[Contribution from the Gates Chemical Laboratory of the California Institute of Technology, No. 63, and from the Chemical Laboratory of the University of California]

THE RATE OF THERMAL DECOMPOSITION OF SULFURYL CHLORIDE. A FIRST-ORDER HOMOGENEOUS GAS REACTION

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Introduction

Recent development of the theory of reaction rate has indicated the importance of data upon gas reactions of the dissociation type whose rate is proportional to the first power of the pressure of the single reacting substance and is independent of the surface of the containing vessel. Thus far, only one clear case of a reaction of this kind has been recorded, namely, the decomposition of nitrogen pentoxide, the measurements of which were published by Daniels and Johnston.[1] The decomposition of phosphine, previously thought to be a reaction of this type, has been shown by Hinshelwood and Topley[2] to be a heterogeneous reaction. The decomposition of sulfuryl chloride gas into sulfur dioxide and chlorine, $SO_2Cl_2(g) = SO_2(g) + Cl_2(g)$, has been shown in the present work to be a homogeneous reaction of the above type, at least within a certain temperature range.

There has been considerable previous work of a different nature upon sulfuryl chloride. Trautz[3] has published some measurements upon the rate of reaction at lower temperatures in the presence of a catalyst of finely divided charcoal, and has previously determined the equilibrium conditions in this reaction,[4] the vapor pressures[5] of liquid sulfuryl chloride and heat data.[5] Trautz[3] and also Le Blanc[6] have determined qualitatively the effect of light upon sulfuryl chloride and its decomposition products. Recently Hinshelwood and Prichard[7] appear to have shown the reaction in glass containers to be heterogeneous at a temperature of about 280°. This point will be referred to later.

At temperatures above 200°, in the dark, the concentration of sulfuryl chloride in equilibrium with sulfur dioxide and chlorine is negligibly small, but the rate of decomposition in the absence of catalysts is very slow until temperatures above 250° are reached. Moreover, many of the usual catalysts were found by Trautz[4] to have no effect; the only catalyst proving satisfactory was a specially prepared charcoal.

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[1] Daniels and Johnston, This Journal, **43**, 53 (1921).

[2] Hinshelwood and Topley, *J. Chem. Soc.*, **125**, 393 (1924).

[3] Trautz, *Z. Elektrochem.*, **21**, 329 (1915).

[4] Trautz, *ibid.*, **14**, 534 (1908).

[5] Trautz, *ibid.*, **14**, 271 (1908).

[6] Le Blanc, *ibid.*, **25**, 229 (1919).

[7] Hinshelwood and Prichard, *J. Chem. Soc.*, **124**, 2725 (1923).

A large part of the present work was done in the Gates Chemical Laboratory of the California Institute of Technology, but many of the later experiments were made while the author was a Fellow of the National Research Council at the University of California, Berkeley. The author wishes to take this opportunity to express his thanks to Professor R. C. Tolman of the California Institute of Technology and to Professor G. N. Lewis of the University of California for their suggestions and interest in the work.

Materials and Apparatus

The sulfuryl chloride used in this work was obtained from a commercial preparation by several distillations through a fractionating column. The final product was a colorless liquid, all of which had twice distilled within a temperature range of less than 0.1°.

The progress of the reaction was followed by measuring the increase of pressure at constant volume. Since mercury is attacked by the chlorine from the decomposition, and also since the sulfuryl chloride distils from the reaction vessel and condenses upon the cold parts, an all-glass pressure-measuring device was used. The details of the apparatus, which was made entirely of Pyrex glass, are shown in Fig. 1. The pressure-measuring device shown at A, which was used in the early part of the work, is similar to that described by Daniels and Bright.[8] The thin glass diaphragm, however, was supported from the inside as shown. This permitted the diaphragm to be made thin enough to be sensitive to 0.2 mm. change in pressure and still be capable of withstanding an atmosphere of pressure in either direction. Also the method of mounting was such that the zero-point adjustment did not change appreciably with changes in temperature. B is the reaction vessel with the filling tube K made of considerable length to provide flexibility and avoid too rigid construction. C connects with a mercury manometer and D with the pressure-regulating device described elsewhere.[9] The sulfuryl chloride is contained in the bulb E attached to the mercury-sealed stopcock as shown. The leads from the pressure-measuring device came from the capillary tubes MM through seals of wax. The making and breaking at the platinized contacts A was indicated by a rough galvanometer in series with a low voltage obtained by tapping off an appropriate length on a resistance wire through which a small current was passing. In the later experiments the pressure-measuring device described by Smith and Taylor[10] was used in place of the device of Daniels and Bright. In order to facilitate changes in the reaction tube, the apparatus was later altered so that the filling tube K communicated

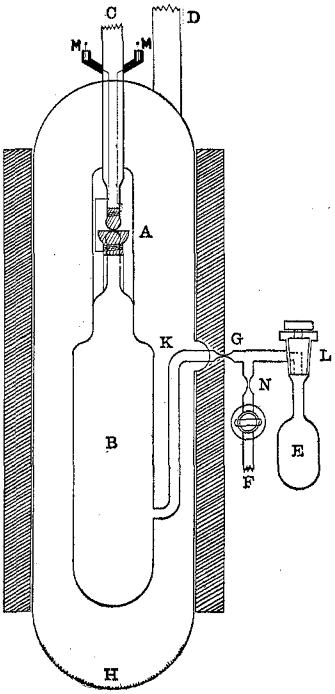

Fig. 1.

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[8] Daniels and Bright, THIS JOURNAL, 42, 1131 (1920).

[9] Smith, *Ind. Eng. Chem.*, 16, 22 (1924).

[10] Smith and Taylor, THIS JOURNAL, 46, 1393 (1924).

with the reaction tube B just below the gage A from which point the small filling tube was led upward close to A and through the outer shell just above A. Also the top of the outer shell, down to within a centimeter or so of K, was made just large enough to pass over the reaction tube. In this way the outer tube could be cut off just below the filling tube and the lower, enlarged part of the outer shell slipped over the reaction tube; this permitted access to the reaction tube and subsequent replacement by sealing together the small diameter part of the outer shell where it had been cut.

The temperature control was obtained by boiling mercury in the outer tube under different constant pressures, the pressures being regulated to 1 mm. or less by the device described by Smith.[9] To the bottom of the outer tube at H was fused a thin coating of finely broken glass which caused the mercury to boil extraordinarily smoothly. From the pressure obtaining in the interior of the apparatus over the mercury could be determined the temperature of the mercury vapor by reference to the accurate vapor-pressure data of Alexander Smith and Menzies.[11] The mercury used was thoroughly electrolyzed and twice distilled. The tube D acted as a condenser for the mercury vapor.

An oil pump was used for evacuating. In the later experiments a charcoal liquid-air trap was placed between the pump and the apparatus to prevent possible diffusion of oil vapors over into the reaction vessel and to prevent the escape of corrosive gases into the pump or the room.

Method of Operation

At the start of an experiment the pressure-regulating device was set to give the desired temperature, the mercury was boiled until it began to condense in the top of the outer tube, which was lagged with magnesia as shown, and until the whole apparatus was up to the desired temperature. The liquid sulfuryl chloride in E was surrounded by a freezing mixture at about —20° or by liquid air, and the apparatus evacuated at F, the connecting tubes being warmed with a flame to remove adhering films of gas and water vapor. The sulfuryl chloride in E was then surrounded by a bath of water at a temperature which would give the desired vapor pressure of sulfuryl chloride, the connecting tubes were warmed to prevent condensation, and the apparatus was washed out several times with sulfuryl chloride by opening the stopcock at L. The apparatus was again evacuated and sealed off at N. Then the stopcock L was opened, filling the reaction vessel B with sulfuryl chloride, and the apparatus was quickly sealed off at G, close to the boiling tube. The pressure of air at the upper surface of the glass diaphragm was increased an appropriate amount and was then read on the mercury manometer. The time when the gage functioned was taken with a high grade split-second stop watch. In this way the reaction was followed throughout its course. The final pressure was obtained by raising the gas to a higher temperature and then bringing it back to the temperature of the experiment or by waiting until the reaction had gone to completion at the temperature of the experiment.

One or two experiments as noted later were made, using for the reaction vessel a 1-liter round-bottom flask in an electric furnace. The furnace was packed with iron nails in the region around the flask in order to ensure uniform temperature. One experiment was made using a reaction tube whose walls were coated with silver chloride by melting the pure dry salt inside the vessel and running it over the surface while the vessel slowly cooled. In this way a fairly thin adherent coating was obtained.

Experimental Results

A few examples of typical experiments are presented in full in Table I. The complete data of the experiments are summarized in Table II. Below

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[11] Smith and Menzies, This Journal, 32, 1434 (1910).

280° the reaction was very slow. Above 330° the reaction had gone practically to completion before the apparatus was sealed off and adjusted for the pressure measurements. All pressures are given in millimeters of mercury, corrected to 0°.

In all, about eight or ten experiments were discarded for various reasons. In several experiments there was a small leak where the apparatus was sealed off at G, which remained unnoticed until the end of the experiment. As a matter of fact considerable care was needed in the sealing-off at this point, since difficulty was experienced due to a small amount of sulfur or of products of reaction of the very hot gas on the glass at the capillary tip which was being heated with an oxygen-gas flame. In other experiments, expecially when the reaction vessel contained glass wool, a small amount of liquid condensed in the protruding capillary stem, probably from incomplete drying and evacuation of the apparatus. Such experiments were always discarded. Some other experiments were discarded due to failure of various parts of the apparatus. However, results of all of the experiments which there was no obvious reason to reject are presented in the table.

A check upon the temperature control was obtained by using the reaction vessel as a gas thermometer. A measurement of the pressure of gas in the tube at 552.3° K. gave 592.4 mm. The same gas at 621.3° K. had a pressure of 665.0 mm., account being taken of the small, measured change in the "zero" adjustment of the pressure gage. Taking the cubical expansion coefficient of Pyrex glass as 0.0000096, the higher pressure becomes 665.4 mm. when reduced to the same volume that the reaction vessel had at 552.3°. Using the gas law, the pressure 665.4 when multiplied by 552.3/621.3, gives 591.5 mm. This difference is small enough to be accounted for wholly by error in the pressure measurements alone. This test was repeated between the temperatures 592.6° K. and 628.5° K. with an equally satisfactory result. It is believed that the temperature control is accurate to a few tenths of a degree at least.

The monomolecular rate constants were calculated from the expression $k_m = \frac{2.303}{t_2 - t_1} \log \frac{p_\infty - p_1}{p_\infty - p_2}$, which is obtained by making appropriate substitutions and integrating the expression $-dp/dt = k_m p$; p_∞ is the final total pressure, p_1 the total pressure at the time t_1, p_2 the total pressure at the time t_2, and p the calculated pressure (at t_1, $p = p_\infty - p_1$) of sulfuryl chloride at any time t. The expression for the bimolecular constants, the pressures having been expressed in millimeters, is

$$k_b = \frac{1}{t_2 - t_1}\left(\frac{1}{p_\infty - p_2} - \frac{1}{p_\infty - p_1}\right)$$

which results from appropriate substitution in and integration of the expression $-dp/dt = k_b p^2$. The tabulated values of the constants are all given in terms of reciprocal seconds. The predominance of the mono-

TABLE I

COMPLETE DATA OF TYPICAL EXPERIMENTS

EXPT. 1

$t = 279.2°$

Total press., mm.		325		335		345		355		365		375		385		395
Time, min.		3.4		15.7		28.1		41.1		54.5		68.3		82.4		96.3
$10^5 k_m$			5.13		5.29		5,25		5.31		5.39		5.52		5.87	
$10^7 k_b$			1.94		..		..		..		..		2.58		..	
Total press., mim.		405		415		425		435		445		484.5		496,6		594.2
Time, min.		110.7		125.0		140.0		155.9		171.8		235.1		260.5		∞
$10^5 k_m$	5.97		6.33		6.38		6.39		6.80		8.15		7.55			Av. 6.09
$10^7 k_b$	.,		..		..		..		..		6.35		..			

EXPT. 5

$t = 278.9°$

8 g. of Pyrex glass wool in tube

Total press., mm.		465.3		474.2		481.4		488.9		504.0		518.1		536.2		555.4		571.6
Time, min.		1.33		2.78		4.00		5.23		7.33		9.50		12.58		16.00		19.08
$10^5 k_m$			31.7*		29.8		30.7		40.2		37.5		36.1		36.2		36.6	
$10^7 k_b$			..		9.4		..		..		..		..		..		15.5	
Total press., mm.		588.8		604.2		622.5		639.7		663.5		683.9		708.9		738.9	...	801.4
Time, min.		23.08		26.15		31.08		36.25		44.40		51.83		61.72		75.95	...	∞
$10^5 k_m$	32.0		37.2		35.2		33.6		32.4		35.8		40.3		45.8	Av. 36.0		
$10^7 k_b$	..		.,		,,		..		.,		..		..		60.7			

EXPT. 7

$t = 299.4°$

Total press., mm.		426.8		433.5		436.9		446.1		454.5		460.3		468.2		473.8
Time, min.		0.73		1.78		2.48		3.58		5.00		5.92		7.58		8.68
$10^5 k_m$			31.4*		24.2*		42.1*		30.8		33.5		25.7		28.2	
$10^7 k_b$			..		..		..		..		10.6		..		..	
Total press., mm.		480.5		488.7		497.1		502.5		516.1		523.0		536.6		545.5
Time, min.		9.85		11.50		12.97		14.20		16.63		18.83		22.15		24.67
$10^5 k_m$	32.5		28.7		34.3		26.8		35.4		20.7		28.2		25.5	
$10^7 k_b$	..		..		,.		,..		13.5		..		..		..	

Total press., mm.		558.3		573.4		587.4		599.7		608.8		620.6		628.2		634.5	
Time, min.		27.72		32.40		37.02		40.93		44.53		48.77		51.07		54.22	
$10^5\,k_m$	31.8		26.1		26.4		29.4		25.1		29.5		37.3		24.0		
$10^7\,k_b$	..		..		..		..		..		18.8		..		..		
Total press., mm.		641.6		651.5		658.5		666.9		696.5		707.5		715.0		...	772.0
Time, min.		59.15		63.43		68.47		74.38		98.10		111.63		119.45		...	∞
$10^5\,k_m$	17.6		30.6		19.9		21.7		23.3		19.4		19.5		Av. 27.1		
$10^7\,k_b$	..		..		..		..		..		..		43.4				

Expt. 10

$t = 320.0°$

3 mm. of H_2O in apparatus

Total press., mm.		469.0		494.5		524.2		545.1		567.4		590.9		607.9
Time, min.		0.58		1.40		2.45		3.27		4.23		5.38		6.35
$10^5\,k_m$			170.7*		169.8*		170.7*		165.9		164.2		156.9	
$10^7\,k_b$			...		...		...		...		79.0		...	
Total press., mm.		625.5		643.6		662.1		671.7		681.2		698.3		705.6
Time, min.		7.48		8.82		10.43		11.47		12.50		14.72		15.90
$10^5\,k_m$	151.8		148.7		142.5		127.8		140.3		132.1		121.2	
$10^7\,k_b$	...		...		...		...		...		137.4		...	
Total press., mm.		721.2		729.0		735.7		744.1		752.5		...		786.9
Time, min.		18.97		20.68		22.60		25.38		29.00		...		∞
$10^5\,k_m$	115.8		121.2		107.2		107.8		100.3		Av. 133.6			
$10^7\,k_b$	...		...		...		...		263.0					

Expt. 24

$t = 328.2°$

Total press., mm.		553.8		591.9		607.8		621.2		631.2		648.6		655.4
Time, min.		1.48		3.02		3.77		4.80		6.00		8.62		10.52
$10^5\,k_m$			398*		453*		342		268		295		230	
$10^7\,k_b$	...		...		541		...		...		...		...	
Total press., mm.		661.1		669.0		673.2		676.4		...		678.0		
Time, min,		12.95		19.63		23.83		32.42		...		∞		
$10^5\,k_m$	200		158		249		214							
$10^7\,k_b$	...		...		3860		...				Av. 244.5			

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* Omitted in calculation of final averages.

molecular mechanism is clear from comparison of the constancy of the values of the two k's which have been tabulated side by side in the experiments in Table I.

It may be remarked that this practice of calculating the constants from neighboring time-pressure measurements rather than from some "initial" time greatly exaggerates the experimental errors. For example, an error of even 1 mm. in the pressure near the end of the experiment causes a disproportionately large error in the constant. Furthermore, if the deviation from the gas law of the mixture of gases at the beginning of the experiment was 2% different from the deviation towards the end, there could easily be introduced 50–100% change in the rate constants. In the case of most of the data here presented, if the constants were calculated from some initial time to several neighboring points well on in the reaction, as is done by Rice and Kilpatrick,[12] for example, there would be but small variation in the constants.

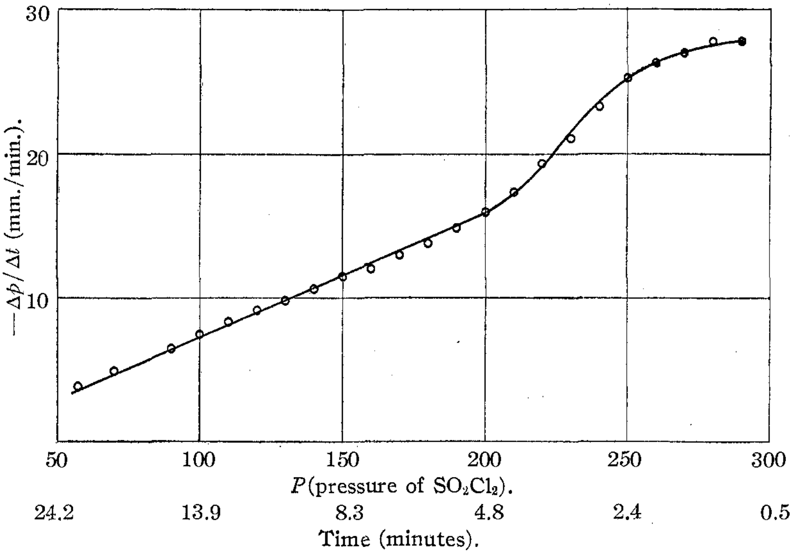

Fig. 2.—From data of Expt. 11.

In taking the final averages for the specific reaction rates from the original data the values of the constants (marked with an asterisk in Table I) which were obtained within three minutes from the beginning of an experiment have been eliminated, since temperature equilibrium may not have been attained in this short time. During this initial time, rise in pressure due to thermal expansion will make the measured rate of reaction too large, while a lower temperature will make the actual rate of reaction too small. Since the tubes leading from the sulfuryl chloride container to the reaction

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[12] Rice and Kilpatrick, This Journal, **45**, 1401 (1923).

vessel were warmed with a flame to prevent condensation, the gases which enter the reaction tube may be either too hot or too cold. The resulting deviations from the correct reaction rate may be quite complicated, as illustrated by Fig. 2, which is constructed from the data of Expt. 11, where the measured values of the rate of decomposition $-\Delta p/\Delta t$ are plotted against the calculated pressure p of sulfuryl chloride. Time intervals are also indicated on Fig. 2 so as to show the portion of the data that are neglected in taking the final average. It will be noted that only the theoretically reasonable straight-line portion of the curve has been used for the final average.

The data recorded for Expts. 1 and 25 were read from the smooth curve obtained by plotting the original data, for the reason that more experimental points were obtained in these particular runs than would warrant calculation of the constant for each pair of values.

In some of the experiments, as indicated in Table II, the reaction vessel contained Pyrex glass wool or broken glass distributed as uniformly as possible throughout the reaction tube. The amount of glass wool varied from 6.5 to 8.0 g. The average diameter of the wool was about 0.0076

Table II

Summary of the Experimental Data

Expt.	t °C.	p range covered, Mm. Hg at 0°	No. of meas.	p_∞ Mm.	Relative area/vol.	Max. range of variation of $10^5 k_m$	Av. dev.	$10^5 k_m$, mean	Remarks
1	279.2	325–497	15	594.2	1.0	5.1–8.1	0.7	6.09	
2	278.6	401–660	18	744.9	1.0	7.4–14.2	1.1	10.71	
3	280.0	186–300	9	353.1	0.2	7.9–13.7	2.0	11.00	In 1-l. flask in furnace
4	278.9	540–858	22	893.3	20.0	9–53	14.7	30.9	Glass wool in tube
5	278.9	474–739	16	801.4	20.0	30–46	2.9	36.0	Glass wool in tube
6	278.8	396–551	10	660.4	20.0	32–54	5.6	40.8	Glass wool in tube
7	299.4	446–715	28	772.0	1.0	18–37	4.3	27.1	
8	300.2	473–587	6	801.3	20.0	85–92	2.1	88.6	Glass wool in tube
9	319.6	115–141	7	145.7	1.0	105–161	17.2	130.0	Gas dried with P_2O_5
10	320.0	545–753	16	786.9	1.0	100–166	18.0	133.6	3 mm. of H_2O in apparatus
11	319.5	655–827	13	875.3	1.0	95–202	23.3	127.9	
12	320.2	426–647	13	652.7	7.5	117–181	15.9	156.0	Tube filled with broken glass
13	320.0	385–582	15	595.0	0.2	70–183	36.4	125.6	In 1-l. flask in furnace
14	320.0	451–654	19	674.3	20.0	106–140	9.0	123.9	Glass wool in tube
15	320.5	597–807	15	819.7	20.0	121–181	16.6	141.0	Glass wool in tube
16	319.9	490–631	16	641.9	1.0	105–149	11.1	121.8	Walls coated with AgCl
17	319.1	838–987	9	1100.6	20.0	121–198	21.1	174.1	Glass wool, p_∞ uncertain
18	320.4	596–743	13	749.6	20.0	132–228	21.6	197.0	Glass wool, p_∞ uncertain
19	319.6	495–758	20	847.8	1.0	85–137	6.1	95.3	9.8 mm. of H_2O in apparatus
20	320.0	1089–1292	11	1327.9	1.0	133–226	33.3	190.7	Very high pressure
21	320.3	427–713	15	743.7	0.8	71–92	4.7	86.0	Large diameter tube
22	320.1	333–451	16	458.4	0.7	66–94	7.2	76.6	Large diameter tube
23	319.5	335–562	22	565.3	1.0	60–88	6.9	78.1	Gas dried with P_2O_5
24	328.2	608–676	9	678.0	1.0	158–342	45.2	244.5	
25	329.3	650–840	10	850.2	1.0	124–308	56.3	251.1	
26	329.7	587–635	6	643.2	1.0	239–346	41.0	294.0	
27	330.1	673–822	7	918.2	20.0	290–343	12.9	307.3	Glass wool in tube
28	329.7	661–855	12	867.2	1.0	225–419	76.9	349.7	Temp. regulation poor
29	328.9	464–725	12	744.7	0.8	122–214	14.0	139.7	Large diameter tube

cm. The surface area of 7 g. of the glass wool, taking the density of Pyrex glass as 2.25 was at least 1660 sq. cm. Due to breaking up of the wool the total area would be somewhat greater than this. The reaction vessel used in most of the experiments was 11 cm. in length and 2.0 cm. in diameter. The internal surface area was about 82 sq. cm. and the volume about 38 cc. The ratio of area to volume was about 2.2. This ratio was set equal to unity in calculating the relative values which are given in Table II. The surface-volume ratio in the vessels containing the glass wool was thus at least 20 times greater than that in the vessels without glass wool. In one experiment the reaction vessel was filled with pieces of 5mm. diameter glass tubing cut in 1cm. lengths. A summary of the experimental data including the relative ratios of area to volume in the different experiments, calculated from the dimensions of the vessels and the amount of glass wool or broken glass, is tabulated in Table II.

Regarding the effect of water vapor on the reaction, Expt. 19 seems to show that the effect is to slow down the reaction somewhat. However, this experiment (19) could never be duplicated, and other experiments both with very dry gas (dried by distilling through phosphorus pentoxide) and with moist gas did not show any consistent effect.

In many of the experiments there seems to be a slight general trend in the values of the constant. This effect could arise among other causes, either through impurities in the sulfuryl chloride, or through a small amount of a side reaction. The sulfuryl chloride used could hardly contain any considerable amount of impurity in view of the method of its preparation. The question of side reactions is one about which we can say that there seems to be some evidence of a small amount of side reaction in the photochemical reaction as might be expected, since sulfur dioxide alone is subject to the action of light, but there is no reason to believe that any side reaction occurs to an appreciable extent in the dark. Further than this we may state that there can be no side reaction that comes to equilibrium with the gaseous mixture, or that produces a volatile solid or liquid product, since in this case the measured pressure of the mixture of the gases inside the reaction vessel at the different temperatures from 279°C. to 355° C. would not be calculable from each other by the gas law as shown above. We have also some additional evidence bearing on this point, as follows. The reaction vessel was filled with pure sulfuryl chloride gas at 100°, where no appreciable dissociation occurs, the pressure was measured and the vessel was then heated at 320° until decomposition was complete. The actually measured final pressure was 2% greater than that which was calculated from the original pressure of pure sulfuryl chloride. It is possible, therefore, that a slight amount of side reaction occurs at 320°, although perhaps adsorption on the glass walls may have been responsible for this result.

Discussion of the Results

The experimental results show that a 20-fold increase of the ratio of area to volume in the reaction vessel increases the rate of reaction from 3- to 4-fold at 280° in some cases and in others a 200-fold increase has about the same effect, while at 320° an increase in this ratio from 0.2 to 20.0 causes no increase in the rate, within the limit of experimental error. This is interpreted to mean that a small fraction of the reaction at the lower temperatures takes place on the walls of the reaction vessel, but at the higher temperatures this fraction is negligible compared to the fraction which is a true gas reaction,

Expts. 21, 22 and 29, which were made in larger reaction vessels, gave lower values for the rate constants. Yet Expt. 13, which was made in a 1-liter, round-bottom flask in an electric furnace, did not give an appreciably lower value. Furthermore, Expt. 23, which was made in a reaction vessel of the usual size, gave a very low value for the constant. Also, Expt. 16, in which the walls of the tube were coated with silver chloride gave the usual rate. It seems, therefore, that at 320° there is no consistent effect due to surface. As yet, we are unable to state why three experiments at 320° (Nos. 21, 22 and 23) and one experiment at 329° (No. 29) should have given much lower than the average results. Further work is being done on this, however, and will be reported later. For the present we prefer to regard these few experimental deviations as accidental, and to take as final values the results given by the majority of the experiments.

As mentioned above, Hinshelwood and Prichard[7] made a few experiments on the rate of decomposition of sulfuryl chloride at temperatures around 280°. They concluded that the reaction was heterogeneous. However, we believe we have shown conclusively that only a part of the reaction at this temperature takes place on the walls. Furthermore, they base their conclusion chiefly upon the high rates they obtained in experiments in which the reaction vessel was filled with glass wool. In the use of glass wool for this purpose we have found it essential to clean and dry very carefully the wool used. In an early experiment in which glass wool was used we obtained an exceptionally high rate, but noticed that a liquid condensed in the protruding stem of the apparatus at G in Fig. 1. When the glass wool was removed, sealed in a tube attached to a vacuum pump and heated with a flame, surprisingly large quantities of gas and liquid were given off, in spite of the fact that the glass wool had previously been heated to 280° in a vacuum for more than an hour. We were careful thereafter to clean and dry thoroughly the glass wool used by heating with a flame and pumping off first, and after introduction into the apparatus, pumping it off for a considerable time at 360° without subsequent exposure to the air. Also, Hinshelwood and Prichard doubtless used soda glass, whereas in the present work Pyrex glass and Pyrex glass wool were used throughout. The high rate they obtained we suggest may be due to spurious effects.

The final averages of the constants are somewhat arbitrary due to the fact that there was a considerable trend in the values of the constants calculated between successive measurements in a single experiment. We have tried plotting log $p_{SO_2Cl_2}$ against t and deriving the constant from the best straight line through the points. But the placing of the straight line through the points is also somewhat arbitrary and in general leads to about the same values as those presented in the table. In most of the experiments the points at the beginning of an experiment are high, and those at the end slightly low, while those in the middle of the run lie very close to a straight line.

In Table III are presented the values for the reaction-rate constants which for the present we will take as best values. The constant tabulated here for temperatures around 320° is the average of the first eight values for this temperature in Table II, and for temperatures around 330° the average of the first four values in Table II. The values given here for the lower temperatures are the smallest observed values, which might be supposed to be those least affected by wall reaction. There are also presented here values for the critical increment or heat of activation q which are calculated by integrating between two temperatures and inserting the respective values of the measured rate constants k_m in the Arrhenius equation, $d\, ln\, k_m/dT = q/RT^2$. The best value of q is probably that calculated from the data at 320° and 330°. It is seen that the values calculated from the data at lower temperatures are slightly lower than this, as we might expect on account of the wall catalysis.

TABLE III

FINAL BEST VALUES OF THE RATE CONSTANTS AND THE HEAT OF ACTIVATION

Temp., ° K.	552.3		572.5		593.1		602.4
$10^5\, k_m$	6.09		27.1		132.1		274.2
q, cal./mole		46,400		51,850		55,700	

A Test of Various Theories of Reaction Rate

Although we are convinced that the "single-frequency" theories of chemical reaction rate can never explain thermal reaction rate in general, it may nevertheless be of some interest to mention briefly the application of these theories to the data here presented.

It was originally assumed by Perrin[13] that the process of activation of a molecule, whereby it acquires the energy q/N, consisted always in the absorption of a single quantum of radiation of frequency ν and thus that $q = Nh\nu$, where h is Planck's constant. On this theory, then, light of

[13] Perrin, *Ann. phys.*, 11, 5 (1919).

the frequency ν should cause photochemical decomposition of the molecule. The value of ν thus calculated from the above value of 55,700 calories per mole for q would give $\nu = 5.86 \times 10^{14}$, or $\lambda = 512\ \mu\mu$. Now, Le Blanc worked with light in the region from 200 to $400\mu\mu$. While he does not mention having tried the effect of light of wave lengths longer than $400\mu\mu$, presumably light of the wave length $512\mu\mu$ would have no effect and, indeed, light of the wave length $400\mu\mu$ has no effect when chlorine is absent. It may be recalled that in the case of nitrogen pentoxide, also, the wave length so calculated was longer than any active wave length. These results indicate that the process of activation is not so simple as was supposed by Perrin. And, indeed, other serious objections have been raised against this theory, so that it now seems evident that the simple theory of Perrin should be abandoned.[14]

Trautz and Bhandarkar[15] have assumed that the dissociation of a molecule depends upon the number of collisions between its constituent parts. The equation they derive on this basis is

$$k_m = \frac{8.72 \times 10^4}{\sigma} \sqrt{\frac{A + B}{AB}}\, T^2\, e^{-\frac{Q}{RT}}$$

where σ is the mean diameter of the reacting molecules, A would be the molecular weight of sulfur dioxide and B that of chlorine. The other symbols have their usual significance. Taking the value of $k_m = 274.2 \times 10^{-5}$ at $T = 602.4°$ K. and $k_m = 132.1 \times 10^{-5}$ at $T = 593.1°$ K. and $\sigma = 4 \times 10^{-8}$, we find $Q = 53{,}350$ cal. per g. mol. Using this value of Q, the value of k_m at the temperature 602.4° is calculated to be 7.2×10^{-3} as compared with the experimental value 2.74×10^{-3}, which is a satisfactory agreement.

W. C. McC. Lewis and McKeown[16] have given the equation $k_m = \frac{8\pi^2 e^2 n_m{}^3 \nu^2}{3me^3} e^{-\frac{h\nu}{kT}}$, in which they interpret the data of Daniels and Johnston on nitrogen pentoxide to indicate that $n_m{}^3$, the cube of the "index of refraction" of the individual molecules, has the value 1.2×10^7. A treatment similar to that given in the case of the equation of Trautz and Bhandarkar gives $Nh\nu = 55{,}700$ cal. per mole and $k_m = 5.94 \times 10^{-6}$ at 602.4° K. as against the experimental value of 2.74×10^{-3}. W. C. McC. Lewis had previously taken the value of n to be unity, but the equation then gave far too low values for k_m. In agreement with Perrin, Lewis assumed that the process of activation for reaction consisted in the absorption of radiant energy of almost monochromatic character. From the present result it appears that even ascribing this large value to n, the

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[14] For a discussion of these objections, see Lewis and Smith, THIS JOURNAL, **47**, 1508 (1925).

[15] Trautz and Bhandarkar, *Z. anorg. allgem. Chem.*, **106**, 95 (1919).

[16] Lewis and McKeown, THIS JOURNAL, **43**, 1288 (1921).

equation gives a far too low value for k_m. This result again seems to show that the process of activation is more complicated than the simple theory of Perrin would indicate.

The equation proposed by Dushman[17] is $k_m = \frac{Q_A}{Nh} e^{-\frac{Q_A}{RT}}$. As before, we calculate Q_A = 55,700 cal. per mole and $k_m = 3.41 \times 10^{-6}$ at 602.4° K. Dushman's equation was first applied to the phosphine reaction, but this reaction, as stated above, was shown to be heterogeneous. Tolman,[18] however, showed that this equation applied approximately to the nitrogen pentoxide reaction. Dushman's equation would seem to involve the idea that the fraction of the molecules which are activated is equal to $e^{-\frac{Q_A}{RT}}$ and that their rate of decomposition is proportional to the energy of activation. It was, however, shown by Lewis and Smith[19] that this form of equation would result from the assumption that reaction takes place whenever collisions occur between molecules in the various energy states and quanta of sufficient additional energy to total the energy of activation and that the motion within the molecule which is important for reaction is one of only two degrees of freedom (one rotational orbit, for example). For complicated molecules which have many degrees of freedom, it is not unreasonable to suppose that many of them may be important for the reaction in question. The equation from this point of view might then give far too low results.

Eliminating the case of the phosphine reaction, since the considerations involved in the various theories apply only to homogeneous reactions, the results of the two available tests on these theories are as follows. The equation of Trautz and Bhandarkar fits the data for sulfuryl chloride, but gives far too high results for nitrogen pentoxide. The equation of W. C. McC. Lewis and McKeown was made to fit the data for nitrogen pentoxide, but gives results for sulfuryl chloride which are a thousand times too low. Dushman's equation agrees with the results for nitrogen pentoxide, but for sulfuryl chloride gives values a thousand fold too low. It seems, therefore, that none of these theories will have more than limited application.

Summary

1. There have been described a satisfactory apparatus and technique providing for a constant uniform temperature and easy temperature control, by which the rates of those reactions that are accompanied by a change of pressure can be measured.

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[17] Dushman, This Journal, **43**, 397 (1921).

[18] Tolman, *ibid.*, **43**, 269 (1921).

[19] It should be clearly noted, however, that the equation derived by Lewis and Smith (Ref. 14) is Dushman's equation in form only. It was derived from wholly different assumptions.

2. The reaction, $SO_2Cl_2(g) = SO_2(g) + Cl_2(g)$, in glass containers at 320° C. has been shown to be a first-order reaction whose rate is uninfluenced by a 200-fold increase of the ratio of surface to volume in the container. At lower temperatures there seems to be a small amount of wall reaction or some spurious effect caused by the large glass surface present.

3. Deviations from the normal rate were observed in a few experiments, but these deviations lacked consistency, and at present cannot be explained. Further work is being done in this connection and will be reported later.

4. The frequency of light, which early theories of reaction rate predict from the temperature coefficient of the reaction velocity, to be photochemically active, probably has no effect on the reaction.

5. Since the phosphine reaction was shown by Hinshelwood and Topley to be heterogeneous, there remain two cases of a first-order homogeneous gas reaction, namely, the decomposition of nitrogen pentoxide studied by Daniels and Johnston and the present reaction of sulfuryl chloride. A summary of the tests of various theories of this type of reaction is as follows. The equation of Trautz and Bhandarkar, based upon a consideration of the number of collisions between the constituent parts of the molecule, fits the data for sulfuryl chloride, but gives far too high results for nitrogen pentoxide. The equation of W. C. McC. Lewis and McKeown, which assumes activation by almost monochromatic light and attributes a very high value to the "index of refraction" of an individual molecule, was made to fit the data on nitrogen pentoxide, since the "index of refraction" was deduced from these data. But this equation gives far too low results for sulfuryl chloride. The empirical equation of Dushman approximately fits the data on nitrogen pentoxide, but gives far too low results on sulfuryl chloride. It thus seems that none of these theories is of general application.

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