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James F. Black and Hugh S. Taylor

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Equilibrium in Hydrogen-Water Systems Containing Tritium

JAMES F. BLACK AND HUGH S. TAYLOR
Frick Chemical Laboratory, Princeton University, Princeton, N. J.

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The equilibrium constant of the reaction $HT+H_2O=H_2+HTO$ involving radioactive hydrogen (T) has been determined over the temperature range 289 to 576°K in contact with a platinum-charcoal catalyst. The results are summarized in the equations:

$$\begin{aligned} \log K &= 0.292 \log T + 336.5/T - 1.055 \\ \Delta F^\circ &= +4.83T - 1.34T \log T - 1540 \\ \Delta H^\circ &= 0.58T - 1540 \\ \Delta S^\circ &= 1.34 \log T - 4.25 \\ \Delta C_p^\circ &= 0.58 \pm 0.05 \text{ cal./deg./mole} \\ \Delta H_o^\circ &= -1540 \pm 160 \text{ cal./mole} \\ I &= 1.055. \end{aligned}$$

Comparison of the experimental results with theoretical calculations by W. F. Libby indicates the correctness of these latter and confirms the assumption with respect to isotopic species that the forces acting within a molecule are unaltered by the change in nuclear mass and that any effects on the properties of the molecule are solely due to a different mass moving in the same force field.

THE object of these experiments is the determination of the equilibrium constant of the reaction $HT+HHO=HH+HTO$, "T" being "tritium," the hydrogen isotope of mass 3, first detected in 1934.[1] The equilibrium can be followed by virtue of the radioactivity of tritium[2] which is evidenced by a weak beta-radiation with a half-life of 31±8 years.[3]

The interest in this determination lies in the effect of isotopic substitution upon the potential function of a molecule. The usual assumption of this effect is that the forces acting within the molecule are unaltered by the change in nuclear mass and that any effects upon the properties of the molecule are solely due to a different mass moving in the same force field. On the basis of this assumption, calculations have been made by W. F. Libby[4] of the equilibrium constant of the reaction investigated in this report. This reaction is simple enough for accurate theoretical treatment and is concerned with a mass difference which should provide the best possible criterion of the assumptions involved concerning isotopes.

EXPERIMENTAL METHOD

The equilibrium constant determined here is written $(HTO)(HH)/(HT)(HHO)=K$. Alter-

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[1] Oliphant, Harteck, and Rutherford, Nature **133**, 413 (1934).

[2] Luis W. Alvarez and Robert Cornog, Phys. Rev. **56**, 613 (1939).

[3] R. D. O'Neal and M. Goldhaber, Phys. Rev. **58**, 574–5 (1940).

[4] W. F. Libby, J. Chem. Phys. **11**, 101 (1943).

nately, this may be put

$$\frac{(\mathrm{HTO})/(\mathrm{HHO})}{(\mathrm{HT})/(\mathrm{HH})}=K,$$

which is the form into which substitution was made in these experiments.

The partial pressure of HTO (or of HT) in a given container is proportional to the number of disintegrations resulting from it per minute. In a sample of radioactive water or hydrogen which will give a convenient counting rate, however, the actual mole fraction of tritium present is of the order of 10^{-12} so that the total pressure of a sample of radioactive hydrogen or water vapor may very safely be used as the partial pressure of the inactive species. Therefore, after equilibrium has been established, by separating the hydrogen, active plus inactive, from the water vapor, active plus inactive, and putting each in turn into the same counter where the counts per minute and the pressure to which the sample had been introduced were noted, we could write counts per minute per cm Hg for water vapor (kHTO/HHO) over counts per minute per cm Hg for hydrogen (kHT/HH) to obtain the desired constant.

The first problem was to obtain equilibrium. This was done for the runs at 16°C, 20°C and 25°C by placing the platinum on carbon catalyst within a water-jacketed condenser. Constant temperature was maintained by running water from a thermostat through the water jacket. The radioactive water was placed immediately on the catalyst with the hydrogen being cycled over it and around a closed system until equilibrium had been reached. A portion of the system, enclosing a sample of the equilibrated hydrogen and water vapor, was now shut off. No further change would occur within this sample since the exchange of hydrogen isotopes between hydrogen and water is not catalyzed by glass.[5] The two gases were separated by freezing out the water vapor with a cold bath, after which each could be counted separately.

For the runs above 25°C, a very active catalyst was used. This was kept at constant temperature in a vapor bath. The inactive hydrogen was bubbled through radioactive water, held at constant temperature, and the mixture passed over the catalyst, where equilibrium was established. It then flowed on through a sample trap where a sample could be closed off and analyzed as in the previous apparatus.

In both these methods it is important that a sample of hydrogen and water *vapor*, in equilibrium, was obtained. Thus, the gaseous equilibrium was investigated. To do this it was necessary to be very careful that none of the water vapor was removed by condensation after equilibrium had been established. Such an occurrence would result in a concentration of tritium within the condensed phase, due to the extreme isotopic effect between tritium and hydrogen, and a constant below the true value would result.

The counting was carried out in a Geiger-Mueller tube counter of one-liter volume. The counting mixture was composed of 0.2-cm water vapor, 2.5-cm alcohol, from 0.8- to 2.0-cm hydrogen and 2.0-cm argon. This mixture was always introduced in the same order, the pressures being measured by a closed-end manometer which was utilized as a McLeod gauge to read the water vapor pressure when that gas was the active material. The tube, so filled, had a plateau (region where the count is independent of the wall voltage) about 20 volts long with a center about 50 volts above the threshold (the wall voltage at which counts first can be detected). In each count, we tried to set the voltage so that the tube would be operating at the center of the plateau, where reproducibility is most easily obtained.

Initially, it was necessary to check the reproducibility of the counting conditions by bringing a standard uranium sample to an exact position near the counter and noting the number of counts per minute it produced in addition to the count being determined. This latter was then corrected by the factor necessary to bring this additional number of counts to a standard value.

This method was used for the first four runs at 20°C, which was the first temperature investigated. For the rest of the runs, however, such a correction was not employed, since it was

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[5] Gould, Bleakney, and Taylor, J. Chem. Phys. 2, 362 (1934).

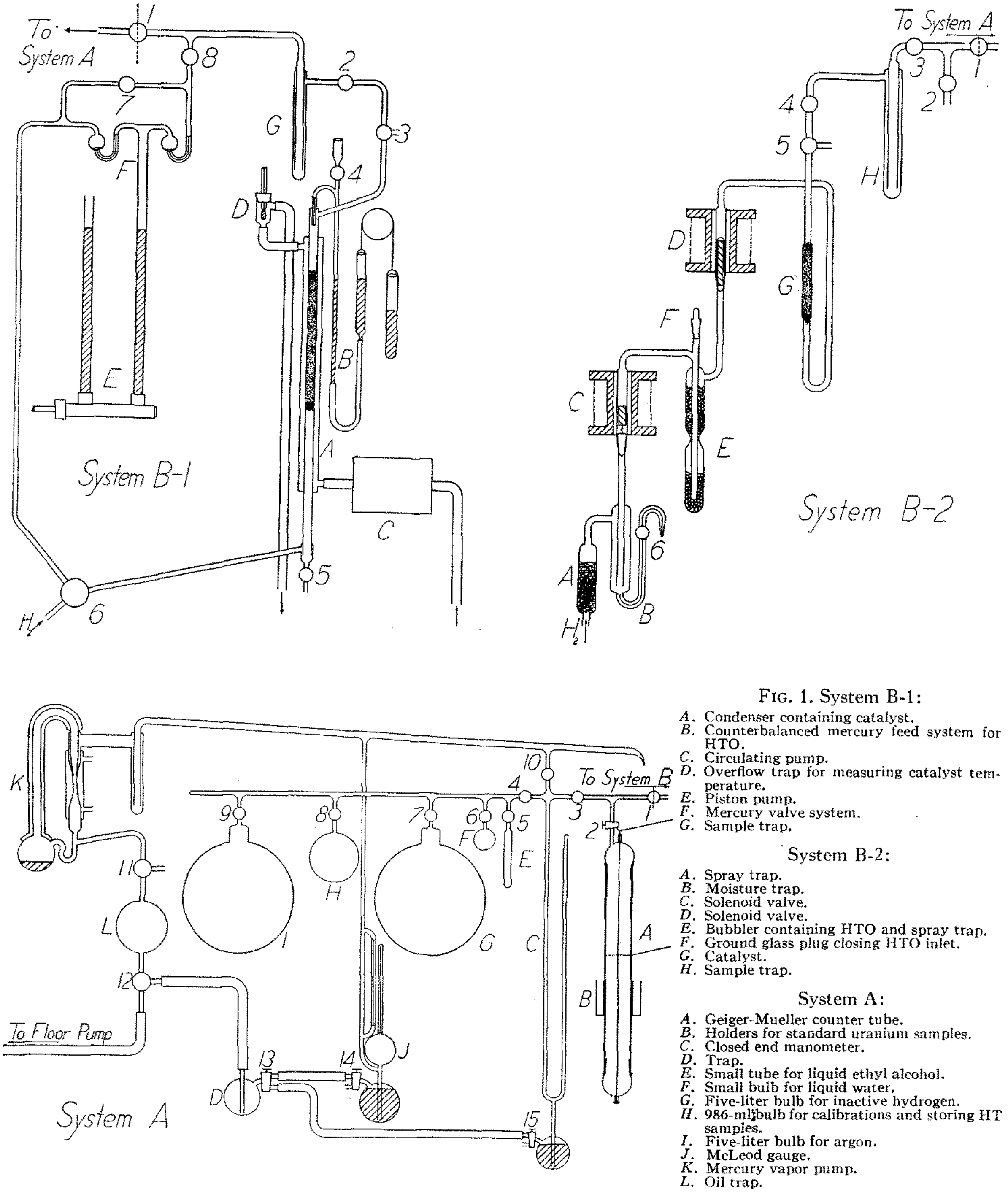


FIG. 1. System B-1:

A. Condenser containing catalyst.
B. Counterbalanced mercury feed system for HTO.
C. Circulating pump.
D. Overflow trap for measuring catalyst temperature.
E. Piston pump.
F. Mercury valve system.
G. Sample trap.

System B-2:

A. Spray trap.
B. Moisture trap.
C. Solenoid valve.
D. Solenoid valve.
E. Bubbler containing HTO and spray trap.
F. Ground glass plug closing HTO inlet.
G. Catalyst.
H. Sample trap.

System A:

A. Geiger-Mueller counter tube.
B. Holders for standard uranium samples.
C. Closed end manometer.
D. Trap.
E. Small tube for liquid ethyl alcohol.
F. Small bulb for liquid water.
G. Five-liter bulb for inactive hydrogen.
H. 986-ml bulb for calibrations and storing HT samples.
I. Five-liter bulb for argon.
J. McLeod gauge.
K. Mercury vapor pump.
L. Oil trap.

found possible to keep the sensitivity actually more constant than the accuracy in this method of determining it.

To get accurate comparisons at the high counting rates involved in these experiments a coincidence correction was employed. This gave, at a given counting rate, the number of counts per minute that had followed too closely after the preceding count for the apparatus to record them both.

APPARATUS AND PROCEDURE

The experiments were performed in two different sets of apparatus shown in Fig. 1.

System A comprises the evacuating devices, counter tube, measuring devices and storage bulbs. These pieces of equipment were maintained as shown throughout the entire series of runs. At the point marked by the inscription "to system B" and by the arrow, system A was sealed to the apparatus in which equilibrium was obtained.

It was in this latter part of the apparatus that two different techniques were involved. The first method, depicted as "system B-1," was used to obtain equilibrium at 16°C, 20°C and 25°C. For higher temperatures, the equipment shown in "system B-2" was employed. Both of these apparatus were joined to system A at the "sample trap," the stopcock labeled "1" and divided by the dotted line being common to both systems A and B in each case.

The auxiliary electrical apparatus necessary for the use of the counter tube in system A was contained in a high speed, Geiger-Mueller counting unit purchased from Herbach and Rademan, Inc.

System B-1

Investigations were first carried out in system B-1. The catalyst was contained in the inner tube of the water-jacketed condenser (*A*). The radioactive water was introduced into the feed system (*B*) through stopcock 4 by lowering the mercury level within the feed system.

The catalyst, kept in good thermal contact with the walls by means of the excess water wetting them both, was held at constant temperature by water from a thermostat. A circulating pump (*C*) forced the water through the outer jacket of the condenser, returning it through the overflow trap (*D*) where the temperature was measured by a thermometer. It was necessary to keep the temperature of the room above that of the catalyst to prevent radioactive water from distilling out of that part of the system.

The hydrogen, generated electrolytically, was passed over platinized asbestos to remove any oxygen impurity. The water was removed from the resulting gas by means of phosphorus pentoxide, after which stopcock 6 gave access to the reaction system. Within the latter, the hydrogen was cycled for several hours, long enough for the isotopic equilibrium to be complete for gas and water vapor.

The cycling was accomplished by means of the piston pump (*E*) and mercury valve system (*F*) shown in the drawing. Each of the two identical mercury valves consisted of a bulb connected to capillary tubing and containing a small amount of mercury. Alternating contraction and expansion of the volume between the valves was produced continually by the piston pump which set the mercury columns into oscillation. With stopcock 7 closed, this resulted in a transfer of gas through the valves from right to left. Since the valves formed part of the closed tubular system containing the catalyst, a continuous transfer of gas around the system was accomplished.

Stopcock 7 was inserted for use in filling the system with hydrogen prior to a run. At such a time the sample trap (*G*) was practically empty because of removal of the sample for counting. Since the apparatus operated at atmospheric pressure, an amount of hydrogen corresponding to the sample removed was inserted. The system, after initially being filled with hydrogen, was so operated that no foreign gases were admitted and only the hydrogen removed as a sample in the previous run had to be replaced to commence a new experiment.

System B-2

The equilibrium was studied at temperatures higher than that of the room by means of system B-2.

The hydrogen was generated electrolytically at about one liter per hour with 2.4 amperes current. The generated gas traversed a spray trap (*A*), and then a liquid-air trap (*B*) to dry it completely. The water collected in the latter could be forced out through the capillary tubing leading to stopcock 6.

The gas next traversed solenoid valve (*C*) which separated the active water from the inactive water when the system was not in operation. Beyond this the hydrogen entered the bubbler (*E*), passing down through the long center tube and bubbling through the glass beads, covered with radioactive water, at the bottom. The radioactive water was added by removing the ground glass tapered plug (*F*) at the bend just above the bubbler. The hydrogen, saturated with radioactive water, next passed through glass wool in the upper half of the bubbler to remove spray. The entire bubbler, including the spray trap, was immersed in a water bath kept at constant temperature in a large Dewar flask.

Traversing solenoid valve (*D*), the gas was introduced into the section heated by the vapor bath and containing the catalyst (*G*). Here it was brought to temperature by passing downward through six-millimeter tubing in which numerous indentations had been punched to facilitate heat exchange. Rounding the bottom "U" of the tube, the mixture of hydrogen and radioactive water vapor passed upward over the catalyst where equilibrium was established.

Passing through stopcock 5, the mixture, now at equilibrium, could either be run out at the exit tube or sent into the sample trap (*H*) through stopcock 4 which was inserted to prevent placing stopcock 5 under the high vacuum sometimes present in the sample trap. The gas left the sample trap via stopcocks 3 and 2, stopcock 1 being closed.

System A

This part of the apparatus was used as depicted throughout the whole series of measurements. It contained the counter tube, storage bulbs, pressure measuring devices, and vacuum equipment. System A was first sealed to system B-1 and later to system B-2, stopcock 1 being the same in all three figures.

The counter tube itself (*A*) was constructed from two-inch o.d. brass tubing one-sixteenth inch thick, and had glass ends. The glass and metal were sealed together with picene wax to give a vacuum-tight container with a volume of about one liter.

Supported very close to but not touching the counter tube wall were the sensitivity holders (*B*). These held two sample tubes of uranium acetate, kept firmly in place in the tube by a layer of paraffin. These tubes were always placed each in the same holder and in exactly the same position as indicated by an arrow on the cork. Thus, they should always give the same number of counts per minute in addition to those being measured inside the counter if other conditions have been reproduced. Their purpose was to check this latter fact.

Gas was admitted to the counter tube through stopcock 2. Stopcock 1 led to the sample trap while stopcock 3 led to the manometer (*C*).

This latter was a closed tube type which could be pulled down by opening stopcocks 12, 13, and 15 to the floor pump. The manometer was used in filling the counter to read the pressures of the gases directly or by the McLeod gauge method. This last was necessary with the radioactive water which was expanded to a pressure of about two millimeters on being introduced into the counter.

Stopcock 4 led to the storage bulbs. Sealed to stopcock 5 was a test tube (*E*) of liquid absolute alcohol, to stopcock 6 a small bulb (*F*) of liquid inactive water, to stopcock 7 a five-liter bulb (*G*) for inactive hydrogen, to stopcock 8 a liter bulb (*H*) for calibration purposes and to store radioactive hydrogen, and to stopcock 9 a five-liter bulb (*I*) of argon. After separation of a sample, the radioactive water vapor was stored in the sample trap which is not shown as part of system A.

Stopcock 10 led to the main vacuum line. A low pressure McLeod gauge (*J*) tapping this line was used to test the efficiency with which the apparatus was being evacuated. The upper end of the main vacuum line was connected to a trap which led into the mercury vapor pump (*K*) backed by a floor pump.

The vacuum system was in continuous operation, since the counter tube had to be evacuating at all times when not in use and for 25 minutes between each individual counting period. Unless the tube were treated to this exhaustive evacuation, the sensitivity would not, in any sense, be reproducible but would depend upon the recent history of the apparatus. The peculiarities in evidence were complex and have not been explained, but the above treatment enabled these measurements to be made with a sensitivity more constant than it was possible to measure.

CALCULATION OF RESULTS

The data which entered immediately into the equilibrium constant were the pressures of HTO and HT samples, the counting rate with these samples and the background counting rate. In the first four runs the counting rates were corrected to a standard sensitivity value of one count per minute.

The constant recorded for each temperature is the average of the successful runs. The constant at 25°C, calculated in this manner, is 6.25±0.05. The error was obtained from the actual deviations of the individual results from the mean. (See Table I.)

INTERPRETATION OF RESULTS

The results of these measurements and their conversion into the form necessary for a plot of log K against $1/T$ are given in Table II. The plot itself appears in Fig. 2. Such a plot is usually a straight line but, in this case, due to the wide temperature range covered by the experiments, a slight curvature is present.

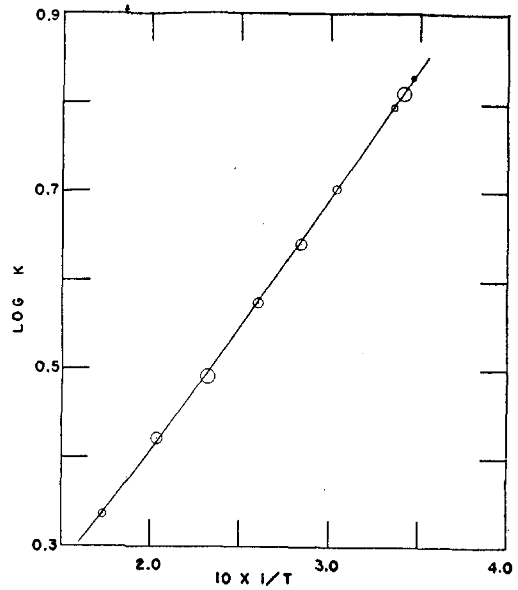
TABLE I. Data and results.

Page	Temp. °C	Back-ground	Obs. H Count	Press. H	HT — cm	Obs. HTO Water	Press. Water	HTO — cm	K
Vol. 2									
14	20.2	0.560	1.873	1.46	0.900	2.002	0.251	5.74	6.38
17	20.2	0.583	1.880	1.46	0.888	1.752	0.218	5.36	6.04
20	20.2	0.560	1.915	1.41	0.961	1.715	0.192	6.01	6.25
23	20.2	0.567	1.903	1.46	0.914	1.658	0.199	5.49	6.01
94	20.2	622	1713	1.45	752	1602	0.179	5475	7.28
97	20.2	626	1846	1.48	824	1584	0.181	5300	6.44
100	20.2	610	1795	1.44	823	1556	0.176	5375	6.54
103	20.2	633	1830	1.47	814	1572	0.176	5340	6.55
106	20.2	612	1785	1.48	792	1546	0.168	5560	7.01
109	20.2	622	1889	1.50	844	1536	0.176	5200	6.16
									Av. $K_{20.2}=6.47\pm0.12$
29	16.0	580	1900	1.48	891	1417	0.140	5980	6.71
32	16.0	588	1900	1.56	841	1323	0.135	5440	6.46
35	16.0	588	1917	1.51	880	1236	0.140	5840	6.63
38	16.0	600	1932	1.57	848	1404	0.140	5745	6.77
46	16.0	603	1764	1.32	879	1460	0.142	6035	6.86
49	16.0	605	1725	1.31	855	1440	0.142	5880	6.88
54	16.0	591	1663	1.27	843	1428	0.148	5655	6.71
58	16.0	596	1690	1.30	841	1367	0.137	5630	6.69
61	16.0	583	1688	1.32	837	1383	0.140	5710	6.82
64	16.0	590	1702	1.33	836	1396	0.143	5640	6.74
67	16.0	585	1640	1.28	825	1386	0.140	5720	6.93
									Av. $K_{16.0}=6.75\pm0.04$
70	25.0	612	2338	1.99	866	1906	0.238	5440	6.28
73	25.0	616	1824	1.43	845	1894	0.244	5240	6.20
76	25.0	600	1860	1.43	880	1968	0.256	5340	6.07
79	25.0	604	1862	1.45	867	1875	0.233	5450	6.28
82	25.0	620	1955	1.47	907	2199	0.282	5600	6.17
85	25.0	603	1896	1.43	884	2082	0.262	5640	6.38
88	25.0	623	1888	1.44	878	2051	0.256	5580	6.35
									Av. $K_{25.0}=6.25\pm0.05$
124	56.3	705	1889	1.01	1172	1698	0.169	5870	5.01
127	56.0	625	1860	0.96	1287	1659	0.166	6230	4.84
133	56.0	665	2094	1.00	1429	1739	0.151	7140	4.96
142	56.2	645	2251	1.01	1590	2168	0.196	7770	4.89
145	56.3	669	2036	0.94	1454	1778	0.151	7340	5.04
148	56.1	675	2131	1.00	1456	1802	0.151	7460	5.12
151	55.8	634	2153	0.99	1533	1893	0.158	7960	5.19
154	55.8	665	2282	1.01	1600	1886	0.146	8360	5.22
156	55.5	720	2333	1.02	1582	1991	0.156	8150	5.15
									Av. $K_{56.2}=5.05\pm0.05$
160	79.8	645	2697	0.99	2073	2500	0.213	8700	4.20
162	79.8	631	2474	0.86	2144	2309	0.186	9020	4.21
165	79.6	631	2400	0.81	2184	2335	0.181	9410	4.52
167	79.5	646	2537	0.94	2012	2249	0.173	9260	4.61
169	79.5	663	2524	0.88	2116	2229	0.171	9150	4.32
171	79.2	642	2532	0.89	2124	2603	0.208	9425	4.44
174	79.6	643	2622	0.94	2105	2445	0.198	9090	4.32
175	79.7	643	2452	0.88	2055	2506	0.208	8955	4.36
									Av. $K_{79.6}=4.37\pm0.05$
177	111.5	676	2585	0.90	2120	2198	0.196	7760	3.66
178	111	673	2460	0.89	2007	2201	0.196	7795	3.88
180	111	673	2367	0.81	2091	2069	0.183	7625	3.65
182	111	671	2334	0.80	2080	2325	0.198	8350	4.01
183	111	671	2537	0.83	2248	2190	0.186	8160	3.63
185	110.0	660	2217	0.80	2217	2255	0.201	7930	3.82
2	111.2	657	2357	0.82	2073	2306	0.208	7925	3.82
4	111.3	657	2365	0.82	2084	2254	0.211	7560	3.63
6	111.2	671	2484	0.83	2185	2618	0.238	8180	3.74
									Av. $K_{111.2}=3.76\pm0.05$
7	158.7	656	2389	0.82	2115	1973	0.191	6900	3.26
9	158.1	656	2332	0.80	2095	1980	0.196	6750	3.22
10	158.2	656	2358	0.82	2076	1994	0.198	6750	3.25
11	158.2	685	2494	0.81	2232	2020	0.201	6640	2.98
13	158.7	656	2384	0.78	2215	2060	0.226	6210	2.81
15	158.6	656	2542	0.80	2358	2178	0.211	7210	3.06
17	158.4	686	2466	0.80	2225	2121	0.204	7030	3.16
18	158.7	686	2532	0.81	2280	2186	0.208	7200	3.06
									Av. $K_{158.4}=3.10\pm0.06$
19	216.9	680	2376	0.77	2200	1903	0.204	6000	2.72
21	217.3	680	2483	0.80	2255	1858	0.204	5770	2.56
22	217.3	680	2450	0.81	2185	1836	0.193	5990	2.74
23	217.3	680	2483	0.80	2255	1756	0.186	5785	2.56
24	217.6	664	2653	0.91	2185	1654	0.176	5625	2.58
26	216.5	664	2394	0.77	2247	1815	0.193	5960	2.65
27	217.0	664	2495	0.80	2288	1820	0.181	6390	2.79
28	217.2	664	2643	0.81	2442	1888	0.201	6090	2.50
									Av. $K_{217.1}=2.64\pm0.04$
30	302.3	660	2545	0.81	2327	1714	0.201	5250	2.26
31	302.3	660	2553	0.81	2338	1720	0.209	5070	2.17
32	303.0	660	2490	0.80	2287	1638	0.188	5200	2.27
33	302.9	660	2600	0.83	2336	1620	0.193	4975	2.13
35	303.6	660	2690	0.86	2360	1611	0.186	5110	2.16
36	303.6	660	2530	0.79	2366	1578	0.186	4935	2.09
37	302.8	660	2698	0.81	2515	1642	0.186	5280	2.10
38	302.1	660	2605	0.81	2400	1627	0.186	5200	2.17
									Av. $K_{302.9}=2.17\pm0.02$

TABLE II.

t°C	T°K	$1/T$	K	log K	±
16.0	289.1	0.003459	6.75±0.04	0.8293	0.0025
20.2	293.3	3409	6.47±0.12	0.8109	0.0080
25.0	298.1	3354	6.25±0.05	0.7959	0.0034
56.2	329.3	3036	5.05±0.05	0.7033	0.0043
79.6	352.7	2834	4.37±0.05	0.6405	0.0049
111.2	384.3	2602	3.76±0.04	0.5752	0.0051
158.4	413.5	2317	3.10±0.06	0.4914	0.0084
217.1	490.2	2039	2.64±0.04	0.4216	0.0065
302.9	576.0	1736	2.17±0.02	0.3365	0.0040

A plot of the slope against temperature is utilized here to obtain an estimate of ΔC_p. The



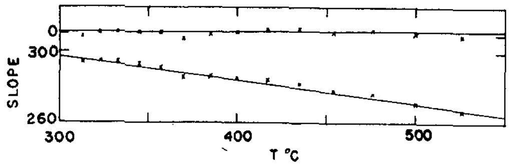


FIG. 2. Upper.
FIG. 3. Lower.

data read from Fig. 2 and the slopes obtained from them are found in Table III. The slopes are plotted against temperature as the lower series of points in the bottom part of Fig. 3. The upper series of points in this section of Fig. 3 represent the deviations of the lower series from the straight line drawn through them. From the two straight lines that are drawn we find the best equation for the data to be slope $= -0.126T + 336 = (d \log K)/d(1/T)$. Multiplying through by $2.303R$, we obtain

$$2.303R\frac{d \log K}{d(1/T)} = -0.58T + 1540. \quad (1)$$

From Eq. (1) we see that ΔC_p is 0.58 cal. per mole and $\Delta H_0°$ is -1540 cal. per mole. Therefore

$$\Delta H° = 0.58T - 1540. \quad (2)$$

Integration of Eq. (1) gives us

$$\log K = 0.292 \log T + \frac{336.5}{T} + I. \quad (3)$$

Substituting into Eq. (3) the experimental values for K with their corresponding temperatures, we obtain the values for "I" shown in Table IV. These values show no drift over the 300° temperature range. We now have the complete equation

$$\log K = 0.292 \log T + \frac{336.5}{T} - 1.055. \quad (4)$$

From the values of ΔC_p and "I" we obtain for the entropy

$$\Delta S° = 1.34 \log T - 4.25. \quad (5)$$

Combining this with our previous expression for $\Delta H°$ we have:

$$\Delta F° = -4.83T - 1.34T \log T - 1540. \quad (6)$$

To test our equations we use them to calculate K and compare the value obtained, K_{calc}, with that of our experiments, K_{exp}, and with that, K_{theo}, calculated from pure theory by W. F. Libby. This comparison is contained in Table V. In each case our calculated value of K lies within the root mean square error of the

TABLE III.

$\log{}'K$	$\log K$	$1/T'$	$1/T$	$1/T$ °K Av.	T °K	$\log{}'K - \log K$	Slope
0.4356	0.3293	0.0021	0.0017	0.0019	526	0.1063	267
0.4630	0.3546	22	18	0.0020	500	0.1084	271
0.4910	0.3816	23	19	21	476	0.1094	276
0.5200	0.4088	24	0.0020	22	454	0.1112	278
0.5486	0.4356	25	21	23	435	0.1130	282
0.5764	0.4630	26	22	24	417	0.1134	284
0.6050	0.4910	27	23	25	400	0.1140	285
0.6344	0.5200	28	24	26	385	0.1144	286
0.6630	0.5486	29	25	27	370	0.1144	286
0.6928	0.5764	0.0030	26	28	357	0.1164	291
0.7224	0.6050	31	27	29	345	0.1174	293
0.7520	0.6344	32	28	0.0030	333	0.1176	294
0.7810	0.6630	33	29	31	323	0.1180	295
0.8105	0.6928	34	0.0030	32	313	0.1177	294

TABLE IV.

T° K	$\log K_{\text{obs}}$	$\log T$	$-0.292 \log T$	$-336.5/T$	I
289.1	0.8293	2.461	0.719	1.164	−1.054
293.3	0.8109	2.467	0.720	1.148	−1.057
298.1	0.7959	2.474	0.722	1.129	−1.055
329.3	0.7033	2.517	0.734	1.022	−1.053
352.7	0.6405	2.547	0.744	0.954	−1.057
384.3	0.5752	2.585	0.755	0.876	−1.056
431.5	0.4914	2.635	0.769	0.780	−1.058
490.2	0.4216	2.690	0.785	0.687	−1.050
576.0	0.3365	2.760	0.806	0.585	−1.054

Av. $I = -1.055 \pm 0.002$

experimental value, with no drift being shown in these slight deviations.

The relationship between the experimental constants and W. F. Libby's theoretical calculations is demonstrated in Fig. 4. In it the lower curve represents the theory and the upper curve these experiments. The radius of the circles represents, in the case of the experiments, the root mean square error of the point while the circles around the theoretical points are an estimate by W. F. Libby of their probable errors. It is interesting to note that in a direction perpendicular to the curves, the "smearing" produced by these errors just overlaps.

The small difference between the two curves corresponds at 16°C to a $\Delta F°$ difference of 24 cal. per mole out of about 1100 cal. This is much too high to be due to error in the fundamental frequencies of the water molecule. The discrepancy, therefore, must be due either to some unaccounted source of systematic error in the experiments or to some inadequacy in the assumptions used in the theoretical calculations. One of the possibilities in the latter case, and the initial interest behind W. F. Libby's calculations, is that the potential function for a molecule may, in fact, be changed by isotopic substitution.

TABLE V.

t °C	log K_{calc}	K_{calc}	K_{exp}	K_{theo}
16.0	0.828	6.73	6.75±0.04	6.47
20.2	0.813	6.50	6.47±0.12	6.24
25.0	0.796	6.25	6.25±0.05	6.01
56.2	0.701	5.02	5.05±0.05	4.84
79.6	0.643	4.40	4.37±0.05	4.23
111.2	0.576	3.77	3.76±0.04	3.64
158.4	0.494	3.12	3.10±0.06	3.03
217.1	0.417	2.61	2.64±0.04	2.54
302.9	0.336	2.17	2.17±0.02	2.08

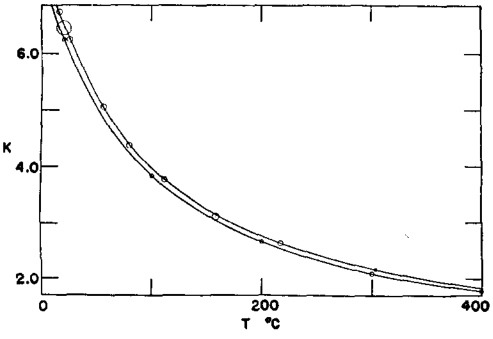


FIG. 4.

The agreement is actually so close, however, as to constitute quite a satisfactory check over the entire temperature range. It can be said with confidence that isotopic substitution by elements other than hydrogen will produce no effect upon the potential function of a molecule.

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