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FIG. 2. $H_2+2DCl=D_2+2HCl$. —, theoretical curve; o, experimental points.

FIG. 3. $H_2+DCl=HD+HCl$. —, theoretical curve; o, experimental points.

process of analysis, or between the measurements on the mixture and the hydrogen standard.

The average values of $\Delta E_0°$, shown in Table I, are higher than the values obtained from band spectra. This might be taken as evide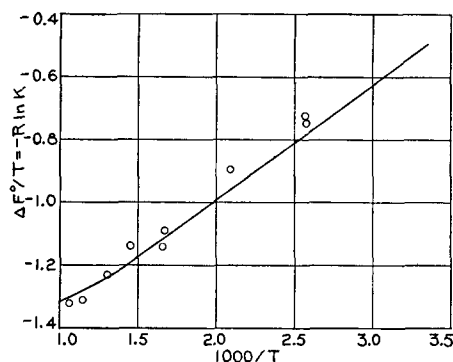nce in favor of Urey and Rittenberg's choice I of the hydrogen constants. However, the authors feel that there may be slight systematic errors in the use of the balance which could account for this discrepancy and too much confidence must not be placed in the accuracy as determined from chance distribution of results.

The Viscosity of Deuterium Oxide and Its Mixtures with Water at 25°C

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The viscosity, η, of 97.6 percent deuterium oxide and six more dilute mixtures with water, as well as that of nearly pure protium oxide, has been determined by comparison with ordinary water, and found to be almost but not quite a linear function of the specific gravity. The relative fluidity, ϕ, has been related to the density by an equation of the type $\phi=1/\eta=1+A(\Delta s)+B(\Delta s)^2$, where (Δs) is the increase in the specific gravity over ordinary water. This equation has been found valid to 0.006 percent over the entire concentration range. Bingham's equation concerning the law of additive fluidities in binary systems, and containing but one arbitrary constant, has been tested and found valid to 0.01 percent.

A SCIENTIFIC problem of great interest and importance is the precise determination of the physical and chemical properties of deuterium oxide and its mixtures with water. Professor Harold C. Urey, who kindly supplied us with liberal amounts of nearly pure deuterium oxide and five other mixtures with water, has made it possible for us to measure the viscosity of these samples. Although the viscosity has been measured before, the viscometric apparatus available in this laboratory should enable us to obtain more precise results than are now extant.

The first measurements on the viscosity of deuterium oxide were made by Selwood and Frost.[1] Lewis and MacDonald,[2] using but a fraction of a cc of liquid, measured the viscosity of 70 and 90 percent samples at various tempera-

[1] P. W. Selwood and A. A. Frost, J. Am. Chem. Soc. **55**, 4335 (1933).
[2] G. N. Lewis and R. T. MacDonald, J. Am. Chem. Soc. **55**, 4730 (1933).

tures. Extrapolating from these values on the assumption that the viscosity-density curve is linear, they estimated the relative viscosity of 100 percent deuterium oxide at 20° to be 1.249, and at 25° to be 1.232. The 20° value did not agree with that previously reported by Selwood and Frost at the same temperature, but it was consistent with the other values on Lewis and MacDonald's viscosity-temperature curve. This suggested that the value of Selwood and Frost was in error. Taylor and Selwood[3] found that the value of Selwood and Frost was vitiated by a calibration error, and have confirmed that of Lewis and MacDonald, for 20°C. Baker and La Mer[4] have measured the viscosity of six mixtures of deuterium oxide, using an instrument having a volume of efflux of 5 cc, and a period of 75 seconds. They have covered the entire concentration range, up to 98 percent, and by extrapolation to 100 percent deuterium oxide estimate the relative viscosity at 25° to be 1.232, which agrees with Lewis and MacDonald.

So far as we know, the viscosity of pure protium oxide has not been measured. Through the kindness of Dr. C. H. Greene and R. J. Voskuyl, we were also able to measure the viscosity of a sample of water from which all or nearly all of the deuterium oxide had been removed by two electrolyses. This sample had a density ($d_{25°}^{25°}$) of 0.99998_2. Greene and Voskuyl will later publish a description of the preparation of this sample and a more precise determination of its density, and further tests as to the amount of deuterium oxide remaining. It seems probable that the deuterium oxide remaining in this sample is so small that its effect on the viscosity would be much less than the limit of error in our viscometric measurements, and therefore the result obtained can be regarded as the viscosity of pure protium oxide.

EXPERIMENTAL

To avoid loss by evaporation or contamination by atmospheric moisture, all samples were transferred from the Pyrex bulbs in which they were received, by distillation in a vacuum line equipped with standard ground glass joints for connecting the pycnometer and viscometer. These joints were mercury-sealed. The pycnometer was furnished with a stopcock, so that the volume could be obtained automatically by closing this stopcock when the contents of the pycnometer were at the proper temperature. A given sample was distilled without ebullition into the pycnometer (capacity 57 cc) by warming the container and chilling the pycnometer sufficiently to effect rapid condensation without freezing the liquid. When filled to a point slightly above the stopcock, distillation was stopped and the pycnometer and contents were allowed to come to the thermostat temperature of 25.00°C. The stopcock was then closed to fix the volume, and the excess liquid was distilled back into the original container, which was then sealed off before the next operation. The pycnometer was detached from the line and weighed. In four calibration runs with water, with the same procedure, the vacuum weights of water contained were 57.2325, 57.2339, 57.2332, 57.2336 g.

After the determination of the density, the filled pycnometer was again attached to the vacuum line and the contents distilled into the viscometer. This operation served to fix the amount of liquid delivered to the viscometer. Any vapors that might have been lost during the pumping out of the line were caught in a trap surrounded by solid carbon dioxide and ether, and this recovered material was also distilled into the viscometer. The viscometer was then removed, placed in the 25° thermostat, and after coming to temperature the viscosity was determined. This was done by the method and apparatus devised by Jones and Talley,[5] and used by them and others in this laboratory for precision measurements on the relative viscosity of electrolytic solutions. Before each run as described above, the viscometer was calibrated with pure, distilled water, using an amount as near as possible to that delivered by the pycnometer. Corrections were applied for any deviation in these volumes. The viscometer, of the Ostwald type and constructed entirely of quartz, had a water time of 533.7 seconds at 25°, an efflux volume of 10 cc, and a working volume of 57 cc.

[3] H. S. Taylor and P. W. Selwood, J. Am. Chem. Soc. 56, 998 (1934).

[4] W. N. Baker and V. K. La Mer, J. Chem. Phys. 3, 406 (1935).

[5] Grinnell Jones and S. K. Talley, J. Am. Chem. Soc. 55, 624, 4124 (1933); Physics 4, 215 (1933).

TABLE I.

$d^{25°}_{5°}$	d_c/d_0	t_c	t_0	$t_c d_c/t_0 d_0$	K.E.	η obs.
0.99998₂	0.99998₂	539.00	539.01	0.99996	0.00000	0.99996
1.00061	1.00061	533.88	533.50	1.00132	.00000	1.00132
1.02368	1.02371	547.12	533.73	1.04939	.00029	1.04968
1.04591	1.04597	559.46	533.70	1.09647	.00056	1.09703
1.05783	1.05790	566.26	533.99	1.12184	.00071	1.12255
1.07556	1.07565	575.33	533.56	1.15986	.00092	1.16078
1.08903	1.08913	582.23	533.50	1.18860	.00109	1.18969
1.10495	1.10508	590.35	533.63	1.22253	.00127	1.22380
(1.10790)			(extrapolated value)			(1.22996)

RESULTS

The fundamental data are shown in Table I. The column headings have the following significance: $d^{25°}_{25°}$ the relative density in vacuum or the specific gravity; d_c/d_0 the relative density in air based on water at 25° as 1.00000; t_c the average period of flow in seconds for the heavy (or light) water; t_0 the corresponding period of flow for ordinary water; $t_c d_c/t_0 d_0$ the relative viscosity without the kinetic energy correction; K.E. the kinetic energy correction; η the observed relative viscosity. The periods given for heavy water, t_c, and the corresponding values for ordinary water, t_0, are comparable, having been determined on the same day with all conditions maintained as nearly uniform as possible. The exceptionally high value for t_0 for the first experiment listed is due to the use of a larger working volume. The differences in the values of t_0 in successive experiments were due to necessary adjustments in the optical and timing systems.

DISCUSSION

The deuterium oxide-water mixtures whose viscosity we have measured are best defined in terms of the specific gravity in vacuum at 25°C. The specific gravity can be easily determined with precision and, except for the slight vagueness as to the relative proportions of the isotopes of oxygen, characterizes the mixture definitely. This is to be preferred to the use of the mole fraction because the estimation of the mole fraction of deuterium oxide in our mixtures would in any case have to be based on an experimental determination of the specific gravity interpreted with the aid of a formula giving the relationship between the mole fraction and the specific gravity. The best formula available for this purpose at the present time is less reliable and precise than our experimental data. Selwood et al.[6] have reported the density ($d^{25°}_{25°}$) of 100

percent deuterium oxide as 1.10790±0.00005. Luten[7] has given a formula relating the mole fraction to the specific gravity, based on the early value of 1.1056 for the density of pure deuterium oxide by G. N. Lewis. La Mer and Baker[8] have revised Luten's equation, using Selwood's value. However, La Mer and Baker did not allow for the 0.02 percent of deuterium oxide present in ordinary water. If their formula is modified to allow for this it becomes,

$$N_{D_2O} = 0.0002 + 9.375\Delta s - 1.03(\Delta s)^2 + 0.2(\Delta s)^3,$$

where N_{D_2O} is the mole fraction of D_2O and $\Delta s = d^{25°}_{25°} - 1$.

The use of specific gravity as a means of identifying any particular deuterium oxide-water mixture is independent of any future revision of the figure chosen for the density of pure deuterium oxide and of the formula expressing the composition as a function of the density.

A plot of the relative viscosity vs. the specific gravity showed this relation to be approximately linear, but there appear to be systematic deviations greater than the probable experimental error. Test of linearity by actual computation showed that the curve deviated systematically from a straight line, giving a bow-shaped curve whose maximum deviation from linearity was 8 parts in 10,000 in the 50 percent region. This is at least 8 times the experimental error. These deviations were exaggerated considerably by plotting the relative fluidity vs. the specific gravity. A plot of $(\eta-1)/\Delta s$ vs. Δs gave a smooth curve but indicated that the relationship between the viscosity and the density would not be a simple one. However, it was found that a plot of $(\phi-1)/\Delta s$ vs. Δs (where $\phi = 1/\eta$ is the relative fluidity) gave a straight line as is shown by the points in circles in Fig. 1. This proves that the desired relationship is

$$\phi = 1/\eta = 1 + A(\Delta s) + B(\Delta s)^2.$$

The data were fitted to this equation by the method of least squares to determine the best values of the constants A and B. The final equation becomes

$$\phi = 1/\eta = 1 - 2.06855(\Delta s) + 3.1122(\Delta s)^2.$$

This equation is tested in Table II. The average

[6] P. W. Selwood, H. S. Taylor, J. A. Hipple and W. Bleakney, J. Am. Chem. Soc. **57**, 642 (1935).

[7] D. B. Luten, Jr., Phys. Rev. **45**, 161 (1934).
[8] V. K. La Mer and W. N. Baker, J. Am. Chem. Soc. **56**, 2641 (1934).

TABLE II.

N_{D_2O}	Δs	ϕ OBS.	ϕ CALC.	$\Delta\phi \times 10^5$
0.0000	−0.00002	1.00004	1.00004	0
.0059	+ .00061	.99868	.99874	−6
.2216	.02368	.95267	.95276	−9
.4285	.04591	.91155	.91159	−4
.5390	.05783	.89083	.89078	+5
.7028	.07556	.86149	.86146	+3
.8268	.08903	.84056	.84051	+5
.9730	.10495	.81713	.81718	−5
1.0000	(.10790)		(.81304)	

deviation of the calculated from the observed is 0.006 percent.

In a private communication Baker and La Mer have given us the specific gravities of their samples whose viscosity they measured. We find that their data are represented by the above equation to 0.1 percent, which is probably the magnitude of their experimental error. Baker and La Mer's data are shown by the crosses on Fig. 1. This private communication also disclosed a typographical error in their published paper. Their figure for viscosity of the sample having a mole fraction of 0.980 should read 1.226 instead of 1.228 as printed.

The following extrapolated values for pure deuterium oxide at 25°C are obtained from our data, based on 1.10790 as the specific gravity of 100 percent deuterium oxide: relative fluidity $\phi = 0.81304$; relative viscosity $\eta = 1.22996$; absolute fluidity $= 90.987$ rhes; absolute viscosity $= 1.0992$ centipoises, based on water as 0.8937 cp., by Bingham.[9]

APPLICATION TO BINGHAM'S LAW OF ADDITIVE FLUIDITIES IN BINARY MIXTURES

Bingham[10] has proposed the following formula for binary mixtures which give no volume change on mixing or which approach this ideal: $\phi = a\phi_A + b\phi_B - K(a-m)(v_A-v_B)$, where ϕ is the absolute fluidity of a mixture, a and b the volume fractions of the components A and B, ϕ_A and ϕ_B the absolute fluidities, v_A and v_B the specific volumes, and m and n the weight fractions. When the single arbitrary constant K is determined, the fluidity of any mixture may be calculated. In applying this formula to the system: protium oxide-deuterium oxide, the following data were used: protium oxide, $\phi_A = 111.914$ rhes, $v_A = 1.00296$ cc/g, molecular weight $= 18.016$; for

[9] E. C. Bingham, *Fluidity and Plasticity* (McGraw-Hill, 1922), p. 340.
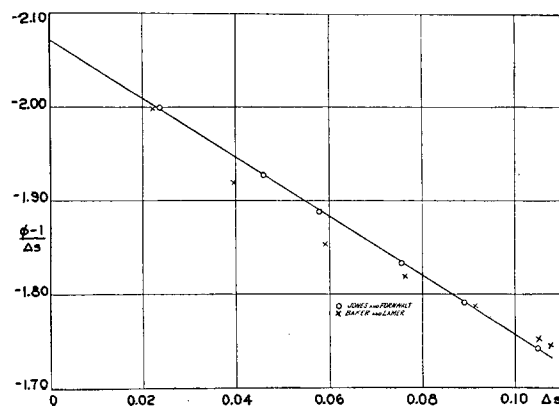[10] Reference 9, p. 165.

FIG. 1

deuterium oxide, $\phi_B = 90.98_7$ rhes, $v_B = 0.90526$, mol. wt. $= 20.027$. The revised Luten equation was used to calculate the mole fractions which in turn were converted to weight and volume fractions. The data were fitted to the Bingham equation by the method of least squares and K was found to be $+373.98$. If A and B are protium oxide and deuterium oxide, respectively, the equation becomes $\phi = 111.914a + 90.987b - 373.98(a-m)(0.09770)$. Since $a = 1-b$ and $m = 1-n$, $\phi = 111.914 + 15.611b - 36.538n$, where b and n are the volume and weight fractions of deuterium oxide, respectively. Table III shows the test of this equation.

TABLE III.

b	n	ϕ CALC.	ϕ OBS.	% DEV.
0.0000	0.0000	111.914	111.914	0
.0002	.0002	111.910	111.910	0
.0059	.0065	111.769	111.762	−0.006
.2222	.2405	106.596	106.613	+.016
.4293	.4546	102.006	102.012	+.006
.5398	.5652	99.690	99.693	+.003
.7035	.7245	96.424	96.409	−.015
.8273	.8415	94.082	94.067	−.016
.9731	.9757	91.455	91.445	−.011
1.0000	1.0000	90.987	90.987	0

The average deviation of 0.01 percent is very satisfactory in view of average errors as high as 0.7 percent upon the application of this same formula to other binary liquid systems, as illustrated by Bingham. Whether the large deviations observed in the study of other binary systems are due to experimental error or mutual interaction between the components is not clear. However, in this case, there is great chemical similarity between the components and the data are more accurate, so that the Bingham equation describes this system with high precision.