

Exchange Reactions with Deuterium I. Deuterium and Hydrogen Chloride

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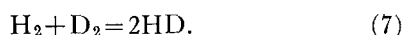
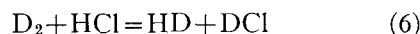
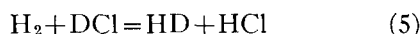
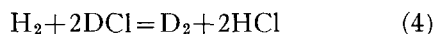
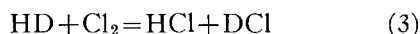
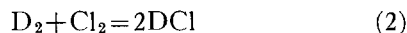
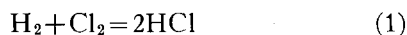
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movable and stationary balance pointers against the gas pressure to obtain an average pressure corresponding to coincidence of the pointers. The statistical accuracy of this procedure was surprisingly good, the probable error usually being <0.1 mm of gas. Nearly all analyses were followed by standardization of the balance on H_2 purified by passing through palladium. These standardizations fluctuated over a range of about one percent of the total H_2 pressure, 154 mm, supposedly due to disturbances of the balance by vibrations between the determinations. No data were taken which give information concerning the absolute accuracy of the balance, but the agreement of the results reported here with the theoretical values is sufficient to warrant further use of the balance as is in the study of exchanges. The authors believe, and the results show, that with care, analyses of deuterium-hydrogen mixtures can be made to within ± 0.2 percent.

Exchanges above $700^\circ K$ were made in a quartz reaction vessel. Those below that temperature were made in a Pyrex cell containing platinum black as a catalyst. The uncatalyzed reaction at $768^\circ K$ in quartz and the catalyzed reaction at $390^\circ K$ in glass each required approximately a day to reach equilibrium to within the accuracy of the analyses.

The following molecular equilibria are established in the reaction vessel:



Reactions (1), (2), and (3) may be assumed to be completely to the right for the purposes of this investigation. The equilibrium (7) is undoubtedly established, through the mechanism of the other reactions if not directly. The theoretical constants of this equilibrium¹ were assumed in order to calculate the equilibria (4), (5) and (6). Furthermore $K_6 = K_5/K_4 = K_7/K_5$.

¹ H. C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933).

TABLE I.

EXP.	T	K_4	K_5	K_6	$\Delta E_0^\circ(4)$	$\Delta E_0^\circ(5)$
1	876	0.96	1.93	2.01	543	342
2	944	0.97	1.94	2.00	544	348
3	768	0.90	1.86	2.07	591	368
4	691	0.83	1.78	2.14	650	400
5	599	0.80	1.73	2.15	611	384
6	496	0.54	1.40	2.59	900*	527*
7	390	0.60	1.44	2.42	625	392
8	604	0.85	1.78	2.09	545	354
9	689	0.77	1.71	2.22	753*	448*
10	478	0.68	1.57	2.30	661	398
11	388	0.61	1.46	2.40	615	380
* Average, omitting Nos. 6 and 9					598 ± 15	374 ± 7
Theoretical ΔE_0° :						
Urey and Rittenberg ¹			I		591.1	373.3
" "			II		579.1	367.4
Farkas ²					579.0	366.9

The results are summarized in Table I. Urey and Rittenberg's¹ calculations on reaction (4) were extended to $1000^\circ K$ where $K_4 = 0.96$. Likewise $K_5(1000^\circ K) = 1.93$ (calculations are for the Cl^{35} isotope). The agreement of the observed equilibrium constants with the theoretical are shown in Figs. 2 and 3 where $\Delta F^\circ/T = -R \ln K$ is plotted against $1/T$ for reactions (4) and (5). Also in the two final columns of Table I there are given the values of ΔE_0° calculated from the experimental measurements. $\Delta[(F^\circ - E_0^\circ)/T]$ values were obtained from Farkas² and Urey and Rittenberg¹ and the value $(F^\circ - E_0^\circ)/T$ for DCl at $1000^\circ K = 47.58_5$.

The results shown in Figs. 2 and 3 (runs 6 and 9 excluded) all agree with the theoretical values of $-R \ln K$ to within an amount corresponding approximately to an accuracy of ± 0.3 percent in the analysis of hydrogen-deuterium mixtures. The sensitivity of $-R \ln K$ to small errors in analysis may be illustrated by the data of run 4. The final percentage of hydrogen was 53.8, $-R \ln K_4$ being 0.37. The theoretical value of $-R \ln K_4$, 0.27, would be obtained from the data on the reaction if the final percentage hydrogen were 53.6.

Experiments Nos. 6 and 9 show deviations from the mean which are so much larger than the other deviations that they may be disregarded in taking the average value for ΔE_0° . These poor results were probably due to a disturbance of the balance, either during the

² A. Farkas, *Light and Heavy Hydrogen* (Cambridge, 1935), p. 166.

³ Reference 2, pp. 155, 179.

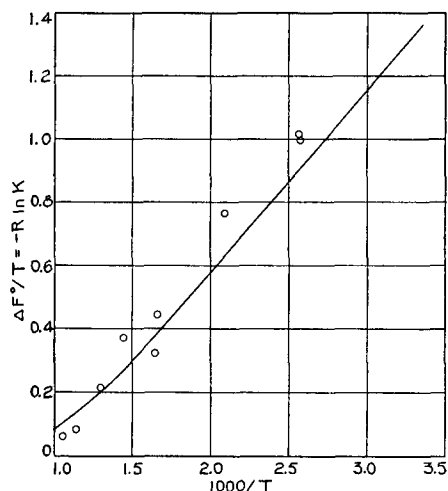


FIG. 2. $\text{H}_2 + 2\text{DCl} = \text{D}_2 + 2\text{HCl}$. —, theoretical curve; o, experimental points.

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

The average values of ΔE_0° , shown in Table I, are higher than the values obtained from band spectra. This might be taken as evidence in favor of Urey and Rittenberg's choice I of the

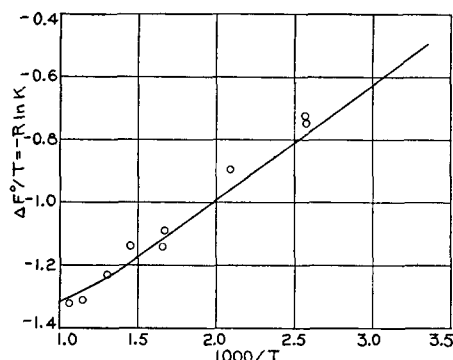


FIG. 3. $\text{H}_2 + \text{DCl} = \text{HD} + \text{HCl}$. —, theoretical curve; o, experimental points.

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.

We are indebted to the Carnegie Institution of Washington for a grant in support of this research, and to Mr. A. I. Rambo for much of the preliminary work in connection with the construction of the balance and apparatus.

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).