

The Rate of Reaction of Deuterium with Hydrogen Chloride

Ph. Gross and H. Steiner

Citation: [The Journal of Chemical Physics](#) **4**, 165 (1936); doi: 10.1063/1.1749814

View online: <http://dx.doi.org/10.1063/1.1749814>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/4/3?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Gaseous Reaction Rates at High Temperatures. II. The Dissociation of Hydrogen Chloride](#)

J. Chem. Phys. **45**, 4053 (1966); 10.1063/1.1727456

[Measurement of the Dissociation Rates of Hydrogen and Deuterium](#)

J. Chem. Phys. **36**, 2923 (1962); 10.1063/1.1732403

[The Relative Rates of the Reactions of Hydrogen Iodide and Deuterium Iodide with Methyl Iodide](#)

J. Chem. Phys. **18**, 797 (1950); 10.1063/1.1747778

[Exchange Reactions with Deuterium II. The Photochemical Exchange Between Deuterium and Hydrogen Chloride](#)

J. Chem. Phys. **6**, 345 (1938); 10.1063/1.1750267

[Exchange Reactions with Deuterium I. Deuterium and Hydrogen Chloride](#)

J. Chem. Phys. **4**, 28 (1936); 10.1063/1.1749742



The Rate of Reaction of Deuterium with Hydrogen Chloride

PH. GROSS AND H. STEINER, *First Chemistry Laboratory, University of Vienna*

(Received December 4, 1935)

The reaction $D_2 + HCl = HD + DCl$ has been investigated at temperatures from 765°K to 843°K. The reaction is almost entirely homogeneous, and, up to temperatures of the order of 830°K, bimolecular. The fraction which proceeds heterogeneously is determined in a vessel packed with tubes. The constant of the homogeneous bimolecular reaction can be represented by the following equation:

$$K_c = 6.27 \times 10^{13} \times T^4 \times e^{-26,200/T} \text{ mole}^{-1} \text{ cm}^3 \text{ sec.}^{-1}.$$

At the maximum measured temperature of 843°K deviations were noticed which may have been due to atomic reaction.

I. INTRODUCTION

THIS investigation into the reaction of heavy hydrogen with light hydrogen halides was undertaken to gain acquaintance with the mechanism of exchange reactions of this nature. After it had been found that the process proceeds substantially homogeneously and bimolecularly, the investigation gained in interest, since the reaction turned out to be a typical example of the few reactions of the type $A_2 + BC = AB + AC$ which proceed without complications.

II. EXPERIMENTAL

(1) Materials used

(a) Deuterium was obtained for the greater part by electrolysis of a 0.3 N solution of heavy sodium hydroxide. The electrolysis vessel consisted of a U-tube into which platinum electrodes were sealed. The escaping deuterium diffused through a heated palladium tube closed towards the U-tube, and was collected in a flask. To equalize the pressure on both sides of the U-tube the oxygen evolved was drawn off by means of a water-jet pump controlled by a valve with precision regulation. By prolonged electrolysis it proved possible to produce gas containing 100 percent D_2 . This gas however was only used for calibration purposes, while for the experiments there was used a gas with an HD content varying from five to ten percent. A small quantity of D_2 was prepared from heavy water containing D_2O to the extent of 99.2 percent by decomposition with the aid of metallic sodium.

(b) Light hydrogen, which was used for cali-

bration purposes, was taken from a cylinder. It diffused from a hydrogen flame through a palladium tube into the apparatus.

(c) Hydrogen chloride was produced from sodium chloride and sulphuric acid (both Merck p.a.) in an apparatus consisting throughout of glass. After passing through a wash-bottle and a vessel cooled to -70°C , the hydrogen chloride was frozen out with the aid of liquid air. After sealing and evacuation, the hydrogen chloride was distilled twice and finally after repeated evacuation conducted into a receiving flask. It was found that dry hydrogen chloride does not appreciably attack mercury and stopcock grease, so that it was possible to work without any particular precautionary measures.

(2) The determination of the deuterium content

The deuterium content of the gas was deduced from its heat conductivity which was determined by Schleiermacher's method¹ of the electrically heated wire. With the aid of the cell, which has been described previously,² it was possible with 0.2 cm³ gas at atmospheric pressure to ascertain the total deuterium concentration to within 0.5 percent and consequently that of HD to within one percent. The resistance of the cell amounted to approximately 85 ohms, and the excess temperature of the wire over that of the wall amounted to approximately 20°C. The voltage applied was measured while the resistance was kept constant, and likewise the temperature of the wall. The wall temperature was kept constant

¹ Schleiermacher, Wied. Ann. **34**, 623 (1888).

² Ph. Gross and H. Steiner, Zeits. f. Mikrochemie **17**, 43 (1935).

TABLE I.

$p(\text{mm Hg})$	$E_{\text{D}_2}^2(99.2)\%$	$E_{\text{H}_2}^2$	$E_{\text{H}_2}^2/(E_{\text{D}_2}^2 \times 0.975)$	Corrected for 100% D_2
200	2353	3188	1.390	1.391
300	2417	3311	1.405	1.407
400	2464	3386	1.411	1.412
500	2484	3423	1.414	1.414
600	2499	3452	1.417	1.417

by immersing the cell in ice water agitated by a current of air. Since only relative values of the heat conductivity were needed, we used the square of the scale divisions (E^2) read off at the potentiometer for our computations, since this square is proportional to the heat conductivity. Fluctuations in the voltage of the accumulator used for compensation were of course allowed for.

Since the heat conductivity thus measured showed some dependence on pressure it was determined at different pressures. Table I shows that from 400 mm Hg upwards the relation given by the kinetic theory of gases,

$$E_{\text{H}_2}^2/(E_{\text{D}_2}^2 \times 0.975) = \sqrt{2},$$

is fulfilled to a great extent at 400 mm Hg and higher pressures, the factor 0.975 being given by the ratio of the specific heats of H_2 and D_2 at 0°C .³ In order to save hydrogen the measurements were made at a pressure of 200 mm Hg, slight deviations from this pressure being allowed for empirically. The values for (E^2) were corrected for each gas separately from a pressure of 500 mm Hg to a pressure of 200 mm Hg. The value for HD was computed at a pressure of 500 mm Hg from the relation

$$E_{\text{HD}}^2/E_{\text{D}_2}^2 = 2/\sqrt{3}$$

and was corrected to a pressure of 200 mm Hg by multiplication by the geometric mean of the factors of correction for D_2 and H_2 . Since the experiments were confined to the start of the reaction, it was assumed that the gas consisted solely of D_2 and HD, and the HD concentration was accordingly determined by linear interpolation between the values for D_2 and HD.

Before each run the value of ($E_{\text{H}_2}^2$) for light hydrogen, which served as a reference value was

determined. Table II shows that in general the fluctuations in the reference value are not very great, greater displacements being however observable at times.

TABLE II.

DATE OF RUN	$E^2\text{H}_2$
Oct. 1	{ 3196
Oct. 2	{ 3198
Oct. 3	{ 3192
Oct. 4	{ 3184
Oct. 5	{ 3185
Oct. 7	{ 3179
	{ 3179

(3) Apparatus

As reaction vessels (Fig. 1, *A*) cylindrical tubes of quartz of approximately 200 cm³ capacity in which there were sealed on the one side a quartz capillary tube for charging, and on the other side a quartz tube *B* for the introduction of the thermocouple were used. Two empty vessels and one packed with quartz tubes were used to determine the fraction of the reaction which proceeded heterogeneously. The ratio between the superficial area of the empty vessels to that of the packed vessel was as 1 : 10.

The reaction furnace consisted of a shell *C* made from "Eternit," into which a firebrick pipe *D* was cemented. In this latter there was disposed an iron tube *E* on which the heating wire was wound with the interposition of an insulating layer of asbestos. The reaction vessel held in position by means of perforated brass disks *F* was suspended inside the iron tube. With the exception of the inner space, the furnace was packed with silicate wool. As a result of this precaution the temperature in the inner space did not vary more than 0.1°C from any one part to another. During the run the temperature could be kept constant within 0.5°C by hand control of the current supply.

A silver-platinum thermocouple the voltage of which was measured in a potentiometer using a galvanometer as a null-point-instrument was used for measuring the temperature. The arrangement used allowed of reading accurately to within 0.1° . The thermocouple was calibrated at the boiling point of benzophenone and melting points of zinc and antimony, and was checked against a platinum-platinum rhodium thermo-

³ See A. Farkas, *Ortho-, Para- and Heavy Hydrogen*, (Cambridge, University Press, 1935).

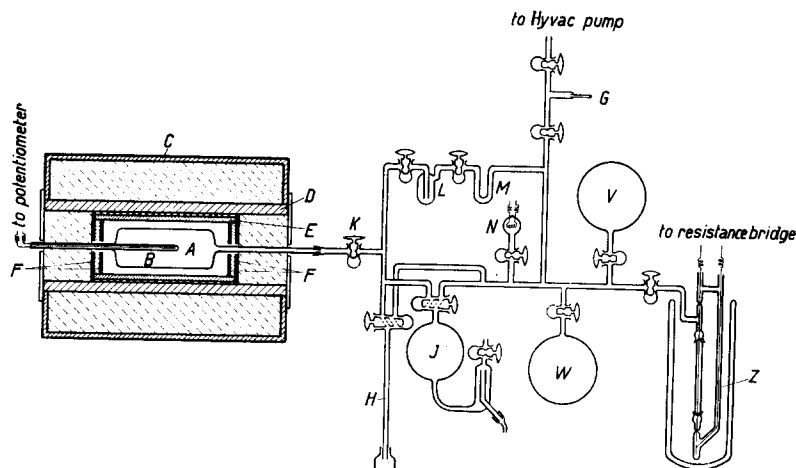


FIG. 1.

couple calibrated by the Physikalisch-Technische Reichsanstalt at Berlin. The maximum deviation was found to be 1°C.

(4) Procedure

The runs were conducted as follows: After evacuation of the apparatus to 10^{-4} mm Hg, the heat conductivity determining cell *Z* was filled with light hydrogen from the palladium tube *G*, for the purpose of determining the reference value of $E_{H_2}^2$.

A manometer *H* which could be selectively connected to the reaction vessel or to the measuring apparatus was used for the adjustment of the temperature. After repeated evacuation, deuterium of known concentration was forced into the reaction vessel from the storage flask *V* with the aid of the Töpler pump *I* and the pressure read off at the manometer. After repeated evacuation, hydrogen chloride was likewise forced into the reaction vessel from the storage flask *W*, the time at which the reaction started being simultaneously noted. After reading off the additional pressure, the stopcock *K* was closed, and the remainder of the apparatus once more evacuated. After conclusion of the run, in order to freeze out the hydrogen chloride, the gas was drawn through the trap *L* and U-tube *M*, (both of which were cooled with liquid air) into the Töpler pump and thence forced into the cell. At high concentrations of hydrogen chloride, even with repeated pumping through the freezing traps, traces of hydrogen chloride were left

behind, the percentage of which was very small but which prevented the measurement of heat conductivity. In this case the gas was introduced into the adjoining sealed-on incandescent lamp *N* the filament of which was heated to white heat. After this treatment the last traces of hydrogen chloride appeared to have been eliminated. It should, however, be noted that at the incandescent filament the equilibrium of the reaction $H_2 + D_2 = 2HD$ becomes established, thus causing an alteration of the heat conductivity of the original gas consisting exclusively of HD and D₂. However these alterations are insignificant at a total-*D*-content of 85–90 percent and come within the limits of error of the heat conductivity determination.

III. EVALUATION OF RESULTS

In Table III complete minutes of two of the runs are given. The constant given in column 13 is calculated from the following equation of differences:

$$\Delta p_{D_2} / \Delta t = K_p \times p_{D_2m} \times p_{HClm}.$$

Since merely the start of the reaction was measured the accuracy of the equation using differences is adequate, as can be demonstrated by series expansion. In Table IV an account of all the runs is given. In this table the first column specifies the vessel used (*e*=empty, *t*=tubes), the second, the mean temperature in degrees

TABLE III.

NO. OF RUN	$T(^{\circ}\text{K})$	t	$E^{\circ}\text{D}_2(100\%)$	E°	% D_2	$p(\text{D}_2+\text{HD})$	$p\text{D}_2$	$\Delta p\text{D}_2$	$p\text{D}_{2m}$	$p\text{HCl}$	$p\text{HClm}$	$K_p \times 10^{-5}$
11	826	0	2364	2404	88.0	162	142.5	18.8	133	142	133	3.47
		30.6		2444	76.3		123.7					
27	826	0	2351	2375	92.5	149	138.0	21.7	127	153	142	3.54
		34.0		2425	78.0		116.3					

Explanation of Table III. In the first column there is given the number of the run, in the second the temperature in degrees K, in the third the duration of the run or the time at which reading was made, in the fourth the value of E° for 100% D_2 , in the fifth the value of E° at the commencement and at the end of the run, in the sixth the resulting percentage of D_2 in the gas, in the seventh the total pressure of D_2+HD , in the eighth the partial pressure of D_2 at the commencement and at the end of the run, in the ninth the decrease in pressure of D_2 , in the tenth the mean partial pressure of D_2 ($p\text{D}_{2m}$), in the eleventh the total pressure of $\text{HCl}+\text{DCl}$, in the twelfth the mean partial pressure of HCl ($p\text{HClm}$) and in the thirteenth the constant K_p .

Kelvin, the third the mean partial pressure of D_2 , the fourth the mean partial pressure of HCl , and the fifth the constant K_p .

IV. RESULTS

It was found that the reaction is bimolecular and for the greater part homogeneous over a range of D_2 and HCl partial pressures from 80 mm Hg to 300 mm Hg. As is shown by the increase of the constants, the conditions appear to change at pressures below 50 mm Hg, but this fact was not followed up for the time being. Measurements made in the packed vessel showed that the reaction proceeded to a slight extent on the wall and that at the most to the extent of 15 percent at the lowest temperature.

In the further evaluation of the results the heterogeneous reaction was included in the cal-

culation, which could all the more easily be done since its order was the same as that of the homogeneous reaction. The constant of the reaction in the empty vessel was subtracted from that in the packed vessel. Seeing that the ratio between the superficial areas was 1 : 10; dividing this difference by ten gave the constant of the heterogeneous reaction in the empty vessel. From the measurements in the packed vessel for two temperatures the values for the remaining temperatures were calculated from the resulting activation energy of the heterogeneous reaction amounting to 44 kcal. In Table V there are given, in the first column the temperatures of the runs in degrees Kelvin, in the second the mean values of K_p with the omission of the values below a pressure of 50 mm Hg, in the third the values of K_p after allowance is made for the heterogeneous reaction, and in the fourth the values for K_c in $\text{mole}^{-1} \text{cm}^3 \text{sec}^{-1}$.

When the values of $\log K_c$ are plotted against $1/T$ (Fig. 2), it is found, that they lie in a straight line, the lowest value deviating somewhat, corresponding to the higher limit of error caused by the long duration of the run and the small amount reacted. On the other hand the value for the highest temperature lies considerably too high, beyond the limit of error. This deviation is believed to be due to atomic reactions occurring when measuring at the highest temperature. The deviations at low pressures may be due to

TABLE IV.

REACTION VESSEL	$T(^{\circ}\text{K})$	$p\text{D}_2$	$p\text{HCl}$	$K_p \times 10^{-5}$
<i>e</i>	843	62.4	72.1	11.4
<i>e</i>	843	39.3	62.0	13.2
<i>e</i>	843	137	146	11.1
<i>e</i>	826	269	312	3.75
<i>e</i>	826	134	133	3.47
<i>e</i>	826	129	142	3.55
<i>e</i>	826	126	138	3.77
<i>e</i>	826	58.2	142	3.74
<i>e</i>	826	39.7	134	4.88
<i>e</i>	826	37.2	148	5.19
<i>e</i>	806	266	319	1.78
<i>e</i>	806	134	176	1.69
<i>e</i>	784	285	291	0.725
<i>e</i>	784	144	156	0.802
<i>e</i>	784	139	157	0.689
<i>e</i>	765	283	306	0.236
<i>e</i>	765	267	311	0.332
<i>t</i>	826	112	215	6.27
<i>t</i>	826	119	140	5.51
<i>t</i>	826	120	123	6.78
<i>t</i>	826	46	124	6.44
<i>t</i>	784	124	248	1.38
<i>t</i>	784	36	243	1.29

TABLE V.

$T(^{\circ}\text{K})$	$K_p \times 10^{-5}$	$K_{p\text{corr.}} \times 10^{-5}$	K_c	K_c theor. I.	K_c theor. II.
765	2.84	2.49	1.99	2.18	2.25
784	7.17	6.48	5.28	5.02	5.08
806	17.4	16.0	13.4	13.2	12.9
826	36.5	33.8	29.0	28.6	27.4
843	112	107	93.8	54.8	51.4

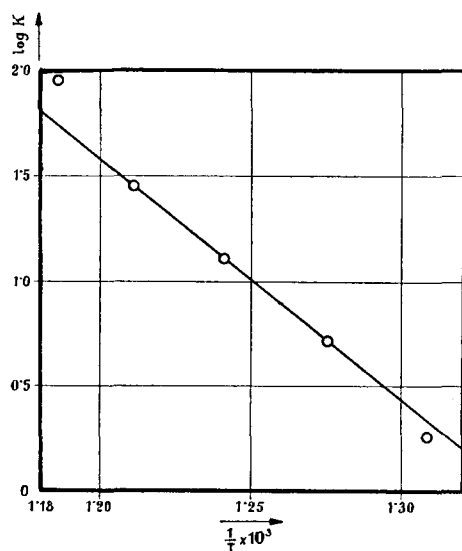


FIG. 2.

the same fact. The authors intend to study this reaction at higher temperatures with modified apparatus. Apart from the change in the energy of activation, there should then be observed a change in the order of the reaction.

The activation energy found from the values determined at the four lower temperatures, taking account of the dependence of the collision number on temperature, amounts to 52.1 kcal./mole. If the collision diameter be calculated according to the simple theory of bimolecular reactions using the formula $K_c = \alpha A e^{-Q/RT}$ (A being the collision number, Q the energy of activation, α the steric factor) there is obtained, assuming $\alpha = 1$, a mean value of 6.5×10^{-8} cm for the collision diameter. By inserting these values in the general equation for the constant of the reaction rate, one obtains

$$K_c = 6.27 \times 10^{13} T^4 e^{-26,200/T} \text{ mole}^{-1} \text{ cm}^3 \text{ sec.}^{-1}.$$

The values calculated from this equation are given in the fifth column of Table V.

V. DISCUSSION

A collision diameter of 6A appears to be too great. At the highest temperatures at which the reaction rate of the hydrogen iodide decomposition has been measured, which approximately correspond to those in the present investigation, collision diameters of the same order of magnitude can be computed with the aid of this simple formula. If the simple theory be modified by the introduction of a part of the non-translational degrees of freedom, which leads to the equation

$$K_c = \alpha A \frac{1}{(S/2 - 1)!} (Q/RT)^{(S/2 - 1)} e^{-Q/RT},$$

in which s is the number of the square terms participating, a steric factor of 0.2 will be found, assuming $s = 6$, the collision-diameter = 3A and the energy of activation = 53.8 kcal. The values for K_c calculated from the latter equation are to be found in the sixth column of Table V. These values appear to be somewhat less in agreement with the experimental results than the values resulting from the former equation. Assuming that a larger number of square terms participate, there are obtained low steric factors and a dependence of the reaction rate on temperature which is out of agreement with the experimental results. In order to arrive at an exact determination of the dependence of the reaction rate on temperature experiments are to be made at lower temperatures in apparatus modified to suit the necessarily long duration of the runs. After conclusion of these experiments, and possibly of similar experiments with other simple hydrogen compounds, the authors intend to furnish a more detailed theoretical discussion.