[Contribution from the School of Chemistry of the University of Minnesota]

Equilibrium Studies on the Exchange Reaction between Acetylene and Heavy Water[1]

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As a result of the discovery in this Laboratory that an isotopic exchange occurs between acetylene and alkaline solutions of heavy water, it was decided to study the equilibria involved. The reaction takes place due to the ionization of the acetylene, but the determination of the change in the density of the heavy water makes it possible to calculate K_X. The results here reported give the values obtained at 0, 25 and 100° using water containing 9.77 and 18.97% deuterium oxide.

Experimental Procedure

A calibrated liter bulb was attached to the high vacuum line shown in Fig. 1, and then thoroughly evacuated and flamed. Dry carbon dioxide-free air was admitted to the bulb before and after flaming. Opening A was stoppered during evacuation but a slow stream of this same air was passed in through A during the cooling of the bulb. About 1 g. of N alkaline solution of known percentage of D_2O was then introduced from a pycnometer through A and A immediately sealed off in such a way that no water from the flame could condense inside the bulb. Part C of the bulb was then immersed in liquid air for from twenty to thirty minutes, after which the bulb was carefully evacuated. Tests made at this point showed no dissolved air. The bulb was now placed in an ice-bath and carefully purified acetylene run in through B from storage bulb Q to the desired pressure. This acetylene was prepared by the action of carefully purified water vapor on the purest of calcium carbide. The gas was further purified by the method recommended for acetylene. After pressure equilibrium had been established the pressure was read, B closed and the contents frozen out at C with liquid air. The bulb was sealed off at D, placed in a thermostat at the desired temperature and occasionally removed and rotated to redistribute the solution over the walls. At the close of the reaction E was sealed to the vacuum line and the system exhausted. The contents of the bulb were frozen out with liquid air and the capillary F broken. The liquid air bath was then transferred to H and about half of the acetylene was distilled over to H. At this point a salt–ice bath of −20° was placed about C and the remaining acetylene distilled. At this point the manometer reading was found to be approximately zero. About a liter of dry carbon dioxide was then condensed in J by a bath of liquid air and all of the non-condensable gases pumped from the system. The carbon dioxide was allowed to warm up and expand into the reaction bulb to a pressure of about 1 atmosphere, when B was closed. The carbon dioxide remained in the bulb for several hours during which time C was warmed to 70–80° occasionally. This treatment converted the sodium hydroxide to sodium carbonate, restoring the combined water.

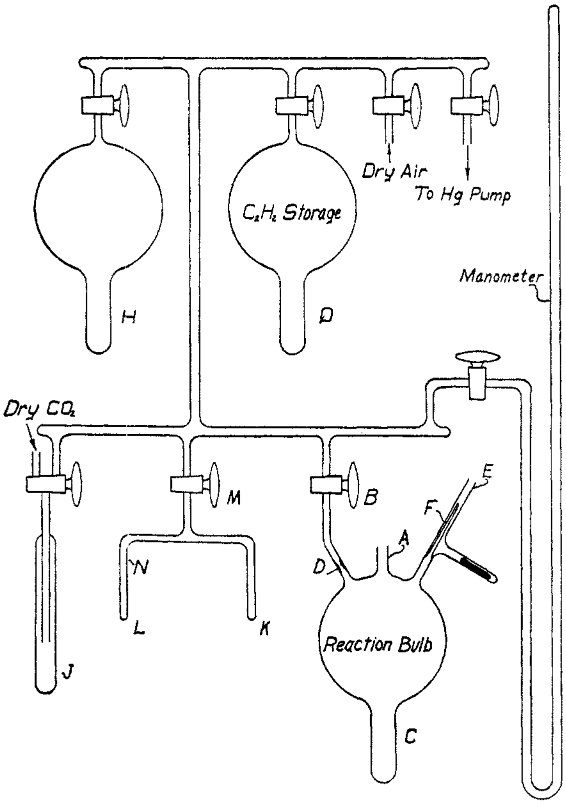

Fig. 1.

The carbon dioxide was removed in the same manner as the acetylene. With K immersed in liquid air the water was then carefully distilled into K from C. K was warmed until the water had melted. With K held at 0° M was cautiously opened to a pressure of about 1 cm. to remove any dissolved carbon dioxide. The pressure external to M was lowered slowly until the water at 0° just started to boil when M was closed, and the water distilled from K to L. Dry carbon dioxide free air was admitted at atmospheric pressure to K and L and L then removed from the system at N and thermostated to constant temperature. The density of the water was determined in a pycnometer of 0.55 cc. capacity. With care the loss of water in the whole operation was of the order of magnitude of 0.1 to 0.15 cc. Finally the reaction bulb was removed, opened at A and D, and the contents washed out with from 8 to 10 small portions of hot freshly distilled water. The washings were combined and titrated with 0.1 N hydrochloric acid using methyl orange as indicator. This gave the amount of alkali used in the original solution.

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EXPERIMENTAL RESULTS

Temp., °C.	Time in hours	Initial concn. of D_2O, %	Corr. press. of acetylene, mm.	Moles at equilibrium C_2H_2	HDO	C_2HD	H_2O	K_X
0	264	9.77	614.05	0.036	0.00667	0.00202	0.0424	0.35
0	288	9.77	361.31	.0212	.00725	.00143	.0417	.38
25	143	9.77	483.6	.0276	.00671	.00184	.0415	.41
25	216	9.77	221.1	.0122	.00753	.00115	.0414	.51
25	113	18.97	733.52	.0398	.01147	.00547	.0378	.45
25	118	18.97	417.38	.0224	.0131	.00369	.0354	.44
100	113	9.77	267.7	.0153	.00736	.00128	.0414	.47
100	168	9.77	562.63	.0323	.0061	.00253	.0433	.55

Results

From the change in density of the water during a given run the amount of deuterium that had reacted with the acetylene could be determined. Table I gives the results of several experiments at the temperatures indicated. The moles of initial and final products of the principal reaction are given and K_X values are calculated for the reaction $C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O$. While there are four possible reactions between solutions of deuterium oxide and acetylene, the concentrations of deuterium oxide justified the calculation for the above reaction alone. Practically all of the deuterium was in the form of HDO at these concentrations. Furthermore, mass spectral analysis of the acetylene at equilibrium showed only a trace of C_2D_2 while the amount of C_2HD present agreed well with the value calculated from the density change. The authors do not attach much significance to the second figure of the K_X values. The averages of the K_X values at the three temperatures are as follows: at 0° K_X is 0.365, at 25° K_X is 0.45 and at 100° K_X is 0.51.

In connection with this investigation, it should be noted that R. P. Bell,[2] as a result of experiments performed at Oxford, questioned the exchange reaction which we had previously reported.[3] In addition to the evidence for this exchange reported in the above equilibrium studies, we have obtained positive proof of the existence of the molecule C_2HD in the equilibrium gas. This was obtained by mass spectroscopic investigation and the amount found compared favorably with the amount determined from the equilibrium study. Furthermore, Glockler and Morrell[4] obtained lines in the Raman spectra for the molecule C_2HD in a sample of gas taken from one of our equilibrium reactions. We feel therefore that the above equilibrium studies represent real equilibrium values within the limit of error of our experimental technique.

The authors wish to acknowledge the valuable suggestions of R. S. Livingston and the assistance of S. T. Yuster which aided greatly in the investigation. Further studies are being carried on at higher deuterium concentrations.

Summary

1. Equilibrium studies have been carried out at 0, 25 and 100° between acetylene and solutions of heavy water.

2. Average values of K_X for the reaction $C_2H_2 + HDO = C_2HD + H_2O$ were found to be 0.365 at 0°, 0.45 at 25° and 0.51 at 100°.

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[2] Bell, THIS JOURNAL, **57**, 778 (1935).

[3] Reyerson, *ibid.*, **56**, 1426 (1934).

[4] Glockler and Morrell, to be published in the *Journal of Chemical Physics*.