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Reaction rate constants have been obtained at seven temperatures between 21° and 200° for the reaction $H + CCl_4 = HCl + CCl_3$. The change of reaction rate with temperature is satisfactorily represented by the classical bimolecular reaction theory with a steric factor of 0.007 and an activation energy of 3.45 kcal. per mole. A comparison of the amount of HCl formed with the number of hydrogen atoms entering indicates that complete conversion of atomic hydrogen into HCl by the reaction may be attained at 150–200° under conditions which are determined in the experiments.

SINCE the original work of Wood on the production of hydrogen atoms in a high voltage discharge, and of Bonhoeffer on the properties of hydrogen atoms, many studies have been made of the various reactions involving them. These reactions, and exchange reactions, seem to be the most suitable ones for testing reaction rate theories. The work on hydrogen atoms, however, has been handicapped to a considerable extent by the difficulty of measuring, conveniently and accurately, the concentration of hydrogen atoms entering a reaction on one hand, and of estimating the concentration gradient of the atoms in the reaction zone on the other. As a consequence of these difficulties, most of the experimental work on atomic reactions involving hydrogen and deuterium has resulted in the determination of the energies of activation rather than in the estimate of the specific reaction rate constants. A few years ago Polanyi,[1] in a study of the reactions of hydrogen atoms with saturated alkyl halides, discovered that the reaction between hydrogen atoms and carbon tetrachloride led to but one product, HCl, within the limits of accuracy of such experiments, and suggested that this reaction might be a convenient means of determining more exactly the concentration of hydrogen atoms entering into a gas reaction. Polanyi and his co-workers were unable to measure the rate or the activation energy of the reaction exactly, due to the limitations of their apparatus, but were able to make an estimate of the activation energy as being less than 2.8 kcal. The present investigation had as its aims the study of this same reaction over a wider range of conditions of temperature, pressure and relative hydrogen-carbon tetrachloride concentrations in order to determine the conditions necessary for the reaction $H + CCl_4 = HCl + CCl_3$ to take place quantitatively. In order to obtain an independent check on the previous results of Polanyi, a different method for the determination of the hydrogen atom concentration was used, namely, the calorimetric method. Further, it was hoped to obtain a more accurate measure of the energy of activation and of the specific rate constant.

APPARATUS

Figure 1 is a scale drawing of the apparatus used in the experiments. Since the primary aim at the beginning of the experiments was to determine the conditions for the complete conversion of hydrogen atoms into HCl, the reaction flask A was made as large as the glass-blowing facilities would allow. This flask was surrounded by an electrically heated furnace whose temperature was manually controlled within ±0.5° of the desired temperature. The $H_2 + H$ and CCl_4 entered concentrically at B, the hydrogen mixture through the inner tube and out through a tapered tip with a minimum inside diameter of 3.5 mm, and the CCl_4 through the outer coiled tube and out through an orifice with an inside diameter of 8 mm. With the assumption that the rate of radiation from the furnace to these tubes

[1] E. Cremer, J. Curry and M. Polanyi, Zeits. f. physik. Chemie **23B**, 445 (1933).
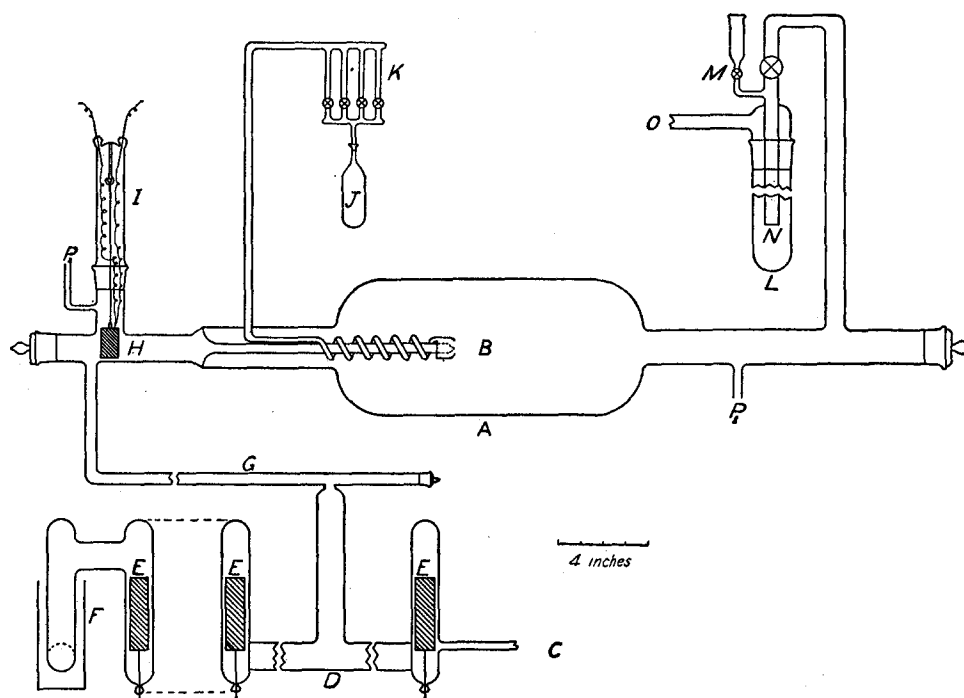
FIG. 1.

was sufficient to maintain the tubes at the furnace temperature, the inlet tubes for both gases were longer than necessary to heat the gases to the furnace temperature before they entered the reaction flask.

Molecular hydrogen entered the system at C and passed through the discharge tube D, the electrodes E of which were mounted in side compartments to prevent spattering of the metal into the main part of the tube. It was found that a discharge tube of this design could be used indefinitely with but a small decrease in efficiency. The discharge tube was cooled by water in the trough F. After leaving the discharge tube, the mixture of H_2+H flowed through a tube G which was 76 cm long and 11 mm inside diameter. This tube was put into the apparatus in order to prevent diffusion effects between the calorimeter bob H and the discharge tube, and was wrapped with asbestos cord.

The calorimeter bob H was a solid piece of silver weighing 116.525 grams and was plated with 0.767 gram of platinum. A copper-constantan thermocouple was soldered into a hole in the bob, and the whole bob was suspended by a cord as shown in the figure. The tube I surround-

ing the calorimeter bob was also wrapped in order to prevent irregularities in the temperature of the thermocouple due to air drafts. The whole assembly of bob and thermocouple could be removed and replaced with a ground stopper.

All glass surfaces in the hydrogen line were coated with phosphoric acid to prevent the recombination of hydrogen atoms on the walls.

CCl_4 was drawn from the reservoir J through the capillaries K. The reservoir was immersed in a beaker thermostat maintained at a constant temperature within $\pm0.1°$. The flow of hydrogen entering the discharge tube was similarly controlled by capillaries which were calibrated as described by Amdur[2] and were checked at regular intervals. Measurements of the hydrogen flow were reproducible to ±1 percent. Tank hydrogen was used without purification. It was saturated with water vapor at room temperature before entering the discharge tube and was kept at atmospheric pressure by an overflow device. CCl_4 was purified by washing with 10 percent NaOH which was then removed by washing with distilled water. After drying, the

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[2] I. Amdur, J. Am. Chem. Soc. **57**, 588 (1935).

CCl₄ was distilled, the first and last 200 cc portions of a liter distillation being discarded.

All thermocouples were calibrated against a standardized platinum resistance thermometer. Thermocouple leads were shielded from stray electric fields. The thermocouples were read on a Leeds & Northrop type K potentiometer of 0–16 mv range.

EXPERIMENTAL PROCEDURE

The range of flows studied was, for the hydrogen atoms 0.5 to 3.5×10^{-3} mole per min., and for the CCl_4 from 8×10^{-5} to 9×10^{-3} mole per min.

With the bob in place the hydrogen atom concentration was determined under conditions of hydrogen flow, pressure, discharge voltage and amperage identical with those in a given experiment. This procedure was particularly satisfactory since it was found empirically that the hydrogen atom concentration varied simply with the pressure in the hydrogen line, making possible small corrections for differences in pressure between actual experiments on the reaction and those experiments on the determination of hydrogen atom concentrations. It was possible to reproduce the hydrogen atom concentrations to within 3 percent for the higher concentrations and to within 5 or 10 percent, at the worst, for lowest concentrations. Over a period of five months it was found that under the same conditions the concentration of hydrogen atoms remained the same, providing that after a period of disuse the discharge was allowed to run for an hour before the measurement. The calculation of the concentration of hydrogen atoms from the temperature rise of the thermocouple was made in the usual way, using the data of Beutler[3] on the heat of dissociation of the hydrogen molecule.

Since it has been indicated in the literature[4] that it is difficult to freeze out HCl quantitatively, careful tests were made. According to the work of Giauque and Wiebe[5] the vapor pressure of solid HCl at liquid-air temperature must be of the order of 10^{-3} mm, so that any difficulty

[3] H. Beutler, Zeits. f. physik. Chemie **B29**, 315 (1935).
[4] H. M. Chadwell and T. Titani, J. Am. Chem. Soc. **55**, 1363 (1933).
[5] W. F. Giauque and R. Wiebe, J. Am. Chem. Soc. **50**, 101 (1928).

must be that of entraining the gas. Several runs were made in which a known volume of standardized HCl solution were evaporated into the system with the pumps running and the HCl frozen out. These experiments gave titrations agreeing within a small fraction of a percent of the HCl taken, so that it may be said definitely that in the presence of an excess of water vapor, HCl is taken out completely in a liquid-air trap. In a typical experiment on the reaction, however, only a small amount of water vapor is present. In this case the HCl may be taken out quantitatively by placing a quantity of snow in the trap. Two sets of experiments checked this. First, an excess of water vapor was introduced into the vacuum line just before the liquid-air trap. This did not increase the amount of HCl frozen out during an experiment. Second, when two successive traps were cooled with liquid air, the second trap showed no trace of HCl. The trap L used in the experiments had a special design, shown in Fig. 1, so that it could be isolated from the system by stopcocks at the conclusion of an experiment. A second large stopcock adjoined the trap at the point O. After an experiment the trap was warmed and the HCl absorbed in the water as the snow melted. When the snow melted more water was introduced through the stopcock M and finally air admitted until the pressure became atmospheric. The trap was then removed and the inner tubes N and O washed. The HCl was titrated with 0.1 N $Ba(OH)_2$.

The procedure in a typical experiment was as follows: Hydrogen was admitted into the system through the desired capillary and was permitted to flow until the pressures at P_1 and P_2 became constant. Then the CCl_4 capillary was opened and again the pressures allowed to become constant. When this had occurred the discharge was turned on and allowed to run for exactly five minutes, following which time the CCl_4 was turned off and a minute later, the hydrogen. After cutting off the discharge the pressures were again read and recorded. The liquid-air trap was then removed and the acid titrated, the whole procedure consuming approximately thirty minutes.

Separate experiments were made to measure the amount of the thermal reaction between H_2 and CCl_4. At the highest temperature studied in

TABLE I. *The reaction of hydrogen atoms with* CCl_4 *at* 21°.

Exp. No.	n_{HCl} $\times 10^5$	n_H $\times 10^6$	P_1 mm	n_C $\times 10^3$	n $\times 10^3$	f	ρ_c $\times 10^9$	k_c $\times 10^{-10}$	k_s $\times 10^{-10}$
322	17.9	45.3	0.78	0.079	3.96	0.396	0.85	7.2	10.6
323	21.4	43.1	.81	.225	4.09	.496	2.44	3.4	4.9
324	22.3	42.5	.82	.295	4.16	.524	3.17	2.9	4.1
325	22.7	41.8	.83	.417	4.27	.543	4.41	2.2	3.1
326	23.2	41.1	.84	.580	4.43	.565	6.02	1.7	2.4
327	24.0	40.4	.86	.783	4.63	.593	7.92	1.4	2.0
328	24.3	38.6	.88	1.265	5.10	.629	11.94	1.0	1.4
329	24.5	38.6	.89	1.433	5.26	.634	13.21	0.91	1.3
330	24.5	38.0	.91	1.655	5.48	.645	14.89	0.82	1.2
161	25.0	35.2	.92	1.980	5.75	.711	17.29	0.90	1.3
163	22.5	31.5	.99	2.980	6.73	.716	23.99	0.61	0.86

the regular experiments, the correction for the amount of HCl due to the thermal reaction was approximately 0.1 cc of 0.1N base.

DATA AND CALCULATIONS

In order to make an estimate of the specific reaction rate, it is necessary to determine the distribution of the reactants in the reaction zone. This involves a study of the stationary state in a streaming, diffusing and reacting gas mixture. The mathematical treatment of this phase of the problem was carried out under the direction of Dr. Lars Onsager, and is described in full in the dissertation of W. C. Bauman on file in the Yale University Library; it will appear in print at a later date. Briefly, the assumptions are that a reacting gas A (in the present instance, CCl_4) is streaming through the reaction zone with a certain linear velocity, and that a second reacting gas B (in the present instance, hydrogen atoms) is introduced into the reaction flask at the center of the vessel and is carried into the reaction flask by component A. It is assumed further that the gas A is in great excess, so that its concentration may be taken as constant throughout the vessel, and that any remaining atoms of B are destroyed by collision with the walls of the vessel. Linear flow is also assumed. While Hartel and Polanyi[6] have studied the stationary state for spherical flames, and Förster and Geib[7] have discussed the distribution of reactants longitudinally in a tube, both of these treatments assume the absence of a wall reaction.

Two cases were considered: the case in which the reaction vessel is a cylinder, the length of

[6] H. v. Hartel and M. Polanyi, Zeits. f. physik. Chemie **11B**, 97 (1931).

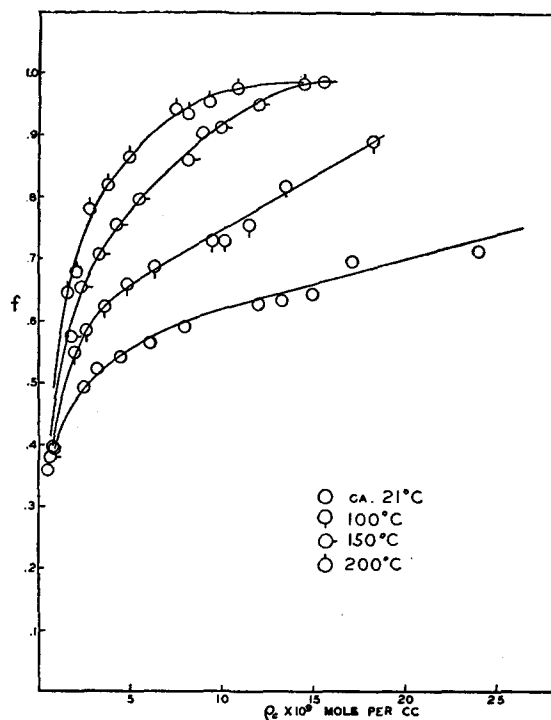[7] v. Th. Förster and K. H. Geib, Ann. d. Physik **20**, 250 (1934).

FIG. 2.

which is much greater than the radius, and the case in which the reaction vessel is a sphere.

The experimental data and the calculated results are shown in Tables I–IV. The experiments included in the tables are all with an approximately constant flow of H_2. Further experiments, not included, with a lower H_2 flow give the same value of the constants. Checking experiments are not shown in the tables. These agreed within 5 percent in the value of f. n_{HCl}, n_H, n_C, and n refer respectively to the mole per minute of HCl, H atoms, CCl_4 and total mole flowing in a given experiment. f is the fraction of hydrogen atoms entering which were converted to HCl, as measured by the titration, thus $f = n_{HCl}/n_H$. ρ_c is the

TABLE II. *The reaction of hydrogen atoms with* CCl_4 *at* 100°.

Exp. No.	n_{HCl} $\times 10^5$	n_H $\times 10^6$	P_1 mm	n_C $\times 10^3$	n $\times 10^3$	f	ρ_c $\times 10^9$	k_c $\times 10^{-10}$	k_s $\times 10^{-10}$
303	15.2	38.3	0.80	0.079	3.81	0.398	0.71	12.2	17.5
304	20.8	37.8	.81	.225	3.95	.550	1.97	7.3	10.5
305	21.5	36.6	.82	.295	4.02	.586	2.59	6.1	8.9
306	22.8	36.6	.82	.417	4.14	.624	3.55	5.1	7.2
307	23.5	35.6	.84	.580	4.34	.660	4.80	4.2	5.9
308	24.1	35.0	.84	.783	4.54	.688	6.26	3.6	4.9
309	25.1	34.4	.87	1.265	5.01	.730	9.40	2.6	3.7
310	25.5	35.0	.85	1.433	5.18	.729	10.12	2.5	3.4
311	26.0	34.4	.87	1.655	5.40	.756	11.40	2.4	3.3
103	27.6	33.6	.88	1.980	5.62	.821	13.36	2.6	3.5
110	27.8	31.2	.95	2.980	6.65	.893	18.18	2.5	3.4

FIG. 3.

EXP. No.	n_{HCl} $\times 10^5$	n_H $\times 10^5$	P_1 mm	n_C $\times 10^3$	n $\times 10^3$	f	ρ_c $\times 10^9$	k_c $\times 10^{-10}$	k_s $\times 10^{-10}$
341	11.7	32.4	0.80	0.079	3.79	0.360	0.57	18.9	27.5
342	20.3	31.5	.82	.225	3.93	.646	1.59	17.4	24.6
343	21.1	31.0	.84	.295	4.00	.679	2.09	14.5	20.4
344	24.2	31.0	.84	.417	4.17	.780	2.84	15.3	21.4
345	25.1	30.6	.84	.580	4.32	.819	3.83	13.2	18.3
346	26.4	30.6	.84	.783	4.53	.863	4.94	12.6	17.2
347	27.6	29.3	.87	1.265	5.07	.941	7.42	13.4	17.9
348	27.4	29.3	.87	1.433	5.17	.934	8.14	11.5	15.4
349	27.1	28.5	.89	1.655	5.39	.953	9.25	11.7	15.2
219	27.1	27.8	.94	1.980	5.79	.975	10.84	12.5	16.3
220	25.9	26.3	.97	2.980	6.77	.983	14.47	10.5	13.7

order and of imaginary argument and is given by:

$$I_0(x) = 1 + \frac{x^2}{2^2} + \frac{x^4}{2^2 \cdot 4^2} + \frac{x^6}{2^2 \cdot 4^2 \cdot 6^2} + \cdots.$$

In either case, $M = (k \cdot \rho_c)/\delta$, where δ is the diffusion coefficient of H in cm^2/sec. The constant calculated from the first equation is designated as k_s and that calculated from the second equation as k_c. For the reaction flask actually used one might expect the proper treatment to be intermediate between these two cases. The difference actually found between k_s and k_c is, however, not large.

If Exp. 261 is taken as a typical caculation, it is found that n_H is 27.1×10^{-5} mole/min. and the HCl found is 9.72×10^{-5} mole/min., giving a value of $f = 0.359$ and of $1/(1-f) = 1.560$. According to Eq. (1) this gives a value of $M = 0.0501$ and according to Eq. (2) a value of $M = 0.0342$ cm^{-2}. Since $k = M\delta/\rho_c$ it is necessary to estimate the diffusion coefficient of hydrogen atoms through almost pure H_2 at a pressure P_1 and at the particular temperature. Taking the values of Steiner[8] at 760 mm and 300°K for the diffusion coefficient of H_2 in H_2 as 1.31 cm^2/sec. and for the diffusion coefficient of H in H as 2.2 cm^2/sec., as well as the diameter of the H_2 molecule, determined from viscosity measurements, as 2.46A,[9] it is possible to calculate the diffusion coefficient of H atoms through H_2. The assumption necessary is that the diffusion coefficient is inversely proportional to the square of the diameter of the diffusing molecule.[10] The values thus obtained are: for the diameter of the H atom, 1.91A; and
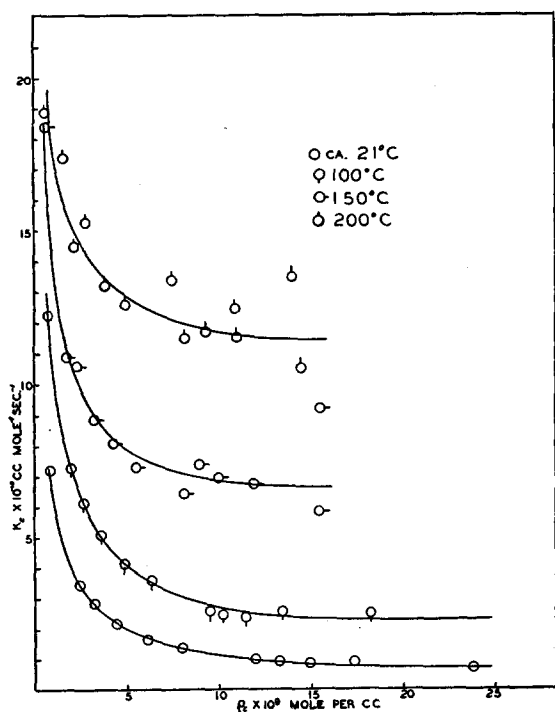
concentration of CCl_4 in mole/cc; k_c and k_s are the specific reaction rate constants calculated on the basis of the theoretical equations. Depending upon the two limiting cases for the shape of the reaction flask, two equations were derived. In the case of a spherical flask the result is:

$$\frac{n_H}{n_H - n_{HCl}} = \frac{1}{1-f} = \frac{\sinh (\sqrt{M} R)}{\sqrt{M} R}, \quad (1)$$

where R is the radius of the reaction flask $= 7.62$ cm. In the case of an infinitely long cylinder, the result is,

$$1/(1-f) = I_0(\sqrt{M}R), \quad (2)$$

where $I_0(x)$ is the Bessel function of zeroth

TABLE III. *The reaction of hydrogen atoms with* CCl_4 *at* 150°.

EXP. No.	n_{HCl} $\times 10^5$	n_H $\times 10^5$	P_1 mm	n_C $\times 10^3$	n $\times 10^3$	f	ρ_c $\times 10^9$	k_c $\times 10^{-10}$	k_s $\times 10^{-10}$
284	13.6	35.7	0.77	0.079	3.67	0.380	0.63	18.4	23.6
285	20.2	35.0	.79	.225	3.82	.575	1.77	10.9	15.4
286	22.0	33.6	.81	.295	3.89	.655	2.32	10.6	14.9
287	23.3	33.0	.82	.417	4.02	.706	3.23	8.9	12.5
288	24.9	33.0	.82	.580	4.26	.755	4.23	8.1	11.3
289	26.2	33.0	.82	.783	4.46	.795	5.46	7.3	10.2
290	27.6	32.0	.84	1.265	4.93	.861	8.12	6.5	8.8
291	28.5	31.6	.84	1.433	5.10	.903	8.91	7.4	10.0
292	28.4	31.1	.84	1.655	5.33	.912	9.92	7.0	9.4
64	24.7	26.0	.83	1.980	5.18	.950	11.97	8.0	10.6
70	25.3	25.6	.91	2.980	6.60	.988	15.50	ʼ 9.2	11.8

[8] W. Steiner, Trans. Faraday Soc. **31**, 623, 962 (1935).
[9] L. Page, *Introduction to Theoretical Physics* (D. Van Nostrand Co., Inc., New York, 1932), p. 309.
[10] H. S. Taylor, *Treatise on Physical Chemistry* (D. Van Nostrand Co., Inc., New York, 1932), Vol. I, p. 214.
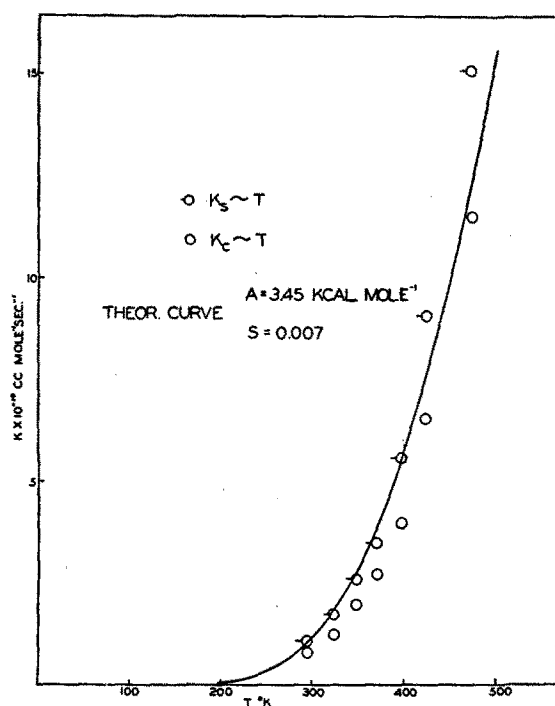
FIG. 4.

for the diffusion coefficient of H atoms through H_2 at 760 mm and 300°K, 1.66 cm²/sec. This leads to a general expression $\delta = 0.2428T^{3/2}/P_1$ cm²/sec. With the values of M obtained above, it is at once possible to calculate k_s and k_c.

DISCUSSION OF RESULTS

Figure 2 is a plot of f against ρ_c at the four temperatures and for the experiments given in the tables, these being all at an approximately constant flow of H_2 of 3.4×10^{-3} mole/min. The experimental points lie on a smooth curve within 5 percent. This may be considered fair accuracy since f depends upon two independent measurements and ρ_c upon three. The results shown in the tables are also plotted in Fig. 3 where the values of k_c are shown as a function of ρ_c. It is entirely evident from Fig. 3 that at the lower values of ρ_c the reaction rate constant increases. This apparent deviation might be expected since the derivation of the equations assumes that ρ_c remains constant, and this, of course, will be true only at higher values of the concentration of CCl_4. Hence the rate constant as calculated from the theoretical expressions

will be constant only for these higher values of ρ_c, and this is seen in Fig. 3. On the basis of a changing and decreasing concentration of CCl_4, we would expect the value of k to decrease, whereas it is actually observed to increase. The explanation is found in the experimental data for those experiments with lowest CCl_4 concentrations, namely Exps. 341, 284, 303 and 322, in which it is seen that the number of mole of HCl found is actually greater than the number of mole of CCl_4 put into the reaction. This evidence would indicate that secondary reactions of the type $H + CCl_3 = HCl + CCl_2$ probably enter at these lower concentrations of CCl_4. Exp. 322 in particular shows that the decomposition of CCl_4 must go beyond the CCl_2 stage at these very low concentrations of CCl_4, since in that experiment the amount of HCl found is more than twice as large as the amount of CCl_4 put into the reaction. While the direct evidence for the existence of such reactions is found only at the lowest concentrations of CCl_4 used, it would be expected that they would occur in all those experiments with low concentrations of CCl_4 and would decrease as the ratio of CCl_4/H increases. These considerations suggest that the limit of k_c or k_s is the actual rate constant for the reaction $H + CCl_4 = HCl + CCl_3$. A plot of k_s against ρ_c gives an exactly similar figure.

Figure 3 shows that there are some appreciable deviations from a smooth curve, particularly at the higher temperatures. This is not because of the failure of the theoretical equations, but rather because of the quantities used in the calculation. The deviations occur in that region where f approaches unity (cf. Fig. 2) and in that region a small experimental error of 5 percent may give rise to an error in the quantity $(1-f)$,

TABLE V. *The specific rate constants at the various temperatures.*

T, °K	k_c cm³ mole⁻¹ sec.⁻¹	k_s cm³ mole⁻¹ sec.⁻¹
294	0.8×10^{10}	1.1×10^{-10}
323	1.3	1.8
348	2.0	2.6
373	2.7	3.5
398	4.0	5.6
423	6.6	9.1
473	11.5	15.1

used in the calculations, of 100 percent or more. This difficulty in the determination of the rate constant may be obviated by changing the design of the apparatus in such a way that f never approaches unity. This change was not made in the present report since one of the principal aims was to determine those conditions which would allow complete conversion of the hydrogen atoms into HCl. Experiments along this line are now in progress.

Experiments exactly similar to those shown in Tables I–IV and in Figs. 1 and 2 were also performed at 50, 75 and 125°. Since the values for f and k show precisely the same dependence upon ρ_c, the data have not been given. In Table V, however, the values of the two constants are given for all seven temperatures as obtained from plots similar to those in Fig. 3. In Fig. 4 the reaction rate constants at all temperatures are plotted as a function of temperature. The curve is the function $k = SZe^{-A/RT}$, S being the steric factor and A the energy of activation, with $Z = 3.1 \times 10^{13}\sqrt{T}$, this latter value being calculated on the usual basis using the values $d_H = 1.91A$ and $d_{CCl_4} = 4.8A$. The values of the constants S and A were obtained from Fig. 5. The straight line in Fig. 5 has been drawn to favor the results at the lower five temperatures and to favor the results calculated on the basis of a spherical flask. This type of weighting, however, does not appreciably alter the values of S and A. The results are $S = 0.007$ and $A = 3.45$ kcal./mole.

It is difficult to make an estimate of the effect of the difference between the actual flow conditions used in the experiments and those assumed in the theoretical derivation of the equations. The primary simplifying assumption of linear flow, which is quite necessary to avoid extreme complexities in the solution of the equations, has not been entirely fulfilled in the present experiments. Further, the glass surface around the jet may recombine some hydrogen atoms. Both effects would tend to make the values of the specific rate constants somewhat too low. These effects would be approximately the same in all experiments.

In all, over two hundred experiments were performed. Those with lower flow rates of H_2 have been mentioned. Other experiments were
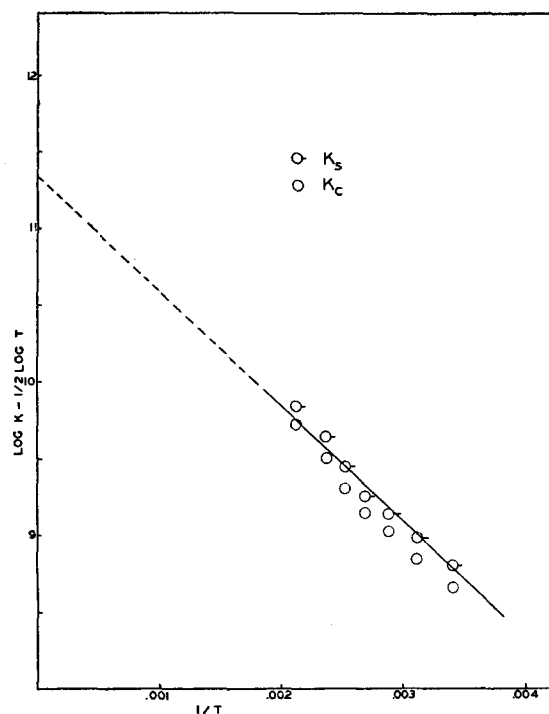

FIG. 5.

carried out in which the concentration of CCl_4 was increased very markedly above the limits of those experiments shown in the tables. In the experiments shown the lower limit of the ratio of CCl_4 : H is approximately 1 : 4, while the upper limit is about 11 : 1. When this ratio, or in general, when the concentration of CCl_4 is increased indefinitely, f suffers a decrease and correspondingly the value of k falls off. For example, when the ratio CCl_4 : H has been increased to 32 : 1, f is found to have decreased by about 17 percent. This decrease is almost certainly because of increased recombination between the calorimeter bob and reaction flask brought about by the increase in pressure. In fact, when the amount of recombination between these two points is calculated from the decrease in f, and plotted against the appropriate function of P_2 and n_{H_2}, the slope obtained agrees with that predicted by Steiner's results[8] within very narrow limits, although the line is displaced by an appreciable amount. This displacement may be partly accounted for by diffusion of hydrogen atoms into the flask, since their concentration is effectively reduced

to zero as they enter, or it might conceivably be due to a constant defect in the calorimetric method of measuring the hydrogen atom concentration.

In a very careful and exhaustive paper by Poole[11] on the general subject of hydrogen atoms, B.S.V.R. Rao points out that Bichowsky and Copeland[12] were in error in their direct determination of the heat of dissociation of the H_2 molecule. In that case there is no longer a direct proof of the correctness of the calorimetric method for estimating hydrogen atom concentrations. It may be pointed out, however, that the agreement between the results of the present paper and the general conclusions of Polanyi,[1] in which the ortho- and parahydrogen conversion

was used as a measure of the hydrogen atom concentration, indicates that the calorimetric method is sound. It seems inconceivable that the reaction of hydrogen atoms with CCl_4 should reach the same limit, namely, 100 percent conversion of the hydrogen atoms into HCl in the range 150–200°, as a result of counter-balancing errors.

The previous discussion of the reaction rate and its calculation may obscure the fact that at intermediate CCl_4 concentrations, the absolute value of n_{HCl} is essentially determined by the absolute value of n_H. In other words, the reaction may be used to determine the concentration of hydrogen atoms actually entering into a reaction with good accuracy and little difficulty. The conditions necessary for apparatus of this design are: a pressure of approximately 0.8 mm, a temperature of 150–200° and a CCl_4 : H ratio of about 10 : 1.

[11] H. G. Poole, Proc. Roy. Soc. (London), **163**, 404 (1937).
[12] F. R. Bichowsky and L. C. Copeland, J. Am. Chem. Soc. **50**, 1315 (1928).

The Calculation of Bond Strengths from Photochemical Evidence

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When predissociation manifests itself in polyatomic molecules by a sudden broadening of the rotation lines of a discrete absorption spectrum, a close correspondence is to be expected between the beginning of the predissociation region and the strength of the bond involved. This principle is used to calculate the bond strengths of C—C in ethane, acetaldehyde, acetone and free acetyl (values: 72.1, 93.1, 96.5 and −19.4 kcal., respectively) and of C—H in methane,
O
acetaldehyde ($CH_3 C—H$), formaldehyde and free formyl (values: 94.8, 114.7, 103.3, and 0.1 kcal., respectively), where the bond strength is defined in reference to the state of the molecule at 0°K. Assuming the validity of the method, the bond strength values given are shown to be accurate within 1.0 kcal. The limitations of the method as well as some implications of the results are indicated.

IT is frequently observed in the absorption spectra of diatomic molecules that within the vibrational bands a sudden blurring occurs because of broadening of the rotational lines as the wave-length is decreased. It has been shown that when predissociation is of this kind in polyatomic

molecules a close correspondence may be expected between the beginning of the diffuse region and the strength of the bond ruptured in the attendant photochemical process.[2] This type of spectrum appears to be present in the cases of formaldehyde, acetaldehyde and acetone. It is proposed in this paper to make the assumption

[1] This paper was begun when the writer was a visitor at the University of California and completed at New York University, which is his present address.

[2] Cf. Burton and Rollefson, J. Chem. Phys. **6**, 416 (1938).