d_{20}^{20} 0.8521 was used throughout this investigation, without purification. The authors feel that the results are not in error more than one per cent. in any case and that the accuracy usually exceeds this.

The tabular data given herewith are for use with the empirical equation $y = a + b\ (10)^{-cx}$, where y = weight percentage of allyl alcohol, x = weight percentage of salt and a, b and c are arbitrary constants.

TABLE I

Dev. curve	Salt	Alcohol rich section a	b	c	Limit for "x"	Salt rich section a	b	c	"x" at plait point
1	$(NH_4)_2HPO_4$	31.99	43.01	0.1837	6.0	0	56.0	0.03225	11.37
9	$Na_2S_2O_3$	35.60	41.67	.1696	5.0	0	66.6	.04025	7.93
8	$MgSO_4$	29.46	32.10	.2460	4.3	− 2.31	52.1	.04107	7.12
4	$NaNO_3$	−70.0	159.0	.00910	26.1	2.90	352.2	.04895	18.96
5	K_2CO_3	32.78	43.96	.1608	4.4	0.44	72.44	.0548	6.24
7	NaCl	17.6	84.50	.0625	8.6	0	128.8	.0565	8.90
6	$SrCl_2$	34.65	102.3	.07116	13.3	0	167.3	.04205	14.87
3	NH_4NO_3	0	112.1	.01402	32.5	0	198.0	.02165	33.45
10	$(NH_4)_2SO_4$	31.30	47.20	.1309	7.0	1.73	74.64	.04677	7.62
2	$CdSO_4$	31.27	30.90	.1545	4.9	−10.0	57.35	.01901	12.55

Summary

Data are given for the ternary systems of water and allyl alcohol with ten salts at 25°. From the qualitative and quantitative data, allyl alcohol seems to be more difficult to salt out than either isopropanol or n-propanol. The exponential function seems to express the relationship between the experimental data the best of any tried. Values for the numerical constants in the empirical equations and deviation charts are given for all of the systems.

GREENSBORO, NORTH CAROLINA

RECEIVED APRIL 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Recombination of Hydrogen Atoms in the Presence of Hydrogen Chloride

BY W. H. RODEBUSH AND M. L. SPEALMAN*

Rodebush and Klingelhoefer[1] measured the rate of the reaction

$$Cl + H_2 = HCl + H \qquad (I)$$

at several temperatures. The rate of the reverse reaction

$$H + HCl = Cl + H_2 \qquad (II)$$

may be calculated from their work, but since it is measurably slow it seemed desirable to measure it in order to reduce the uncertainty in the data for this reaction, especially as regards the temperature coefficient. A number of experimental difficulties were encountered which need not be detailed here. The equilibrium constant for (II) above may be calculated to lie between the values 1.6 and 8.5. The measurement is therefore made more difficult by the danger of approaching equilibrium. This difficulty was not encountered, however. What was actually observed was that the amount of chlorine obtained was a great deal less than the limiting equilibrium amount. At the same time, it was observed that a great deal of heat was liberated at the point in the apparatus where the hydrogen atoms came into contact with the hydrogen chloride, and the number of hydrogen atoms recombining was many times the number of hydrogen chloride molecules, so that the recombination would not be explained by any single simple mechanism. The recombination and heat evolution ceased on stopping the flow of hydrogen chloride. The problem, therefore, became one of determining in what way the hydrogen chloride brought about the recombination of the hydrogen atoms.

Experimental

In order to obtain a minimum of catalytic activity for the recombination of hydrogen atoms, the glass to be used was cleaned with hot chromic–sulfuric acid cleaning solution, rinsed with distilled water, then with acetone, and finally dried in a current of air. After *all* glassblowing operations (except, of course, connecting to the pumps and the leaks) were completed, the cleaning, rinsing and drying operations were repeated.

Hydrogen atoms were produced by means of the electrodeless discharge. It was found that a high degree of

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(1) THIS JOURNAL, **55**, 130 (1933).

dissociation could be obtained with a low partial pressure of water vapor by passing hydrogen saturated with water at room temperature and atmospheric pressure into the discharge bulb and then reducing the partial pressure of water vapor to approximately 0.0004 mm. of mercury by means of a trap, cooled with a solid carbon dioxide–acetone mixture, directly following the discharge bulb. The dissociation into atoms is about three times greater with this procedure than it is when the water vapor content is lowered before the hydrogen reaches the discharge bulb.

The measurement of the percentage dissociation of the hydrogen into atoms was done with a Wrede gage connected to an oil manometer. The oil levels in the manometer were read to ±0.01 mm. by means of a cathetometer. A liquid air or carbon dioxide–acetone trap was always used to prevent oil from getting into the reaction chamber. Either "Stanolind" or *n*-dibutyl phthalate was used in the manometer, both of which were satisfactory. "Stanolind" has the advantage of a lower specific gravity—0.879 compared to 1.047 for *n*-dibutyl phthalate, both measured at 25°—while the *n*-dibutyl phthalate has the advantage of a low viscosity compared to "Stanolind."

The hydrogen chloride was prepared by the action of concentrated sulfuric acid on a slurry of sodium chloride in concentrated hydrochloric acid.

In the experiments dealing with the reaction of hydrogen atoms with hydrogen chloride, the amounts of hydrogen chloride and chlorine leaving the reaction chamber were found by freezing out both substances in a liquid air-cooled trap during a run, breaking the vacuum at the end of the run, vaporizing the chlorine and hydrogen chloride in a current of hydrogen, absorbing them in a neutral solution of potassium iodide, and titrating with solutions of known strength. The chlorine was titrated with sodium thiosulfate, either with or without a starch indicator. The hydrogen chloride was titrated with sodium hydroxide, using methyl orange as an indicator. Conductivity water was used in making all solutions. The hydrogen was admitted in measured quantities from a buret.

For regulating the flow of hydrogen and hydrogen chloride, small Hoke needle valves with stainless steel stems were used.

The reaction was carried out by mixing the hydrogen from the electrodeless discharge and the hydrogen chloride in a tube 2.6 cm. in diameter and 40 cm. long. The percentage of atoms in the gas entering the tube was determined by the Wrede gage. The approximate length of the tube required to complete the reaction was easily determined by placing the hand on the tube, since the walls quickly become warm. A silver wire placed at the far end of the tube was found to be a satisfactory means of testing for the complete recombination of atoms, since the rise in temperature will indicate a smaller percentage of atoms than can be determined with certainty by a Wrede gage.

In the absence of hydrogen chloride the tube remained cool, showing that no appreciable recombination of hydrogen atoms was taking place on the walls. This is to be expected when the walls have been rendered catalytically inactive, since the number of triple collisions and double collisions near the wall is too small to produce much recombination. Under these conditions, the silver wire at the end of the tube became very hot. When the hydrogen chloride was admitted, a portion of the tube warmed up quickly and no heating of the silver wire could be detected. When the flow of hydrogen chloride was stopped, the tube became cool throughout its length in a short time, and the heating of the silver wire showed a large percentage of hydrogen atoms to be passing through the tube without recombination. There could be no doubt that, in the presence of the hydrogen chloride, the recombination of hydrogen atoms was practically complete. The data for a number of experiments are given in the table.

Difficulty was encountered in eliminating entirely the formation of ammonium chloride during these tests. Atomic hydrogen reacts with nitrogen to form ammonia which, in turn, reacts with hydrogen chloride to form ammonium chloride. The nitrogen probably came in through small leaks in the apparatus, although there is the additional possibility that it got into the line from the electrolytic hydrogen generator by diffusion.

The ammonium chloride formed was too small in amount to have used up enough hydrogen chloride to make any difference, but there was the possibility that it was ammonium chloride rather than hydrogen chloride which was responsible for the recombination. In order to test this point, the lower half of the reaction tube was entirely covered with ammonium chloride by sublimation of some of the salt from a side-tube and then atomic hydrogen was sent through the tube. There was some reaction of the atomic hydrogen with the ammonium chloride, but most of the atoms passed through the tube and recombined on the silver wire as was shown by the rise in temperature of the wire. Additional information on this question was secured by using tank hydrogen in tests 8, 11 and 12, and tank hydrogen to which about 3% of tank nitrogen was added in tests 9 and 10. Tank hydrogen itself contains about 0.5% of nitrogen. Evidently, ammonium chloride is not the catalytic agent nor does the presence of a considerable quantity of nitrogen in the hydrogen influence the behavior of the phenomenon appreciably.

The condition of the glass surface apparently played a very important role. After an apparatus had been in use for a considerable length of time, the amount of hydrogen chloride required to cause recombination was observed to be greater than for a newly built apparatus. Furthermore, after an old apparatus was "torched," the amount of hydrogen chloride required was smaller than before the heating. For example, the apparatus was "torched" after test 8. The reduction in the amounts of hydrogen chloride required in tests 9, 10, 11 and 12 to effect recombination are presumably the result of this heat treatment.

The Adsorption of Hydrogen Chloride on Pyrex Glass.—The results of the study on recombination indicated that adsorbed hydrogen chloride might play a role in the recombination. Accordingly, an elaborate series of experiments was performed to measure the amount of adsorption. Because of the small amount of adsorption, the results obtained were not highly consistent, but were of sufficient accuracy for the present use.

The adsorption measurements were made by admitting a measured quantity of hydrogen chloride into a flask of known surface and volume, and observing the pressure with an oil manometer. In order to increase the surface

TABLE I

Test	1	2	3	4	5	6	7	8	9	10	11	12
Apparatus number	1	1	2	2	2	3	3	3	3	3	3	3
(H_2 flow in moles per sec.) × 10^7	207	207	204	204	222	197	218	218	160	160	160	160
(HCl flow in moles per sec.) × 10^7	0.75	0.75	6.4	6.4	5.3	8.2	14.0	19.2	8.5	4.5	6.0	10.5
HCl converted to Cl_2, %	13.3	13.3	9.3	9.3	7.8	3.1	8.1	3.6	...	...	...	...
Part. press HCl, mm. × 10^3	1.1	1.3	7.6	5.7	5.8	12	15	29	10	5.5	7.1	14
H_2 dissociated, %	31	23	41	50	43	38	31	21	27	27	26	24
Pressure in mm.	0.336	0.416	0.272	0.205	0.269	0.305	0.266	0.366	0.220	0.220	0.220	0.260
Length of tube warm, cm.	28	23	24	35	33	38	36	27	21	24	28	27
(Moles H_2 recombined per sec.) × 10^7	64	48	84	102	95	75	68	52	43	43	42	38
Moles H_2 recombined per sec. per mole HCl entering per sec.	85	64	13	16	18	9	5	3	5	10	7	4
Initial partial pressure of H atoms, mm.	0.16	0.16	0.16	0.13	0.16	0.16	0.12	0.12	0.091	0.091	0.089	0.099
(Fraction of surface covered by HCl) × 10^3	1.0	1.2	7.3	5.6	5.6	10	11	15	9	5.3	6.8	11

various amounts of glass tubing were packed into the flask. The glass surfaces were treated in the same way as the reaction tube in the recombination experiments. The results obtained indicated that the adsorption was proportional to the amount of surface used, and independent of the amount of water present. A check run with air showed no adsorption. The apparatus was exhausted to a "stick" vacuum between runs. A careful check was made of all possible sources of error in the determination of the amount of adsorption. The results are shown in Fig. 1.

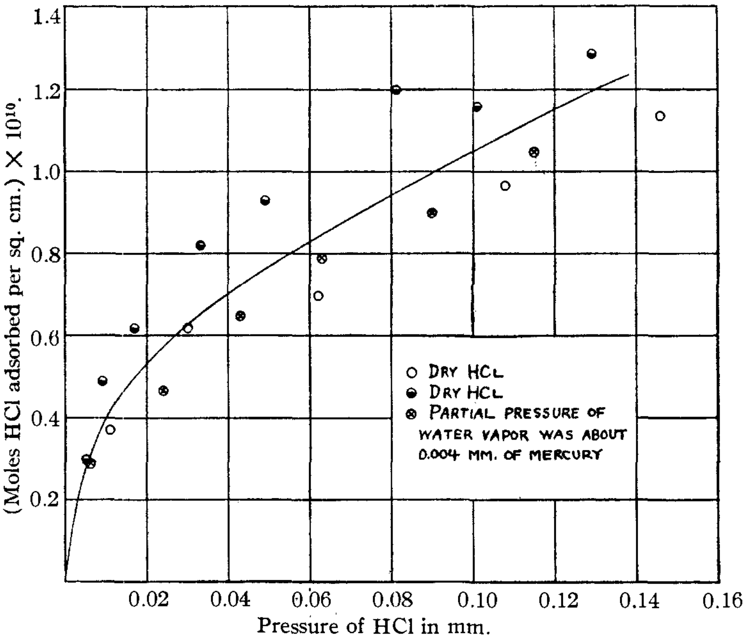

Fig. 1.—The adsorption of hydrogen chloride on Pyrex glass at 25°.

Discussion of Results

While individual runs varied, it was clearly shown by preliminary experiments that, when relatively large amounts of hydrogen chloride were admitted, the recombination took place very rapidly, and the tube became very warm, but only for a short distance from the point of mixing. The studies were made, therefore, with small amounts of hydrogen chloride. The first thing to be observed is that even then only a small amount of chlorine was produced. The partial pressure of hydrogen chloride may, therefore, be assumed to remain nearly constant throughout the tube. It might be that the hydrogen chloride did not take part in the reaction, but it seems more likely that reaction II takes place, and the hydrogen chloride is regenerated by a second reaction. This cannot be I, of course, since no hydrogen atoms would be used up nor would any heat appear. The reaction

$$H + Cl = HCl \qquad (III)$$

may be expected to occur on the walls following II, since it was shown by Rodebush and Klingelhoefer that chlorine atoms are adsorbed to a considerable extent on the walls. The hydrogen atoms cannot, of course, be adsorbed or recombination would take place in the absence of hydrogen chloride. Reaction III should be so rapid as to keep the concentration of chlorine atoms small. There appear to be no other possible mechanisms.

It remains, therefore, to discuss the conditions under which II occurs. From the rate of reaction I, as measured by Rodebush and Klingelhoefer, and the equilibrium constant it is possible to calculate the rate of reaction II. An upper value at 40° (assuming the equilibrium constant of II to be 5) for the constant k_1 in the equation

$$-\frac{d[H]}{dt} = k_1[H][HCl]$$

is 1.074×10^{-13}; the concentration expressed in molecules per cc. The integrated equation using partial pressures instead of concentrations and assuming the partial pressure of hydrogen chloride constant is

$$\ln p/p_0 = -2.5\,Pt$$

where p_0 is the initial pressure of atomic hydrogen, p the pressure at time, t, and P the pressure of hydrogen chloride, all quantities in c. g. s. units. From the data of a typical run (No. 5) the time required for the gas mixture to pass through the reaction zone is estimated as 0.11 sec. Remembering that for each hydrogen atom that reacts according to II another disappears by the rapid following reaction III we calculate that the concentration of hydrogen atoms could be reduced to a per cent. or so of its initial value in a typical run. It is, therefore, possible but not certain that the entire reaction may take place in the gas phase.

The only other possibility is that hydrogen atoms may react with hydrogen chloride molecules adsorbed on the walls of the tube. If we calculate again the results to be expected for a typical run (No. 5) we find that 1.4×10^{13} molecules of hydrogen chloride are adsorbed per sq. cm. Estimating the cross section of a hydrogen chloride molecule as 4 (Å.) we find that the area actually covered is 5.6×10^{-3} times the total area. The number of hydrogen atoms hitting the walls per square centimeter per second is given by the expression

$$p/\sqrt{2\pi mkT}$$

Allowing for the dimensions of the tube and substituting in the expression for the rate of a first order reaction we obtain

$$\ln\frac{p}{p_0} = 2 \times 5.6 \times 10^{-3}\sqrt{\frac{RT}{2\pi M}}\,Kt$$

The factor 2 is introduced because of the rapid following reaction III, and K is the reaction probability per collision. If we assume K of the order of magnitude 10^{-1} then the speed of the reaction on the walls is comparable to the speed of the gas phase reaction. An assumption of $K = 10^{-1}$ amounts to an assumption of a very small heat of activation. The heat of activation in the gas phase is calculated from the results of Rodebush and Klingelhoefer to be about 6000 calories. The heat of adsorption of hydrogen chloride on the walls as calculated from the rate of evaporation by the relation[2]

$$\text{Rate of evaporation} = \nu n e^{-\Delta H/RT}$$

is found to be about 11,000 calories. There is no thermodynamic relation valid here, of course, but it seems not unreasonable that the heat of activation of II may be very small when the hydrogen chloride is adsorbed on the wall.

Since very little heat is produced by II, the chlorine atom would probably remain on the wall until struck by a hydrogen atom when III would take place with the evolution of a large quantity of heat. The heat evolved may result in the desorption of the hydrogen chloride molecule.

Summary

The recombination of hydrogen atoms in the presence of gaseous hydrogen chloride is believed to be due to the reaction

$$H + HCl = H_2 + Cl$$

followed by the rapid reaction

$$H + Cl = HCl$$

The first reaction probably takes place both in the gas phase and on the walls. The second reaction takes place on the walls only. These results constitute an indirect confirmation of the results of Rodebush and Klingelhoefer.

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[2] For a derivation of this relation, see Rodebush, THIS JOURNAL, **45**, 606 (1923); *J. Chem. Physics*. A similar relation has been derived by Frenkel, *Z. Physik*, **26**, 117 (1924).