.980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ $18.981$ $0.5802$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.390$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.390$ $0.2895$ $0.00117$ $4.34$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$	26.869	1 2764	0.00303	3 38	21.35	3.2
25.873 $1.1539$ $0.00285$ $3.39$ $19.80$ $3.1$ $25.873$ $1.1506$ $0.00285$ $3.39$ $19.75$ $3.1$ $25.853$ $1.1506$ $0.00285$ $3.39$ $19.75$ $3.1$ $25.000$ $1.0564$ $0.00211$ $3.40$ $18.54$ $2.9$ $24.879$ $1.0438$ $0.00269$ $3.40$ $18.38$ $2.9$ $24.862$ $1.0406$ $0.00268$ $3.41$ $18.33$ $2.9$ $23.997$ $0.9555$ $0.00224$ $3.43$ $17.21$ $2.8$ $23.003$ $0.8651$ $0.00239$ $3.47$ $15.99$ $2.6$ $21.961$ $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ $20.980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.975$ $0.3197$ $0.00126$ $4.30$ $7.496$ $1.5$ $11.379$ $0.2727$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ <t< td=""><td>26.845</td><td>1 2730</td><td>0.00303</td><td>3 38</td><td>21.30</td><td>3.2</td></t<>	26.845	1 2730	0.00303	3 38	21.30	3.2
25,853 $1,1506$ $0.00285$ $3.39$ $19.75$ $3.1$ $25,853$ $1.1506$ $0.00285$ $3.39$ $19.75$ $3.1$ $25,000$ $1.0564$ $0.00271$ $3.40$ $18.54$ $2.9$ $24,879$ $1.0438$ $0.00269$ $3.40$ $18.38$ $2.9$ $24,862$ $1.0406$ $0.00258$ $3.41$ $18.33$ $2.9$ $23,997$ $0.9555$ $0.00239$ $3.47$ $15.99$ $2.6$ $21.961$ $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ $20,980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ $18.981$ $0.5802$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.381$ $0.3013$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ <t< td=""><td>25.873</td><td>1 1539</td><td>0.00285</td><td>3 39</td><td>19.80</td><td>3.1</td></t<>	25.873	1 1539	0.00285	3 39	19.80	3.1
25,000 $1,0564$ $0,00271$ $3,40$ $18,54$ $2.9$ $24,879$ $1,0438$ $0,00269$ $3,40$ $18,54$ $2.9$ $24,862$ $1,0406$ $0,00268$ $3,41$ $18,33$ $2.9$ $23,997$ $0.9555$ $0,00254$ $3,43$ $17,21$ $2.8$ $23,003$ $0,8651$ $0,00239$ $3,47$ $15.99$ $2.6$ $21.961$ $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ $20.980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ $18.981$ $0.5802$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$	25.873	1.1506	0.00285	3 39	19.75	3.1
24.879 $1.033$ $0.00219$ $3.40$ $18.38$ $2.9$ $24.862$ $1.0406$ $0.00268$ $3.41$ $18.33$ $2.9$ $23.997$ $0.9555$ $0.00254$ $3.43$ $17.21$ $2.8$ $23.003$ $0.8651$ $0.00239$ $3.47$ $15.99$ $2.6$ $21.961$ $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ $20.980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ $18.981$ $0.5802$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $12.975$ $0.3197$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00120$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.0096$ $4.65$ $5.990$ $1.3$ $9.144$ $0.2180$ $0.0089$ $4.79$ $5.536$ $1.2$ $7.997$ $0.19324$ $0.0089$ $4.79$ $5.513$ $1.2$	25.000	1.0564	0.00271	3.40	18 54	2.9
24.862 $1.0406$ $0.00268$ $3.41$ $18.33$ $2.9$ $23.997$ $0.9555$ $0.00254$ $3.43$ $17.21$ $2.8$ $23.003$ $0.8651$ $0.00239$ $3.47$ $15.99$ $2.6$ $21.961$ $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ $20.980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ $18.981$ $0.5802$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.981$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $0.983$ $0.2622$ $0.00199$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.55$ $5.990$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0$	24.879	1.0438	0.00271	3.40	18 38	2.9
23.997 $0.9555$ $0.00254$ $3.43$ $17.21$ $2.8$ $23.003$ $0.8651$ $0.00239$ $3.47$ $15.99$ $2.6$ $21.961$ $0.7800$ $0.00224$ $3.52$ $14.82$ $2.5$ $20.980$ $0.7074$ $0.00211$ $3.57$ $13.80$ $2.4$ $19.971$ $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ $18.981$ $0.5802$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.981$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.55$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.534$ $1.2$ $7.997$ $0.19429$ $0.00089$ $4.80$ $5.513$ $1.2$	24.862	1.0406	0.00269	3.40	18.33	2.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	23,002	0.9555	0.00254	3.43	17.21	2.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	23.003	0.9555	0.00234	3.43	17.21	2.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21.961	0.7800	0.00232	3.57	14.82	2.5
20300 $0.7074$ $0.00211$ $3.07$ $15.00$ $2.7$ $19.971$ $0.6401$ $0.00198$ $3.64$ $12.83$ $2.2$ $18.981$ $0.5802$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.379$ $0.2727$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $0.9977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.961$ $0.19324$ $0.00089$ $4.80$ $5.513$ $1.2$	20.980	0.7074	0.00224	3.52	13.80	2.5
177,71 $0.0401$ $0.00176$ $3.04$ $12.63$ $2.2$ $18.981$ $0.5802$ $0.00186$ $3.71$ $11.95$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19429$ $0.0089$ $4.79$ $5.536$ $1.2$ $7.961$ $0.19324$ $0.0089$ $4.80$ $5.513$ $1.2$	10 071	0.6401	0.00211	3.64	12.83	2.4
16.761 $0.5062$ $0.00160$ $3.71$ $11.73$ $2.1$ $17.972$ $0.5250$ $0.00174$ $3.78$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.961$ $0.19324$ $0.00089$ $4.80$ $5.513$ $1.2$	19.971	0.5802	0.00176	3.71	11.05	2.2
17.972 $0.3230$ $0.00174$ $5.76$ $11.12$ $2.0$ $16.972$ $0.4753$ $0.00163$ $3.87$ $10.35$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.961$ $0.19324$ $0.00089$ $4.80$ $5.513$ $1.2$	17 072	0.53502	0.00130	3.78	11.75	2.1
10.712 $0.4753$ $0.00105$ $5.87$ $10.53$ $1.9$ $15.968$ $0.4303$ $0.00153$ $3.95$ $9.640$ $1.8$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.961$ $0.19324$ $0.00089$ $4.80$ $5.513$ $1.2$	16 972	0.4753	0.00174	3.87	10.35	1.0
13.300 $0.4505$ $0.00135$ $3.35$ $7.040$ $1.6$ $14.987$ $0.3905$ $0.00143$ $4.04$ $8.998$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.991$ $0.19324$ $0.00089$ $4.80$ $5.513$ $1.2$	15.968	0.4303	0.00103	3.07	9 640	1.9
14.767 $0.3505$ $0.00145$ $4.04$ $0.756$ $1.7$ $13.963$ $0.3527$ $0.00134$ $4.14$ $8.372$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $0.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.997$ $0.19429$ $0.00089$ $4.80$ $5.513$ $1.2$	1/ 987	0.4505	0.00133	4.04	8 998	1.0
13.303 $0.3327$ $0.00134$ $4.14$ $0.312$ $1.6$ $13.383$ $0.3329$ $0.00129$ $4.20$ $8.038$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.961$ $0.19324$ $0.00089$ $4.80$ $5.513$ $1.2$	13 963	0.3527	0.00134	4.14	8 372	1.7
12.905 $0.3197$ $0.00125$ $4.20$ $0.0515$ $1.6$ $12.975$ $0.3197$ $0.00125$ $4.24$ $7.813$ $1.6$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.534$ $1.2$ $7.997$ $0.19429$ $0.00089$ $4.80$ $5.513$ $1.2$	13 383	0.3329	0.00129	4.14	8.038	1.0
12.381 $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $12.381$ $0.3013$ $0.00120$ $4.30$ $7.496$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.534$ $1.2$ $7.997$ $0.19429$ $0.00089$ $4.80$ $5.513$ $1.2$	12 975	0.3197	0.00125	4.20	7 813	1.6
11.980 $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.980$ $0.2895$ $0.00117$ $4.34$ $7.289$ $1.5$ $11.379$ $0.2727$ $0.00112$ $4.40$ $6.993$ $1.4$ $10.983$ $0.2622$ $0.00109$ $4.44$ $6.806$ $1.4$ $9.977$ $0.2371$ $0.00102$ $4.56$ $6.348$ $1.3$ $9.144$ $0.2180$ $0.00096$ $4.65$ $5.990$ $1.3$ $7.998$ $0.19422$ $0.00089$ $4.79$ $5.534$ $1.2$ $7.997$ $0.19429$ $0.00089$ $4.79$ $5.536$ $1.2$ $7.961$ $0.19324$ $0.00089$ $4.80$ $5.513$ $1.2$	12.373	0.3013	0.00120	4.30	7 496	1.5
11.3790.27270.001124.406.9931.410.9830.26220.001094.446.8061.49.9770.23710.001024.566.3481.39.1440.21800.000964.655.9901.37.9980.194220.000894.795.5341.27.9970.194290.000894.805.5131.2	11 980	0.2895	0.00117	4 34	7 289	1.5
11.5130.26220.001094.446.8061.49.9770.23710.001024.566.3481.39.1440.21800.000964.655.9901.37.9980.194220.000894.795.5341.27.9970.194290.000894.795.5361.27.9610.193240.000894.805.5131.2	11 379	0.2727	0.00112	4 40	6 993	1.5
10.3050.20220.001094.440.0009.9770.23710.001024.566.3481.39.1440.21800.000964.655.9901.37.9980.194220.000894.795.5341.27.9970.194290.000894.795.5361.27.9610.193240.000894.805.5131.2	10.983	0.2622	0.00109	4 44	6 806	1.1
9.1440.21800.000964.655.9901.37.9980.194220.000894.795.5341.27.9970.194290.000894.795.5361.27.9610.193240.000894.805.5131.2	9 977	0.2371	0.00102	4 56	6 348	13
7.9980.194220.000894.795.5341.27.9970.194290.000894.795.5361.27.9610.193240.000894.805.5131.2	9.144	0.2180	0.00096	4.65	5.990	1.3
7.9970.194290.000894.795.5361.27.9610.193240.000894.805.5131.2	7 998	0 19422	0.00089	4 79	5 534	12
7.961         0.19324         0.00089         4.80         5.513         1.2	7 997	0 19429	0.00089	4 79	5 536	1.2
	7.961	0.19324	0.00089	4.80	5.513	1.2
6,993 0,17549 0,00083 4,92 5,165 1,1	6.993	0.17549	0.00083	4.92	5.165	1.1
6.974 0.17483 0.00083 4.93 5.148 1.1	6.974	0.17483	0.00083	4.93	5.148	1.1
5.936 0.15773 0.00077 5.05 4.805 1.1	5.936	0.15773	0.00077	5.05	4.805	1.1
5.895 0.15668 0.00077 5.07 4.780 1.1	5.895	0.15668	0.00077	5.07	4.780	1.1
5.068 0.14436 0.00072 5.17 4.526 1.0	5.068	0.14436	0.00072	5.17	4.526	1.0
5.014 0.14322 0.00072 5.19 4.499 1.0	5.014	0.14322	0.00072	5.19	4.499	1.0
4.032 0.12985 0.00067 5.31 4.216 1.0	4.032	0.12985	0.00067	5.31	4.216	1.0
3.987 0.12904 0.00067 5.32 4.196 1.0	3.987	0.12904	0.00067	5.32	4.196	1.0
3.485 0.12256 0.00064 5.39 4.054 0.93	3.485	0.12256	0.00064	5.39	4.054	0.93
3.392 0.12142 0.00064 5.41 4.029 0.93	3.392	0.12142	0.00064	5.41	4.029	0.93
3.383 0.12131 0.00064 5.41 4.027 0.93	3.383	0.12131	0.00064	5.41	4.027	0.93
3.284 0.12009 0.00063 5.42 4.000 0.92	3.284	0.12009	0.00063	5.42	4.000	0.92
3.190 0.11895 0.00063 5.43 3.975 0.92	3.190	0.11895	0.00063	5.43	3.975	0.92
3.097         0.11782         0.00062         5.45         3.950         0.91	3.097	0.11782	0.00062	5.45	3.950	0.91
2.998 0.11664 0.00062 5.46 3.923 0.91	2.998	0.11664	0.00062	5.46	3.923	0.91
2.895 0.11541 0.00062 5.48 3.896 0.90	2.895	0.11541	0.00062	5.48	3.896	0.90
2.798 0.11427 0.00061 5.49 3.870 0.90	2.798	0.11427	0.00061	5.49	3.870	0.90

Table	6.	Properties	of	gas	and	aqueous	phases	in	the	$(s_1 l_1 g)$	equilibrium.
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Temperature	$f_2$	$f_1$	<i>y</i> <sub>1</sub>	$x_2^{11}$	x <sub>3</sub> <sup>11</sup>
(°C)	(MPa)	(MPa)	$(\times 10^{3})$	$(\times 10^{3})$	$(\times 10^{6})$
3.8061	0.00176	0.00066	273.0	0.058	0.11
3.7967	0.00497	0.00066	117.0	0.163	0.19
3.7614	0.01484	0.00066	42.6	0.487	0.32
3.7160	0.02762	0.00066	23.4	0.908	0.44
3.6741	0.04067	0.00065	16.0	1.338	0.54
3.6291	0.05306	0.00065	12.3	1.748	0.61
3.5866	0.06544	0.00065	10.0	2.159	0.68
3.5285	0.08204	0.00065	7.98	2.711	0.76
3.5264	0.08270	0.00065	7.92	2.733	0.76
3.4953	0.09158	0.00064	7.16	3.030	0.80
3.4540	0.10363	0.00064	6.33	3.432	0.86
3.3917	0.12142	0.00064	5.41	4.029	0.93

corresponds with the 0.030% accuracy of the 500 psi gauge (11). The parameter -2160.7 has SE 1.2 K. The fifth column shows the SE on the pressure calculated from eq. [11].

The vapor pressure of the mixed liquids,  $P(l_1l_2g)$ , is less than that of pure deuterium sulfide (11),  $p_2^{\circ}$ , and the ratio of pressures in this temperature range is best represented by

[12]  $\ln [P(l_1 l_2 g) / p_2^{\circ}] = -0.09553 + 25.7 / T$ 

where  $p_2^{\circ}$  has been evaluated using eq. [2] from ref. 11 and has a SE of 0.027%. The combined SE on an observed single ratio of pressure is 0.037%, and the parameter 25.7 has SE 1.7 K.

At 25°C the computed ratio of  $P(l_1l_2g)/p_2^{\circ}$  is 0.99074 with SE 0.000088 and 17 degrees of freedom; this gives the deviation (1 – 0.99074), a student *t* ratio of 106, which confirms that  $P(l_1l_2g)/p_2^{\circ}$  is significantly less than unity at a very high level of probability.

Table 4 presents values for the intensive properties of the equilibrium  $(l_1l_2g)$  phases under the conditions of Table 1. Values in columns three to seven are, respectively, for the fugacities  $f_2$  of deuterium sulfide and  $f_1$  of deuterium oxide, for the gas-phase mole fraction  $y_1$  of deuterium oxide, for the mole fractions  $x_2^{11}$  of undissociated deuterium sulfide and  $x_3^{11}$  of deuterium sulfide anion in the liquid deuterium oxide phase  $l_1$ . In column eight the saturation mole fraction  $x_1^{12}$  of deuterium sulfide as  $(1 - (f_2/f_2^{\circ}))$ , using fugacities assuming the deuterium sulfide solvent obeys Raoult's law. Column two provides the required Redlich–Kwong fugacity  $f_2^{\circ}$  for pure deuterium sulfide at its saturation vapor pressure  $p_2^{\circ}$  (11).

The saturation solubility  $x_1^{12}$  of deuterium oxide in liquid deuterium sulfide  $l_2$  is best discussed in terms of the Henry's law constant,  $H_1^{12} = f_1/x_1^{12}$  MPa, for transfer of deuterium oxide from phase  $l_2$  into the gas phase. Comparison of our 19 estimates of  $f_1/x_1^{12}$  for deuterium oxide in liquid deuterium sulfide with 27 similar estimates of  $f_1/x_1^{12}$  for water in liquid hydrogen sulfide, derived from the vapor pressure data of Scheffer (6), shows that  $f_1/x_1^{12}$  for deuterium oxide in deuterium sulfide and for water in hydrogen sulfide are equal within experimental error at the same temperature between 33 and 19°C. Combination of our 19 estimates of  $f_1/x_1^{12}$  for deuterium oxide in deuterium sulfide with five estimates of  $f_1/x_1^{12}$  for water in hydrogen sulfide, derived from the direct phase analyses of  $x_1^{12}$  between 40 and 105°C by Carroll (22), gives the best representative equation

[13] 
$$\ln [f_1/x_1^{12}] = 9.0634 - 3102/T$$

for the Henry's law constant of deuterium oxide in liquid deuterium sulfide with SE of 3.6% on a single determination between 33 and 19°C: the parameter -3102 has SE 67 K. At 25°C the Henry's law constant  $H_1^{12}$  for deuterium oxide in deuterium sulfide is 0.261 with SE 0.0022 MPa, that evaluated from ref. 6 for water in hydrogen sulfide is 0.261 with SE 0.0073 MPa.

The temperature dependence of  $x_1^{12}$ , the saturation mole fraction of deuterium oxide in liquid deuterium sulfide between 33 and 19°C, is best represented by

[14] 
$$\ln x_1^{12} = 2.7474 - 2182/T$$

with SE of 4.6% on a single determination: the parameter -2182 has SE 70 K. At 25°C  $x_1^{12}$  for deuterium oxide in deuterium sulfide is 0.0103 with SE 0.00011, that evaluated from (6) for water in hydrogen sulfide is 0.0119 with SE 0.00034: the difference 0.0016 of  $x_1^{12}$  is significant.

### $D_2S$ D-hydrate – liquid $D_2O$ – gas (hl<sub>1</sub>g) equilibrium

Table 2 presents 58 equilibrium determinations of  $P(hl_1g)$ , the saturation vapor pressure of deuterium sulfide D-hydrate in contact with liquid deuterium oxide between 30.666 and 2.798°C. The seven determinations below 3.392°C are in metastable equilibrium.

The second column denotes the pressure gauge used, data marked 500, 200, and 16 used the 500 psi, 200 psi, and 16 psi gauges, respectively. The third column gives the square root of the weights used to combine the data from the various gauges into a properly weighted least-squares regression of the logarithm of pressure as a function of temperature.

The fourth column lists the observed  $P(hl_1g)$ , the fifth gives  $P(hl_1g)$  calculated from the best model of the form (21)

which is mathematically equivalent to

[15b] 
$$\ln P(\mathrm{hl}_1\mathrm{g}) = A + B/T + C \ln T + DT + ET^2 + FT^3 + GT^4$$

and which required seven parameters for a proper representation of the 58 data. The percentage differences between observed and calculated pressures, shown in the sixth column, yield an overall SE of 0.013% for a single determination of unit weight with 51 degrees of freedom. The seventh column shows the percentage error on the pressure estimated from the weighted regression model.

The 14 residuals using the 16 psi gauge indicate a SE of 0.013%, the 19 residuals at highest pressure using the 200 psi gauge indicate a SE of 0.018%, and the 14 residuals at highest pressure using the 500 psi gauge indicate a SE of 0.039%. Comparison of these SE estimates with the gauge accuracies (11) shows that (*i*) the data at low pressure are properly represented with SE 0.013% and a 0.020% accuracy of 16 psi gauge calibration, (*ii*) the data at intermediate pressure with SE 0.018% are somewhat more precise than the 0.030% accuracy of 200 psi gauge calibration, and (*iii*) the high-pressure data with SE 0.039% are slightly more variable than the 0.030% accuracy of 500 psi gauge calibration.

The six temperature variables u1-u6 in eq. [15*a*] are defined in ref. 21 with x = (T - 298.15)/298.15, and the parameters b0-b6 with their (SEs) are b0 = 0.157129 (0.000090), b1 = 33.0126 (0.010), b2 = 232.179 (1.2), b3 = 5590.55 (84), b4 = 121 174 (5900), b5 = 1 619 360 (130 000), and b6 = 8 860 000 (890 000). We note that the deuterium sulfide D-hydrate pressures properly define six temperature parameters b1-b6 at 25°C, that all parameters are positive with no alternation of sign, and that the value of the least significant parameter b6 could arise by pure chance at a probability level of less than one in  $10^{15}$  times.

Regression of the 58 data, each assumed equally probable with unit weight, (*i*) gave an unrealistic poor fit of the 14 most accurate determinations at low pressure by the 16 psi gauge and (*ii*) indicated an unrealistic high SE estimate of 0.057% for a single determination, but (*iii*) still required a seven-parameter model (21) with b1-b6 all positive and highly significant.

The requirement of a seven-parameter model together with the unusually large positive values of b1-b3 show that the  $P(hl_1g)$  data contain information of significant composition change with temperature for deuterium sulfide D-hydrate between 2.8 and  $30.7^{\circ}$ C.

Table 5 presents values for the intensive properties of the equilibrium  $l_1$  and g phases under the conditions of Table 2. The values listed under  $f_2$ ,  $f_1$ ,  $y_1$ ,  $x_2^{11}$ , and  $x_3^{11}$  have the same meaning as in Table 4.

The saturation vapor pressure  $P(hl_1g)$  of deuterium sulfide D-hydrate is about 88% of that for hydrogen sulfide hydrate (6, 7) at the same temperature. This ratio of  $P(hl_1g)$  is similar to the ratio of 81% exhibited by the Structure I cyclopropane D-hydrate relative to its cyclopropane hydrate (23) at the same temperature between 6 and  $16^{\circ}C$ .

# D-Ice – liquid $D_2O$ – gas $(s_1l_1g)$ equilibrium

Table 3 presents 11 determinations of  $t(s_1l_1g)$ , the equilibrium temperature of D-ice with a deuterium oxide solution saturated with deuterium sulfide at total pressure  $P(s_1l_1g)$  between 0.00242 and 0.10542 MPa. The final row presents the temperature  $t(hs_1l_1g)$  determined at the total pressure  $P(hs_1l_1g)$  0.12364 MPa. The third column shows calculated temperatures from the representative equation

[16] 
$$t(s_1l_1g) = 3.81473 - 3.4258 P(s_1l_1g)$$
  
(0.00047) (0.0067)

with  $t(s_1l_1g)$  in °C and  $P(s_1l_1g)$  in MPa: the SEs are shown in parenthesis below the parameters. Differences between observed and calculated temperatures, shown in the fourth column, indicate a SE of 0.00090°C on a single temperature determination, with 10 degrees of freedom. The fifth column shows the SE estimate on the temperature evaluated from eq. [16].

The first row of Table 3 shows an estimated triple-point temperature of 3.8125 with SE  $0.00047^{\circ}$ C: this disagrees significantly with our first direct measurement of the triple-point at 3.800 with SE  $0.0005^{\circ}$ C in a preliminary experiment in 1963. We suggest in that first experiment, where we were unaware of the need to bracket the thermostat temperature both above and below the stirred reactor temperature, we unwittingly had applied a "too large" cooling differential to the stirred reactor, and that had caused the negative bias  $-0.0125^{\circ}$ C on the observed temperature. We note that the 12 determinations presented in Table 3 were made at the end of our study in 1966, with more experience and with temperature bracketing, and therefore probably with less bias.

Table 6 presents values for the intensive properties of the equilibrium  $l_1$  and g phases under the conditions of Table 3.

#### Upper quadruple point $Q(hl_1l_2g)$

The upper quadruple point  $Q(hl_1l_2g)$  is the invariant fourphase point at the highest temperature where the D-hydrate can coexist in equilibrium with a gas phase: it is located at the cut of the two univariant three-phase curves (hl\_1g) and (l\_1l\_2g). The (hl\_1g) curve has been defined by the upper 14 determinations using the 500 psi gauge between 25.000 and 30.666°C and indicated a SE of 0.042% on a single pressure determination with 10 degrees of freedom. The (l\_1l\_2g) curve has been defined by eq. [11]. The quadruple-point temperature  $t(hl_1l_2g)$  is 30.770 with SE 0.0043°C and the quadruplepoint pressure  $P(hl_1l_2g)$  is 2.3263 with SE 0.00018 MPa.

Comparison of  $Q(hl_1l_2g)$  for deuterium sulfide D-hydrate with that for hydrogen sulfide hydrate, reported by Scheffer (6) at 29.5°C and at 2.24 MPa, shows a difference of temperature of 1.27°C and a difference of pressure of 0.09 MPa.

#### Lower quadruple point $Q(hs_1l_1g)$

The lower quadruple point  $Q(hs_1l_1g)$  is the invariant fourphase point at the lowest temperature where the D-hydrate coexists in stable equilibrium with a liquid deuterium oxide phase: it is located at the cut of the two univariant threephase curves (hl\_1g) and (s\_1l\_1g). The (hl\_1g) curve has been defined by the lower 10 determinations using the 16 psi gauge between 3.987 and 2.798°C and indicated a SE of 0.0072% on a single pressure determination with 8 degrees of freedom. The  $(s_1l_1g)$  curve has been defined by eq. [16]. The lower quadruple-point temperature  $t(hs_1l_1g)$  has been evaluated at 3.3912 with SE 0.00057°C and the quadruple-point pressure  $P(hs_1l_1g)$  at 0.12363 with SE 0.000002 MPa.

The lower quadruple point, determined directly, has given the temperature  $t(hs_1l_1g)$  at 3.3917 with SE 0.00090°C and the pressure  $P(hs_1l_1g)$  at 0.12364 with SE 0.000011 MPa.

Comparison of  $Q(hs_1l_1g)$  for deuterium sulfide D-hydrate with that for hydrogen sulfide hydrate evaluated by Scheffer and Meyer (7) at -0.4°C and at about 0.094 MPa, indicates a difference of temperature of 3.79°C and of pressure of about 0.030 MPa. The ratio of  $P(hs_1l_1g)$  for deuterium sulfide Dhydrate relative to hydrogen sulfide hydrate at their quadruple points is equal to that 1.31 ratio exhibited by Structure I cyclopropane D-hydrate (23) relative to cyclopropane hydrate at their quadruple points.

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