WATER IN SILICA GELS

AND

SODIUM SILICATE IN WATER

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Following an investigation of the effect of some addition agents (mono- and polyhydric alcohols, aldehydes sugars and some ketones) on the time of set of silica gels of different pH values and at various temperatures, it seemed that data on the state of the water in the gels would be of value when correlated to the results observed.

Satisfactory data on bound and free water in silica gels was not available in the literature. Therefore, this study was planned to try to obtain the desired data by calorimetric measurements.

For this purpose a new calorimeter was designed, incorporating several new features, not recorded in the literature, that should increase the accuracy of the results and decrease the difficulties in manipulation.

Urgent war research prevented construction of the calorimeter.

To carry out the above study it was necessary to have some knowledge of the behavior of sodium silicate in water.

Sodium silicate has been reported by some to be colloidal, by others to be ionic in nature, when in water.

Plans were made to study this system when titrated by acids.

Urgent war problemsprevented completion of the study, but it was observed that Baker's 'crystalline sodium silicate, $Na_2SiO_3.9H_2O$' behaved in water as if H_2SiO_3 were a dibasic acid.

WATER IN SILICA GELS

Introduction

Although Graham's work is generally considered as being the starting point of present day studies on silica sols and gels, Hurd (1) points out that colloidal silicic acid has been known for over 200 years. He refers to work by Meyer and Bergmann before 1800 on solutions of colloidal hydrated silica and by Berzelius on "soluble silicic acid".

Within recent years silica gel has received considerable attention because of its use as a sorbent, catalyst and catalyst support. The sorption of about fifty materials on silica has been recorded (2).

There is an analogy between gelation of silica sols and many physiological functions; such as, deposition of bone and cartilage, formation of mucus, etc. (3). The reverse of gelation, i.e., the peptization of silica gel, is involved in the disease known as silicosis.

Gelation is also involved in the setting of concrete and cements, solidification of many minerals, rubber, plastics and foods (e.g. jellies).

The structure of a gel when formed might, by analogy, give an insight into the structure of many of these substances. Bound water in gelatin has been studied in an attempt to gather information regarding bound water in fish muscle (4).

From these few examples it will be realized that gelation and gel structure is of interest in many fields. The study of bound water in silica gels should contribute information on the structure of not only silica but other gels.

Little is known about the factors governing bound water in gels in general and less is known about bound water in silica gels in particular. A survey of the literature will show some of the factors governing the gelation process and will give an insight into some of the factors that may affect bound water in silica gels. There are no satisfactory theories of gelation and gel structure because of the lack of adequate knowledge in this field. Theories of silica gel structure will not be discussed here as the information is available elsewhere (1).

Definitions

A 'colloidal solution' is called a 'sol'. A sol consists of particles ranging in size from 5×10^{-7} to 200×10^{-7} centimeters (the disperse phase) in a liquid (the dispersion medium). Particles of hydrated silica are the disperse phase in a 'silica sol'.

At gelation or setting the silica sol becomes a semi-rigid translucent or transparent solid. This mass is called a 'silica gel'.

It follows from this, that to prepare silica gels one must first obtain a silica sol. A gel will result from a silica sol if the concentration of silica is not less than 0.5% and the pH is less than 11 (approx.) (5,6).

Preparation of Silica Sols

Silica sols have been prepared in a number of ways:

(a) Graham prepared silica sols by the action of an acid on sodium or potassium silicate. This is the most common method.

(b) Another very common method is by the addition of an ammonium salt to sodium or potassium silicate (7,8,9,10,11).

(c) Berzelius obtained silica sols by treating hydrofluosilicic acid with ammonium hydroxide.

(d) Treadwell removed the sodium from solutions of sodium silicate by electrolysis and deposition of the sodium in a mercury cathode. This was also used by Kröger (12). It is not satisfactory as other ions are also removed from the solution.

(e) Recent experimenters (13) following work done much earlier by Langlois and by Fremy, have tried preparing silica sols by the hydrolysis of silicon compounds. Grimaux has also prepared silica sols by the hydrolysis of silicate esters.

Dialysis is generally used to remove the electrolytes formed, but it is doubtful if the electrolytes are completely eliminated, so this does not result in pure silicic acid sols.

(f) A very pure silicic acid sol has been prepared by oxidizing silane (SiH_4) with ozonized oxygen in the presence of water (14).

(g) Probably the purest silicic acid sol was prepared by grinding Ottawa sand to a fine powder and heating it at 300° - 400°C. with water in a bomb (15).

Properties of Silica Sols

While studies on the molecular weight of freshly prepared silicic acid are complicated by the presence of a certain amount of impurities (electrolytes) and possibly water of hydration, attempts have been made to determine the molecular weight. Two values have been observed for the 'molecular weight' of freshly prepared silicic acid, 60 (26,27) and 149 (28). The 'molecular weight' has been reported to increase with time reaching a value of 8260 after 45 days (29).

Further support for these observations arises from the fact that membranes used for dialysis retain the silica particles in aged sols but silica in freshly prepared sols passes through.

There is no Tyndall cone in freshly prepared silica sols but it develops as they stand (30). This seems rather astonishing when water alone is believed to show a Tyndall cone.

The conductivity of silica sols has been studied and is reported to vary very little with time, even when the sol becomes a gel (31,32,33).

Methods of Measuring the Sol-Gel Transformation

The time required for the sol to form a gel has been measured in various ways:

(a) The time required for the gel to reach a rigidity such that when the container was inverted the mixture would not run out has been used as a criterion of the time of set (34).

(b) Batchelor (20) describes "... a mechanism by which several bottles are rotated at a slow uniform speed at an angle of about 30 degrees from the horizontal with suitable provision for counting the number of revolutions of each bottle." The gelation time can be calculated from the number of rotations before flow stops.

(c) It has been suggested that the setting point of the gel should be that at which the pressure, required to blow a bubble of air, or of mercury or of chloroform colored with iodine through the gel forming mixture, reaches a maximum value (35).

(d) Hurd and Letteron (36) use the "tilted rod method". It is described thus: "... rod is thrust into gel at an angle of 20 degrees with the vertical. The gel is considered set when the rod fails to fall over."

(e) An optical method of determing the time of set has been used (37). The sol is considered to have set when the opacity reached a constant value.

Factors Affecting the Sol-Gel Transformation

Among the factors that govern the rate of conversion of silica sols to gels are the concentration of silica, temperature, acid, hydrogen-ion concentration and the presence of other materials. Ultraviolet radiations (38,39) and ultrasonic radiations (40) also affect the time of set.

It has been known for some time that the greater the concentration of silica the more rapidly would the gel set. There is an excellent quantitative picture of this in the literature (20,cf. also 19).

Maschke is credited as being the first (1808) to show that increase in temperature increased the rate of transformation of silica sols (1). Recent experiments using Graham's method of preparing sols, showed that the relation between the temperature and the time of set of the sol-gel transformation could be treated mathematically by the Arrhenius Equation (36). This study however was limited to acid gels. The value obtained for the 'energy of activation' for the process is a constant and is independent of the concentration of the silica on the gel-forming mixture. Further it was found that the value was independent of the soda-silica ratio of the silicate used.(41). For weak acids (acetic, tartaric, succinic, citric), it was shown to be independent of the acid used (42) but the value varied with the acid when H_2SO_4, H_3PO_4, HNO_3 and HCl were employed (43,44,45). It appears, however, that the Arrhenius Equation does not apply to alkaline silica gels when acetic acid is used (46), but does apply to alkaline gels when phosphoric acid is used (45).

There is a linear relation between time of set and pH of acid gels (47). A similar relation was reported to exist for alkaline gels (1). Many experimenters (eg. 8,19) show that there is a minimum when the pH of alkaline gels is plotted against time of set (or log time of set).

Hurd (1) finds considerable disagreement in the data available upon the effect of electrolytes and non-electrolytes on the silica sol-gel transformation.

Certain electrolytes decrease the set of silica gels (47). In most sols the addition of electrolytes causes coagulation of the disperse phase. In silica sols the addition of electrolytes merely causes an increase in the rate of sol-gel transformation. This would indicate that the silicic acid particle, even on its formation, must be highly hydrated.

The addition of a potassium salt has a greater effect in decreasing the rate of the transformation than the addition of a sodium salt and the acid radical effect is in the order,- chloride > nitrate > sulphate (11). Also, the use of different acid acids in preparing gels (with and without pyridine as an addition agent) decreases the setting time as follows: $H_2SO_4 >$ HCL $> HNO_3$. In all alkaline gels, the order was $HNO_3 >$ HCL $> H_2SO_4$. For acid gels containg pyridine the effect in decreasing the time of set was citric acid > acetic > trichloroacetic > formic > tartaric acid, while for alkaline gels containing pyridine the order of effect was trichloroacetic acid > acetic > formic > tartaric > citric (10). In gels without pyridine the order for weak acids was the same as reported elsewhere (48), that is, the order of effect varies depending on the concentration of the acids used in the mixture. Some of this work has recently been repeated (49).

The effect of methyl, ethyl and n-propyl alcohols on the alkaline gels was reported to be opposite to the effect on acid gels (10).

Hurd and Carver (50) show the effect of ammonia, amines, pyridine and aniline on acid gels. They observe, here, that the above mentioned lack of agreement may arise from neglect of pH changes caused by the addition agents. They also note that the addition of ethyl alcohol increased the time of set of acid silica gels while glycerol had a negligible effect, and at the same time the pH of the gel was unaltered.

Hurd failed to realize that the effect of an addition agent might vary with the pH of the gel itself.

Munro and students (51,52,19,46) obtained a regular decrease in the time of set of alkaline silica gels with increasing molecular weight of the monohydric alcohols. They observed that the gels of high pH became more alkaline on setting and that the effect seemed to be increased in the presence of addition agents. It was also observed that while glycol decreased the time of set of these gels, its effect was not nearly so great as that of monohydric alcohols. With glycerol the time of set was lengthened i.e. the effect was similar to that brought about by addition agents in acid gels. Hurd and Carver's (50) observations on the effect of glycerol on acid gels were reinvestigated and their findings confirmed.

The effect of glycerol was found to be merely a part of a further and regular increase in the time of set when higher polyhydric alcohols were added to alkaline gels. It was also noted that glycol changed from an accelerator of gelation to a retarder in the neighborhood of pH 8.2 (52).

Further work (19) showed that the total effect and the divergance of the individual behavior of both monohydric and polyhydric alcohols becomes greater as the alkalinity of the gel is increased. When the time of set with addition agent is plotted as percentage of the original time of set, there is a constant effect for an equal number of alcohol molecules at pH 7. When the system is acidic, all the alcohols behave as retarders; when it is alkaline, only the higher polyhydrics act in this manner. The monohydric alcohols and glycerol change from accelerators to retarders at pH values between 7.4 to 8.5.

When this study was extended to different temperatures (46), the alcohols were observed to have similar behavior at temperatures from 0 to 50°C. For alkaline gels the effects observed decreased in specificity as the temperature increased. For acid gels the effects were approximately the same at all temperatures.

Similar effects were observed when aldehydes and sugars are used as addition agents (53).

The Point of Minimum Set and the Isoelectric Point

A minimum set on the alkaline side of the neutral point was first noticed by Flemming (34) and later by Holmes (48), Hurd and Letteron (36) and Prasad (8,9). There was much confusion as to the hydrogen- or hydroxyl- ion concentration at which this minimum set occurred. This confusion was dispelled when it was shown (20) that the pH at which the minimum set occurred decreases with increasing dilution of the silicate used (cf. also 19).

The isoelectric point is defined as that state of the fluid phase at which there is no potential difference between it and the solid phase. At this point the stability of the sol is a minimum (54, p.126 et seq). In aqueous dispersion media this corresponds to a definite pH. Therefore it might be expected that for gels of each concentration the minimum set would be observed at a pH corresponding to the isoelectric point. Flemming (34) studying one concentration of silica came to the conclusion that the isoelectric point was in the alkaline region.

Silica particles are negative in alkaline, neutral and weakly acid solution and positive in more strongly acid solution (31). This would put the isoelectric point on the acid side at about pH 6.0.

This range has been defined from consideration of pH changes of the gel during setting as pH 5.5-6.2 (20). Slightly different ranges have been noted (55),(8) as pH's 4.6 to 5.9 and 5.2 to 6.1 respectively. This contradicts Flemming and indicates that for silica gels the region of minimum set and the isoelectric region do not coincide.

Properties of Silica Gels

Five properties of gels will be discussed in relation to silica gels. The properties discussed will be opacity, thixotropy, elasticity, syneresis and bound water.

1. The opacity of silica gels has received the attention of Prasad (8,9,10,11,37) who found that during the setting of acid gels the mixture was transparent for a considerable time then increases in opacity slowly reaching a maximum value. For alkaline gels; the period of transparency is much shorter, the increase in opacity is much more rapid and maximum value of the opacity is much greater than for acid gels.

Photometric measurements indicate that the opacity of acid gels increases only slightly with the decrease in acidity and from about pH 6.5 to pH 10. the opacity increases over one hundred times (5).

2. Hurd (1) after studying only acid gels considers that silica gels only show the phenomenon of thixotropy in the early stages of setting. However, it is known that silica gels between pH's 8.5-9.5 are liquified by ultrasonic vibrations (40).

With this in mind it will be recalled that many of the methods (a,b and c) of measuring the time of set could not be valid for measuring the set of these alkaline gels and (d) can only be valid if the gel is not excessively disturbed.

3. Elasticity has been studied for a few silica gels by Hatschek (56) who found thatgels obey Hooke's Law and that they have a low elastic limit. Young's modulus of silica gels has been studied, and for acid gels there is a slower rate of change of the modulus value with pH than for alkaline

gels (57).

4. The work of Ferguson and Appleby (58) and Bonnel (59,60, 61,62) is probably the best of the published work on syneresis of silica gels.

The former report that the volume of the gel before syneresis is equal to the volume of the gel after syneresis plus the volume of syneretic liquid and that the velocity of syneresis approximately doubles for every 10^{o} rise in temperature.

The latter finds an induction period between setting and the onset of syneresis. The induction period is longer for acid gels. The volume of liquid synerized varies with the silica concentration and when the volume synerized is plotted against the pH of the gel there is a pronounced minimum at about pH 8. It was concluded that this pH must be the isoelectric point. It is reported here that syneresis in silica gels is reversible.

The addition of salts is reported to have no effect on the total volume of liquid synerized although the setting time and induction period are decreased. There is evidence to indicate that the addition of alcohols does not alter the volume of liquid synerized (63).

5. It is believed that there is both free and "bound" or "fixed" water in silica gels (64,74). Part of the latter maybe considered as chemically combined.

Water in silica gel has been studied by the dilatometric method (75,76). The silica gel used for this study was the coagulum formed when acid or ammonium salts are added to a solution of sodium silicate. The coagulum was filtered from the supernatent liquid. It can be seen from the previous discussion that unless rigid control of pH and other factors is maintained reproducibility in the surface features of the gel can not be obtained.

It was observed during this study that repeated freezing and thawing does not alter the ratio of free and bound water in the gel. When silica (sand) and water were studied the water was observed to freeze about -4°C. In the silica coagulum 0.7 g. H_2O /gram of silica froze at temperatures below -6°C and about 25% could not be frozen. It was suggested from these results the one mole of water was combined with the silica and remained combined in definite proportions, the remainder being present in indefinite proportions.

The bound water in silica gels prepared by allowing 'Xerogels' to swell in water has been studied (73). To attack the problem in this way, although valuable, does not permit a control of such variables as pH or the presence of added substances. It is impossible to correlate such phenomena as time of set or syneresis to the bound water data. Such correlation of data from various phenomena is necessary in any colloidal study.

Description of the Apparatus

The lack of data on bound water in silica gels makes a study in this field seem unusually attractive. Such a study might explain the difference in behavior of acid and alkaline gels.

Of the many methods of determining bound water, the calorimetric method (65) was chosen since it had been applied satisfactorily to gelatin (66,67,68).

For this work, a calorimeter was designed which incorporates several new features which should make it more accurate and considerably simpler in manipulation. While the design was completed, construction of the calorimeter was not commenced owing to urgent war problems.

The transfer of the container for the gel (67) from the thermostat to the calorimeter must be made as rapidly as possible to avoid heat change during the transfer. In the old calorimeter this was done by hand and considerable skill and practice were required to make the transfer rapidly. During the transfer, the container was exposed to the air for a minimum period of several seconds, during which heat losses or gains could occur.

A mechanical arrangement has been designed by which the transfer can be effected very rapidly and up to the moment that it enters the calorimeter, the container is enclosed in an envelope, which protects it from the condensation of atmospheric moisture on its surface during the transfer.

In the earlier calorimeter a reciprocating stirrer was used; supported by copper wires which passed through openings in the lid of the calorimeter vessel. A method of stirring has been devised which avoids any direct connection between the interior of the calorimeter and the outside. This makes it possible to close off the inner vessel completely except while the container is being dropped into it.

Figure 1 shows the calorimeter diagramatically.

The inner calorimeter vessel is of rolled copper (10 cm. in diameter and 14 cm. high) with a tight fitting cover and a reinforced bottom. The cover is fitted with a bakelite chimney. This vessel rests on triangularly shaped bakelite supports that fit firmly into the bottom of the calorimeter vessel and the jacket.

A brass jacket surrounds the calorimeter vessel leaving an air space of 2 cm. between the vessel and the jacket. It is believed (69) and (70, p.74) that air spaces between 2 and 4 cm. do not introduce any serious errors due to convection.

As a means of detecting temperature differences between the calorimeter and bath, radiation thermels are used (71).

The opening at the upper end between the calorimeter vessel and jacket chimneys is closed with a brass and bakelite funnel shaped cap.

The jacket is supported on a drive shaft by a "spider" arrangement. Through the center of the drive shaft the leads from the thermels are drawn. The drive shaft passes through a packing box in the water bath wall and is supported

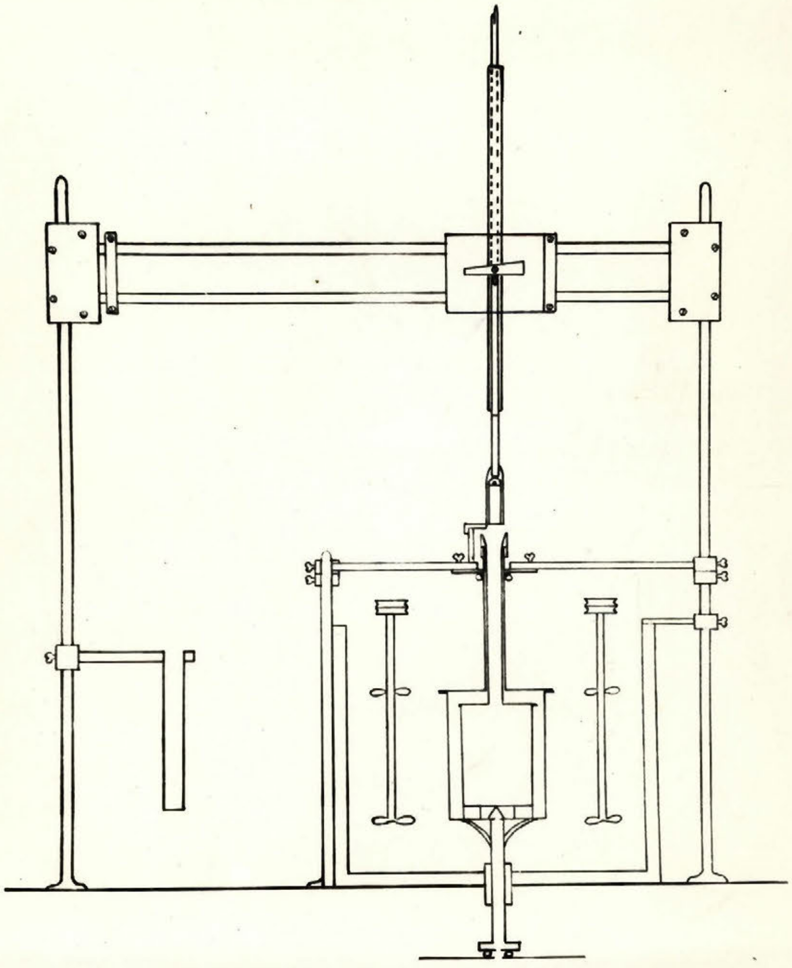

Figure 1

General details of the proposed calorimeter.

on a thrust bearing. By means of suitable gearing the whole calorimeter is made to oscillate back and forth about five times per minute. Removable vanes in the inner vessel provide the means of stirring its contents.

The chimney of the jacket is steadied by a bearing clamped to uprights.

The water bath is stirred by four stirrers and regulated by jets of hot and cold water.

For transferring the container from the low temperature bath (described in 66) the container is fitted into a close fitting brass case with a sliding bottom. The upper end of the case is fitted into a bakelite rod that joins on to a brass shaft. The bfass shaft slides in a tube fastened to a "trolley arrangement" and is raised by a small handle. As the trolley is moved to position over the calorimeter chimney a stop pulls out the sliding bottom allowing the container to slip into the chimney.

To prevent splashing as the container falls into the water in the inner vessel a weighted device grasps the container and slowly pulls it under the surface of the water.

Summary

1. There is need for a thorough study of bound and free water in silica gels.

2. The calorimetric method is considered the most promising method of studying bound water.

3. A new adiabatic calorimeter was designed for this study. Several original features were incorporated in the design which should give somewhat higher accuracy and much greater ease of manipulation than calorimeters previously used for measurements of this kind.

SODIUM SILICATE IN WATER

Introduction

Since the preparation of silica sols by Graham's method is the most common, a discussion of sodium silicate in water is pertinent.

Vail (16) discusses the properties of sodium silicate in water at great length. There is experimental evidence indicating that sodium silicate in water is a true solution, other evidence points to the particles being of colloidial size. Other authorities (17, Vol.2. p.563 et seq.; 18, Vol.2. pp. 193 -- 198) believe alkali silicates to be silica particles stabilized by negative hydroxide ions.

If this is the case, titration of sodium silicate solutions against acids and, vice versa, titration of acids by sodium silicate solution might give curves similar to those for sodium hydroxide i.e. curves with only one point of inflection when a monobasic acid is used. Curves of this type have been observed (77;19;16;20, private communication).

Numerous workers have observed a second inflection point when titrating sodium silicate with a monobasic acid and some have calculated values for the dissociation constants of silicic acid (21,22,23,24).

In connection with this work on bound water some work was done on titrating sodium silicate in water with monobasic acids. Before this study was completed, Chatterjee (25) published the results of his titrations of dialysed, acidified sodium silicate solutions with various bases. He concludes that silicic acid solutions are colloidal but that the colloidal particles behave as a true dibasic acid. If this is the case, the neutralization reaction is essentially a reaction at a solid-liquid interface and the observed results of such a reaction should vary with the conditions of the experiment, i.e. whether one is titrating from acid to base or vice versa.

An hysteresis has been observed in curves obtained from such titrations (20, cf. above).

As the titration curve reported by Munro and Pearce (19) had been drawn from pH measurements on the gels studied, only a few points were recorded and a smooth curve drawn. Therefore, titrations of sodium silicate with acetic and hydrochloric acids were carried out to see if the second inflection point found by others had been overlooked for the above reason.

Experimental

A vacuum tube voltmeter was renovated in an attempt to get accurate pH measurements. This apparatus has a greater sensitivity than was required for this purpose and was cumbersome to manipulate. Its use was abandoned in favor of a Coleman glass electrode potentiometer, when it was found possible to borrow the latter from the Forest Products

Laboratory. To make the potentiometric studies as complete as possible, Baker's best grade of "crystalline sodium silicate $Na_2SiO_3.9H_2O$" was purchased and National Silicates Limited kindly donated the following brands:

"Metso Crystals ($Na_2SiO_3.5H_2O$)"
"Metso 99 ($3Na_2O:2SiO_2$)"
"O" (Na_2O : SiO_2 - 1:3.22)
"S" (Na_2O : SiO_2 - 1:3.90)
"K" (Na_2O : SiO_2 - 1:2.90)
"C" (Na_2O : SiO_2 - 1:2.00)
"BW" (Na_2O : SiO_2 - 1:1.60)
"Star" (Na_2O : SiO_2 - 1:2.50)

Here too, urgent war research prevented carrying out this study on anything but Baker's material.

Stock acetic and hydrochloric acids were used.

The concentrations of all solutions used were obtained by analysis and are recorded in the tables.

Results

The results are tabulated in tables I - IV and figures 2 - 5.

The presence of sodium ion in solutions of pH greater than 9.0 makes the pH reading recorded by the glass electrode somewhat smaller than the true value. Corrections for the presence of sodium ion are available (72, p 12). The pH's recorded here are not corrected for the presence of sodium ion.

The following will show the magnitude of the correction when applied to the first row of table I :

Na-ion (N.)	pH(obs.)	pH(true)
0.0486	11.83	12.16
0.0972	11.85	12.37
0.1458	11.85	12.60
0.1942	11.78	12.70
0.2428	11.76	12.84

TABLE I

Titration of 25 cc. of Na_2SiO_3 solutions of strength indicated (diluted to 250 cc.) by 1.739 M. HOAc solution.

1		2		3		4	
0.243 M.		0.486 M.		0.729 M.		0.971 M.	
cc.	pH	cc.	pH	cc.	pH	cc.	pH
0.0	11.83	0.0	11.85	0.0	11.85	0.0	11.78
1.0	11.72	1.0	11.77	5.0	11.78	10.0	11.64
2.0	11.57	2.0	11.68	6.0	11.75	11.0	11.56
3.0	11.20	3.0	11.60	7.0	11.69	12.0	11.48
4.0	11.49	4.0	11.57	8.0	11.64	13.0	11.32
4.5	10.24	5.0	11.45	9.0	11.55	14.0	11.23
5.0	9.96	6.0	11.23	10.0	11.38	15.0	11.08
6.0	9.56	7.0	11.00	11.0	11.19	16.0	10.97
7.0	7.00	8.0	10.81	12.0	11.00	17.0	10.84
8.0	5.48	9.0	10.49	13.0	10.78	18.0	10.74
9.0	5.16	10.0	10.30	14.0	10.67	19.0	10.72
10.0	4.97	11.0	10.02	15.0	10.55	20.0	10.50
15.0	4.55	12.0	9.78	16.0	10.44	21.0	10.39
20.0	4.30	13.0	9.35	17.0	10.26	22.0	10.28
25.0	4.21	14.0	7.60	18.0	10.12	23.0	10.18
		15.0	5.87	19.0	9.80	24.0	10.00
		16.0	5.51	19.5	9.57	24.5	9.91
		17.0	5.23	20.0	9.20	25.0	9.79
		18.0	5.15	20.5	8.50	25.5	9.66
		23.0	4.88	21.0	7.39	26.0	9.41
		28.0	4.58	21.5	6.53	26.5	9.15
		33.0	4.45	22.0	6.17	27.0	8.67
				23.0	5.78	27.5	8.07
				24.0	5.61	28.0	7.20
				25.0	5.46	28.5	6.53
				30.0	5.09	29.0	6.20
				35.0	4.87	30.0	5.82
				40.0	4.74	31.0	5.69
						35.0	5.28
						45.0	4.88

Do. for NaOH

5	
1.510 M.	
cc.	pH
0.0	11.90
5.0	11.90
10.0	11.90
15.0	11.82
19.0	11.66
20.0	11.34
20.5	11.02
21.0	10.11
21.5	6.99
22.0	6.12
23.0	5.76
25.0	5.40
30.0	5.03
35.0	4.77
40.0	4.72

TABLE II

Titration of 25 cc. of Na_2SiO_3 solutions of strength indicated (diluted to 250 cc.) by 2.253 M. HCl solution.

1

0.486 M.

cc.	pH
0.0	11.85
1.0	11.85
2.0	11.81
3.0	11.75
4.0	11.63
5.0	11.38
6.0	11.03
7.0	10.89
8.0	10.51
9.0	10.21
10.0	9.54
10.5	8.48
11.0	3.67
11.5	2.82
12.0	2.59
13.0	2.29
14.0	2.12
20.0	1.71
25.0	1.55
30.0	1.46

2

0.729 M.

cc.	pH
0.0	11.85
5.0	11.72
6.0	11.68
7.0	11.58
8.0	11.40
9.0	11.21
10.0	11.03
11.0	10.88
12.0	10.69
13.0	10.50
14.0	10.28
15.0	9.77
15.5	9.30
16.0	8.27
16.5	5.91
17.0	3.04
18.0	2.55
19.0	2.31
20.0	2.16
25.0	1.81
30.0	1.66
36.0	1.52

3

0.971 M.

cc.	pH
0.0	11.78
5.0	11.65
6.0	11.62
7.0	11.59
8.0	11.50
9.0	11.40
10.0	11.31
11.0	11.21
12.0	11.16
13.0	10.96
14.0	10.82
15.0	10.58
16.0	10.54
17.0	10.42
18.0	10.27
19.0	10.06
20.0	9.75
20.5	9.16
21.0	8.10
21.5	7.03
22.0	3.20
23.5	2.38
25.0	2.12

4

1.214 M.

cc.	pH
0.0	11.76
10.0	11.60
11.0	11.58
12.0	11.50
13.0	11.41
14.0	11.33
15.0	11.21
16.0	11.11
17.0	11.01
18.0	10.90
19.0	10.80
20.0	10.70
21.0	10.59
22.0	10.45
23.0	10.31
24.0	10.10
25.0	9.41
26.0	9.00
26.5	8.31
27.0	7.44
27.5	3.81
28.0	2.79
29.0	2.35
30.0	2.16
35.0	1.71
40.0	1.58
50.0	1.39

Do. for NaOH

5

0.998 M.

cc.	pH
0.0	12.00
9.0	11.71
10.0	11.55
10.5	11.43
11.0	10.86
11.5	3.13
12.0	2.45
13.0	2.28
14.0	2.08
20.0	1.65
30.0	1.39

TABLE III

Titration of 25 cc. HOAc solutions of strength indicated (diluted to 250 cc.) by 0.984 M. Na_2SiO_3 solution.

1		2		3		4	
0.436 M.		0.872 M.		1.308 M.		1.743 M.	
cc.	pH	cc.	pH	cc.	pH	cc.	pH
0.0	2.90	0.0	2.79	0.0	2.72	0.0	2.70
3.0	4.52	9.0	5.09	14.0	5.17	15.0	4.84
4.0	4.88	10.0	5.40	15.0	5.44	17.0	5.02
5.0	5.42	11.0	6.20	16.0	5.88	18.0	5.18
6.0	8.70	12.0	8.83	17.0	7.41	19.0	5.31
7.0	9.81	13.0	9.77	18.0	9.22	20.0	5.49
8.0	10.21	14.0	10.11	19.0	9.86	21.0	5.74
9.0	10.44	15.0	10.35	20.0	10.12	22.0	6.36
10.0	10.68	20.0	10.91	30.0	11.06	23.0	8.03
11.0	10.89	21.0	10.99	31.0	11.09	24.0	9.33
12.0	11.09	22.0	11.04	32.0	11.11	25.0	9.86
13.0	11.21	23.0	11.11	33.0	11.13	26.0	10.14
14.0	11.31	24.0	11.21	34.0	11.20	27.0	10.35
15.0	11.38	25.0	11.25	35.0	11.21	40.0	11.10
25.0	11.54	26.0	11.30	36.0	11.22	42.0	11.16
		50.0	11.48	37.0	11.30	43.0	11.19
				38.0	11.30	44.0	11.20
				50.0	11.41	45.0	11.24
						46.0	11.29
						47.0	11.30
						48.0	11.31
						49.0	11.32
						50.0	11.34

TABLE IV

Titration of 25 cc. HCl solutions of strength indicated (diluted to 250 cc.) by 0.971 M. Na_2SiO_3 solution.

1		2		3		4	
0.435 M.		0.870 M.		1.305 M.		1.739 M.	
cc.	pH	cc.	pH	cc.	pH	cc.	pH
0.0	1.39	0.0	1.10	0.0	0.99	0.0	0.89
3.0	1.68	9.0	1.78	10.0	1.29	10.0	1.10
4.0	1.92	10.0	2.10	13.0	1.58	12.5	1.19
5.0	2.38	10.5	2.39	15.0	1.91	15.0	1.34
5.5	3.60	11.0	3.51	16.0	2.35	16.0	1.40
6.0	8.78	11.5	7.96	16.5	3.24	17.0	1.48
7.0	9.88	12.0	9.15	17.0	7.32	18.0	1.56
8.0	10.31	13.0	9.90	17.5	8.60	19.0	1.69
9.0	10.59	14.0	10.22	18.0	9.28	20.0	1.82
10.0	10.80	15.0	10.44	19.0	10.90	21.0	2.10
11.0	11.02	16.0	10.58	20.0	10.20	22.0	3.00
12.0	11.21	17.0	10.68	21.0	10.40	22.5	6.88
13.0	11.33	18.0	10.79	22.0	10.51	23.0	8.08
14.0	11.43	19.0	10.86	23.0	10.62	24.0	9.34
20.0	11.64	20.0	10.95	24.0	10.70	25.0	9.90
50.0	11.66	21.0	11.02	25.0	10.76	26.0	10.21
		22.0	11.11	26.0	10.82	27.0	10.39
		23.0	11.19	27.0	10.87	28.0	10.51
		24.0	11.26	28.0	10.91	30.0	10.63
		25.0	11.31	29.0	10.95	40.0	11.02
		30.0	11.38	30.0	11.00	41.0	11.09
		50.0	11.55	31.0	11.05	42.0	11.11
				32.0	11.11	43.0	11.17
				33.0	11.17	44.0	11.20
				34.0	11.21	45.0	11.26
				35.0	11.25	46.0	11.28
				40.0	11.39	47.0	11.31
				50.0	11.50	50.0	11.35

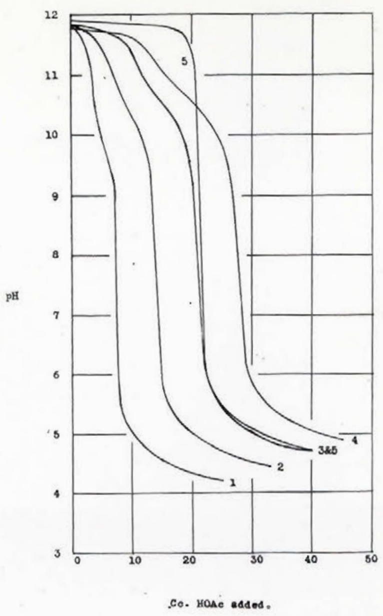

Figure 2

Titration of 25 cc. of Na_2SiO_3 solutions of strength indicated (diluted to 250 cc.) by 1.739 M. HOAc solution.

1. 0.243 M.
2. 0.486 M.
3. 0.729 M.
4. 0.971 M.
5. Do. for NaOH 1.510 M.

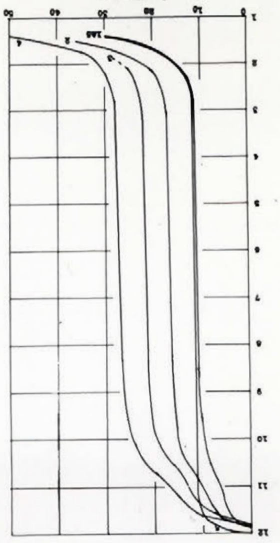

Figure 3

Titration of 25 cc. of Na_2SiO_3 solutions of strength indicated (diluted to 250 cc.) by 2.253 M. HCl solution.
1. 0.486 M.
2. 0.729 M.
3. 0.971 M.
4. 1.214 M.
5. Do. for NaOH 0.998 M.

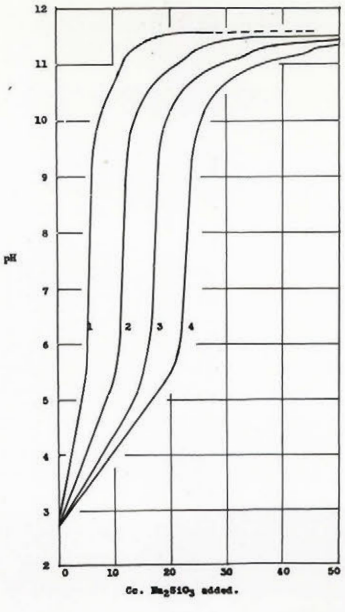

Figure 4

Titration of 25 cc. HOAc solutions of strength indicated (diluted to 250 cc.) by 0.984 M. Na_2SiO_3 solution.

1. 0.436 M.
2. 0.872 M.
3. 1.308 M.
4. 1.743 M.

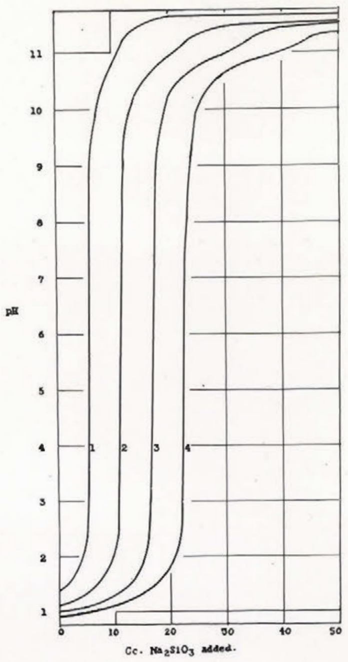

Figure 5

Titration of 25 cc. HCl solutions of strength indicated (diluted to 250 cc.) by 0.971 M. Na_2SiO_3 solution.

1. 0.435 M.
2. 0.870 M.
3. 1.305 M.
4. 1.739 M.

Discussion

From these data it can be seen that there is a definite inflection in the alkaline region. For titrations with acetic acid this inflection occurs between corrected pH 11.06 - 11.95 and with hydrochloric acid between corrected pH 11.21 - 12.07. The observation of an alkaline inflection between pH 11.33 - 11.70 (25) is in excellent agreement with the results recorded here.

The second inflection point is emphasized when the curves for sodium silicate solutions are compared with the curves for sodium hydroxide solution.

From this it is apparent that in previous work (19) this inflection was not observed due to the lack of a sufficient number of experimental points.

Conclusion

Titrating Baker's sodium silicate in water with acids indicates that H_2SiO_3 has the characteristics of a dibasic acid.

REFERENCES

(1) Hurd, C.B.: Chem. Rev.; 22,403 (1938)

(2) McBain, J.W.: Sorption of Gases by Solids, Routledge & Sons, London (1932)

(3) Hurd, C.B.: Sigma Xi Quarterly; 26,28 (1926)

(4) Mennie, J.H.: Can. J. Res.; 7, 178 (1932)

(5) Pearce, J.A.: Dissert. Queens University (1939)

(6) Tourky, A.: Zeit. anorg. allgem. Chem.;240, 198 (1939)

(7) Bhatnagur, S.S. and Mathur, K.K.: Koll.-Z.; 30, 368 (1922)

(8) Prasad, M., and Hattiangadi, P.B.: J. Ind. Chem. Soc.; 6, 653 (1929)

(9) Prasad, M. and Hattiangadi, P.B.: J. Ind. Chem. Soc.; 6, 893 (1929)

(10) Prasad, M. and Hattiangadi, P.B.: J. Ind. Chem. Soc.; 6, 991 (1929)

(11) Prasad, M. and Hattiangadi, P.B.: J. Ind. Chem. Soc.; 7, 341 (1930)

(12) Kröger, M.: Koll.-Z.; 30, 16 (1922)

(13) Ebler, E. and Fellner, M.: Ber.; 44, 1915 (1911) C.A., 5,3206

(14) Kargin, V.A. and Rabinovich, A.J.: Trans. Farad. Soc.; 31, 284 (1935)

(15) Lenher, V.: J. Am. Chem. Soc.; 43, 391 (1921)

(16) Vail, J.G.: Soluble Silicates in Industry, Chem. Catalogue Co. New York (1928)

(17) Bogue, R.H.: Theory and Applications of Colloidal Behavior, McGraw-Hill Book Co. New York (1924)

(18) Weiser, H.B.: Inorganic Colloid Chemistry, Wiley and Sons, New York. (1938)

(19) Munro, L.A. and Pearce, J.A.: Can. J. Res.; B, 17, 266 (1939)

(20) Batchelor, H.W.: J. Phys. Chem.; 42,575 (1938)

(21) Joseph, A.F., and Oakley, H.B.: J. Chem. Soc.; 127, 2813 (1925)

(22) Hägg, G.: Z. anorg. Chem.; 155, 21 (1926)

(23) Harman, R.W.: J. Phys. Che.; 31, 616 (1927)

(24) Treadwell, W.D. and Wieland, W.: Helv. Chem. Acta; 13, 842 (1930)

(25) Chatterjee, B.: J. Ind. Chem. Soc.; 16, 589 (1939)

(26) Gruner, E. and Elöd, J.: Z. anorg. allgem. chem.; 203, 317 (1932)

(27) Willstätter, R., Kraut, H., and Lobinger, K.: Ber.; 58B, 2462 (1925)

(28) Treadwell, W.D.: Trans. Farad. Soc.; 31, 297 (1935)

(29) Brintzinger, H. and Brintzinger, W.: Z. anorg. allgem. Chem.; 196, 44 (1931)

(30) Krishnamurti, K.: Proc. Roy. Soc. (London); A122, 76 (1929)

(31) Losenbeck, K.: Kolloid-Beiheft; 16, 27 (1922)

(32) Mylius, F. and Groschuff, F.: Ber; 39, 116 (1906)

(33) Ghosh, S., and Dhar, N.R.: J. Phys. Chem.; 33, 1905 (1929)

(34) Flemming, W.: Z. physik. Chem.; 41, 427 (1902)

(35) Fells, H.A. and Firth, J.B.: Trans. Farad. Soc.; 23, 623 (1927)

(36) Hurd, C.B. and Letteron, H.A.: J. Phys. Chem.; 36, 604 (1932)

(37) Prasad, M., Mehta, S.M. and Desai, J.R.: J. Phys. Chem.;1324 (1932)

(38) Ray, R.C. and Ganguly, P.B.: J. Phys. Chem.; 34, 352 (1930)

(39) Ray, R.C. and Ganguly, P.B.: J. Phys. Chem.; 35, 596 (1931)

(40) Freundlich, H.: J. Chem. Soc. 1938, 546

(41) Hurd, C.B. and Miller, P.S.: J. Phys. Chem.; 36, 2194 (1932)

(42) Hurd, C.B.: J. Phys. Chem.; 40, 21 (1936)

(43) Hurd, C.B., Fredrick, K.J. and Haynes, C.R.: J. Phys. Chem.; 42, 285 (1938)

(44) Hurd, C.B., and Barclay, R.W.: J. Phys. Chem.; 44, 847 (1940)

(45) Hurd, C.B., and Marotta, A.J.: J. Am. Chem. Soc.; 62, 2769 (1940)

(46) Munro, L.A., and Pearce, J.A.: J. Phys. Chem.; 44, 1024 (1940)

(47) Hurd, C.B., Raymond, C.L., and Miller, P.S.: J. Phys. Chem.; 38, 663 (1934)

(48) Holmes, H.N.: J. Phys. Chem.; 22, 518 (1918)

(49) Davis, H.L., and Hay, K.D.; J. Am. Chem. Soc.; 61, 1020, (1939)

(50) Hurd, C.B. and Carver, D.H.: J. Phys. Chem.; 37, 32 (1933)

(51) Munro, L.A. and Alves, C.A.: Can. J. Res.; B, 15, 353 (1937)

(52) Munro, L.A. and Pearce, J.A.: Can. J. Res.; B, 16, 390 (1938)

(53) Munro, L.A. and Pearce, J.A.: Can. J. Res.; B, 17, 404 (1939)

(54) Ware, J.C.: The Chemistry of the Colloidal State, Wiley and Sons, New York, (1936)

(55) Hurd, C.B. and Griffith, R.L.: J. Phys. Chem.; 39, 1155 (1935)

(56) Hatschek, E.: Trans. Farad. Soc.; 12, 17 (1916)

(57) Munro, L.A. and McNab, J.: Unpublished data

(58) Ferguson, J., and Appleby, M.P.: Trans. Farad. Soc.; 26, pt.II, 624 (1930)

(59) Bonnell, D.G.R.: Trans. Farad. Soc.; 28, pt.I, 1 (1932)

(60) Bonnell, D.G.R.: Trans. Farad. Soc.; 28, pt.I, 12 (1932)

(61) Bonnell, D.G.R.: Trans. Farad. Soc.; 29, pt 1, 1217 (1933)

(62) Bonnell, D.G.R.: Trans. Farad. Soc.; 29, 1221 (1933)

(63) Munro, L.A. and Pearce, J.A.: Unpublished data

(64) Schwarz, R.: Z. Eliktrochem.; 32, 415 (1926)

(65) Thoenes, F.: Biochem. Z.; 157 (174) (1925)

(66) Hampton, W.F. and Mennie, J.H.: Can. J. Res.; 7: 187 (1932)

(67) Hampton, W.F. and Mennie, J.H.: Can. J. Res.; 10: 452 (1932)

(68) Horn, W.R. and Mennie, J.H.: Can. J. Res.;12: 702 (1935)

(69) Barry, F.: J. Am. Chem. Soc.; 44, 899 (1922)

(70) White, W.P.: The Modern Calorimeter, Chem. CatalogueCo. New York (1928)

(71) Barnes, W.H. and Maass, O: Can. J. Res.; 3, 70 (1930)

(72) Dole, M.: Measuring pH with the Glass Electrode Coleman Electric Co., Maywood, Ill. (1937)

(73) Jones, I.D., and Gortner, R.A.: J. Phys. Chem.; 36, 387 (1932)

(74) Fells, H.A. and Firth, J.B.: J. Phys. Chem.; 31, 1230 (1927)

(75) Foote, H.W. and Saxton, B.: J. Am. Chem. Soc.; 38, 588 (1916)

(76) Foote, H.W. and Saxton, B.: J. Am. Chem. Soc.; 39, 1103 (1917)

(77) Vail, J.G.: Sodium Metasilicate Philadelphia Quartz Co., Philadelphia, (1930)

THE CHLORINATION OF TETRACHLOROETHANE

by

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Submitted to the Faculty of Graduate
Studies and Research in partial fulfilment of the requirements for the
degree of Doctor of Philosophy.

McGill University

1941.

TABLE OF CONTENTS

Ph.D. Chemistry

J.A.Pearce

I. THE CHLORINATION OF TETRACHLOROETHANE

There is little information on the conversion of liquid tetrachloroethane to hexachloroethane, and the method used commercially is somewhat involved. The object of this work was to obtain information that could be used in designing a plant to convert tetrachloroethane to hexachloroethane in the liquid phase in as few steps as possible.

As a result of this study it was observed that:

1.(a) The thermal reaction was not satisfactory for commercial development. The dark reaction was very slow.

(b) In the thermal reaction added materials do not give a rate faster than the fastest rate obtained without added materials.

2. Photochemical chlorination in the liquid phase may be made to give satisfactory rates.

3. The characteristics of the photochemical change, some of which may favour, others hinder technical development are briefly:

(a) Small temperature coefficient.

(b) Reaction proceeds rapidly only in thin layers.

(c) Indications that the rate $\propto (I)^{\frac{1}{2}}$.

I. INTRODUCTION

(a) General

In spite of the fact that chlorinations have been studied since Faraday's time, in both gas and liquid phases, catalyzed by added materials and accelerated by light, there is much contradictory information in the literature. Egloff, Schaad, and Lowry, reviewing the halogenation of aliphatic hydrocarbons (2), point out some of this contradictory information.

Hexachlorethane has been prepared in the past by the following methods:

(i) Acetylene was led into S_2Cl_2 containing iron powder. Allowing the reaction to proceed at the boiling point formed hexachloroethane while allowing the reaction to proceed with gentle cooling produced tetrachloroethane (C.A., 1, 950^2. German patent).

(ii) Tetrachloroethane was chlorinated using ultra violet light or other light source rich in active rays to produce penta- and hexachloroethane (C.A., 6, 2824^5. German patent. C.A., 7, 2286^8. British patent.)

(iii) Tetrachloroethane was chlorinated using vegetable charcoal, animal charcoal, bleaching powder, $FeCl_3$ and $AlCl_3$ as catalysts. It was reported here that only hexa-, no pentachloroethane, was formed. (7).

(iv) Miller (9) used a flow method for preparing hexachloroethane from ethylene and chlorine with active charcoal as a catalyst. At 200°C. a poor yield was obtained. But at 300-350°C., admitting ethylene at the rate of 60 c.c./min. and chlorine at 325-250 c.c./min., 92% of the ethylene was converted to hexachloroethane. The conversions were of approximately five hours duration.

(v) Illuminating a solution of tetrachloroethylene in CCl_4 with light (4358Å Hg line) while chlorinating produces hexachloroethane (8). The quantum yield was found to vary from 2500 to 300. The temperature coefficient for the reaction was small (1.16±.08). The rate was believed to vary as $(I_{abs})^{1/2}$. (I_{abs} = rate of absorption of radiation in einsteins/litre/sec.)

(vi) Dickinson and Carrico (1) prepared hexachloroethane in the gas phase from tetrachloroethylene and chlorine illuminating the system with 4358Å Hg light. They found a quantum yield here of only 171 to 287. (cf. (v) above). In line with the results of Gibson and Bayliss (4) they observe that there is little change in the absorption coefficient of chlorine with temperature and established the value of ϵ for chlorine at λ = 4358A° as 1.64. Oxygen was found to inhibit this reaction.

(vii) Ethylene chloride and chlorine have been found to produce hexachloroethane in the gas phase and trichloroethane in the liquid phase at room temperature (5). In the liquid phase the reaction appears to take place at the interface and is accelerated by the presence of HCl.

(viii) Natural gas has been chlorinated to produce 18-20% hexachloroethane, and ethane on chlorination over charcoal at 350°C. produces 70-75% hexachloroethane. O_2 inhibits this reaction. (C.A. 31, 8502[3]).

(ix) Hexachloroethane has been prepared commercially from tetrachloroethane by breaking the tetrachloroethane down to trichloroethylene, chlorinating this to pentachloroethane, breaking the pentachloroethane down to tetrachloroethylene and chlorinating this to hexachloroethane.

(b) Statement of the Problem

Since there is little information on the conversion of liquid tetrachloroethane to hexachloroethane and the method in use commercially is somewhat involved, the object of this work was to obtain information that could be used in designing a plant to convert tetrachloroethane to hexachloroethane in the liquid phase in as few steps as possible.

II EXPERIMENTAL

(a) Apparatus.

Apparatus A, a 500 cc. pyrex flask with a chlorine inlet and condenser attached by ground glass joints, was designed to follow the rate of chlorination by the change in weight as hexachloroethane was formed.

Apparatus B,C,D,E,F, were of pyrex constructed as shown in Figure 1. They were designed to follow the rate of chlorination by the change in boiling point as hexachloroethane was formed.

In the figure: A has a capacity of about 50 cc.; B is a bulb to help eliminate bumping of the material into the condenser C when the material is boiling; D is a chlorine inlet connected to the cylinder by a piece of rubber tube provided with a screw clamp. The screw clamp shut off the chlorine flow during a reading (otherwise the temperature read was lower than it should have been) and made D an enclosed space which helped prevent superheating.

E is a thermometer-well which contained a clear high boiling oil to facilitate temperature equilibrium. F served to introduce tetrachloroethane and catalyst and to facilitate cleaning. G conducted away the excess chlorine. All rubber tubing and corks (H) had to be changed frequently.

The surface to volume ratio of apparatus C was somewhat greater than the others.

Apparatus G was of similar design. The A,B,D,F portions were of quartz; the condenser, of pyrex, joined to the quartz by a mercury seal. The mercury was kept covered with tetrachloroethane, but had to be changed after every run.

Apparatus H was similar to the others but the A and B portions were seven feet long. Its purpose will be discussed later.

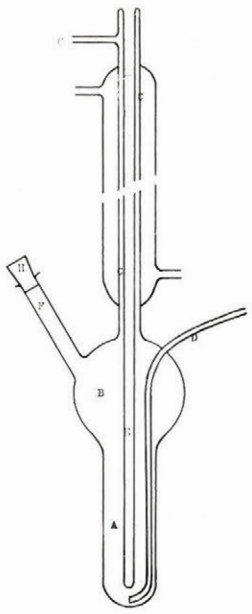

Figure 1

Apparatus used to study the conversion of liquid tetrachloroethane to hexachloroethane

Apparatus I was constructed to study the rate in thin illuminated layers of the liquid. (Solubility data had indicated that light could only penetrate a few millimeters of solution saturated with chlorine.) It consisted of a pyrex tube 8 cm. in diameter. On the bottom was sealed a flat plate. The upper part was drawn down to a neck. Chlorine inlet and condenser were attached by ground glass joints. The samples were removed and their composition determined in the apparatus used to establish the calibration curves. The The upper portions of the flask and condenser were blackened to prevent stray light affecting the reaction.

The determinations for boiling point - composition curves were made in an apparatus similar to B, C etc. This apparatus was much smaller than the others, the A portion having a capacity of only 10 cc. The tube D was permanently sealed off.

The thermometers used were from Fisher Scientific Co., No.405 and No.406, reading 120-230°C. Thermometer No.405 had been compared with a standard thermometer by the company. The results were as follows:

Reading of Standard Thermometer	Reading of Thermometer No.405
+230°C.	+230.00°C.
+218°C.	+218.00°C.
+200°C.	+200.00°C.
+160°C.	+160.10°C.
+140°C.	+140.00°C.

(b) Materials

Work was commenced using crude tetrachloroethane as supplied by Canadian Industries Limited. It was impossible to use this material without purification due to cracking and charring when it was heated.

Attempts to purify the material by letting it stand over KOH and $CaCl_2$ were futile. NaOH is known to cause tetrachloroethane to crack (C.A., 25, 276[7]).

For ease in recording results the polychloroethanes finally used are classified as follows:

Material I - Tetrachloroethane from Canadian Industries Limited. The fraction distilling at 144-148°C. was used.

Material II - The same as material I, the fraction used being dried over $CaCl_2$ to remove any traces of water that may have been present. (This material was used to check the possibility that pentachloroethane was obtained on chlorinating the material treated in this way.)

Material III - Tetrachloroethane from Dow Chemical Company. This was a very pure sample and was further purified by fractionating on a Whitmore column. The fraction taken off at 146.3°C. was used.

Material IV - as $AlCl_3$ caused charring in tetrachloroethane at about 50°C., a sample of III containing $AlCl_3$ was distilled and the sample taken off at 144-148°C. used. (To see if previous history had any effect on the chlorination rate.)

Material V - This was a sample of Material II which had been partly chlorinated and was believed to contain pentachloroethane. Fractionation on the Whitmore Column showed about 5% hexachloroethane. If pentachloroethane was present, the amount was too small to be observed. The tetrachloroethane fraction taken off at 145-147°C. was used in several rate determinations.

Material VI - The variety of rates obtained caused interest in the rate of chlorination of pentachloroethane. This material was supplied by Canadian Industries Limited and fractionated on the Whitmore column. The fraction used boiled at 161.7°C.

Material VII - In establishing calibration curves hexachloroethane was necessary. This was obtained from Dow Chemical Co. and sublimed at 187± 0.5°C.

Cylinders of chlorine were supplied by Canadian Industries Limited. The chlorine was used without purification.

The catalysts used were obtained from various chemical supply houses and were used with purification.

(c) <u>Other Experimental Details</u>

Unless otherwise mentioned, the amount of tetrachloroethane used in a rate determination was 50±1 gms.

The reacting mixture was kept saturated with chlorine during the course of a run.

The vessels were heated in oil baths rather than with the direct flame, and, for reactions at 100°C. water baths were used.

The time periods are recorded in hours to the nearest quarter of an hour. In the last phase of the work, time was determined accurately with a good pocket watch.

Many of the runs may appear to be unusually short. This is due to accidents such as the closing off of the rubber inlet tube by action of chlorine, the material sucking back up the inlet tube or some other similar cause.

The reaction vessels were always cleaned with acetone, following removal of the tetra- and hexachloroethane in ether, and dried in a current of air.

III RESULTS OF DETERMINATIONS BY WEIGHT

For the sake of completeness results obtained with apparatus A are included (Table I). In both cases Material I was used. The conversion was carried out at 100°C., without added materials. A Cenco "Trip Scales" was used for these weight measurements.

The weight increments have not been converted to percent hexachloroethane.

Reliable results were not obtained, owing to loss of chlorine from solution on standing, to changes in chlorine solubility as hexachloroethane is formed and to varying weight of hydrogen chloride in solution.

During these determinations the following solubilities were observed:

At 25°C., - tetrachloroethane dissolved 7.0 g. Cl_2/100 g.

At 25°C., - 66.6% hexa- in tetrachloroethane dissolved 3.7g. Cl_2/100 g.

At 100°C., - tetrachloroethane dissolved 2.1 g. Cl_2/100 g.

At 100°C., - the mixture dissolved 217 g. Cl_2/100 g.

As these were very rough measurements more accurate determinations at a later date indicated the following solubilities of chlorine in tetrachloroethane:

At 23.2°C., - 5.02 g./100 g.
75.0°C., - 2.26 g./100 g. ($\sim$ 0.5 mol/l.)
100.0°C., - 0.71 g./100 g. ($\sim$ 0.16 mol/l.)

Solutility data for HCl is available in the literature (C.A., 29, 2832^3, 7170^5).

TABLE I

Following Conversion of Material I by Weight.

1. 225 gms. of Tetrachloroethane

Time (hrs.)	Wt. increase (g.)
4.25	13.5
8.00	21.2
11.00	28.5
Stand overnight	
14.50	27.5
17.00	41.0
22.00	49.6
25.00	55.5
Stand overnight	
27.25	52.0
28.50	54.0
30.75	56.5
33.50	60.2
37.75	61.0
Stand overnight	
40.25	60.6

2. 296.5 gms.of Tetrachloroethane

Time (hrs.)	Wt. increase (g.)
2.75	8.5
6.00	12.3
8.75	15.0
12.00	15.5
Loss overnight to	12.5
15.00	20.0
Loss overnight to	17.8
23.25	31.0
Loss overnight to	30.0
29.00	38.0
31.75	42.0
36.25	47.0
Loss overnight to	45.5
39.75	52.5
47.75	60.5
Loss overnight to	55.5
51.50	65.0
57.00	72.0
Loss overnight to	69.5

IV ESTABLISHING CALIBRATION CURVES

To follow the rate more conveniently, boiling point - composition curves were established for the systems Hexachloroethane - Tetrachloroethane and Hexachloroethane - Pentachloroethane, Materials VII - III and VII - VI respectively.

The results, expressing % by weight of hexachloroethane, are given in Table II and the curves obtained are shown in Figure 2.

TABLE II

Hexa- in Tetrachloroethane

% Hexa-	B.Pt.°C.
0.0	146.3
12.8	148.8
29.6	154.5
40.9	157.2
55.9	165.2
74.4	172.9
90.5	180.6
100.0	sublimes 187.

Hexa- in Pentachloroethane

% Hexa-	B.Pt.°C.
0.0	161.7
13.6	164.3
29.5	167.6
46.1	171.4
64.3	175.2
100.0	sublimes 187.

Each of the above recorded points is the mean of at least three determinations. The maximum deviation in temperature readings is ±0.5°C.

These curves were used to determine the % conversion in the remainder of the work.

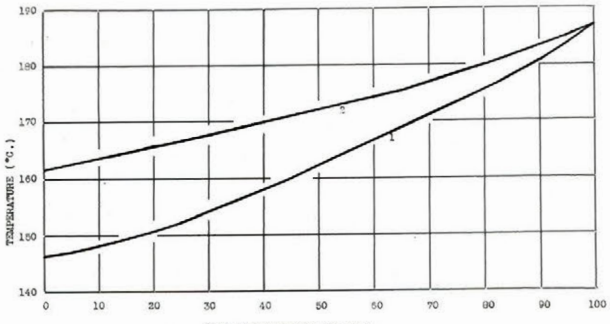

Figure 2

Boiling Point Composition Curves

Curve 1 - Hexa- in Tetrachloroethane
Curve 2 - Hexa- in Pentachloroethane

V RESULTS OF CONVERSIONS AT BOILING POINT

(a) Without added materials.

In the beginning a study of the rate of chlorination at the boiling point (which changes, of course, as hexachloroethane is formed) was attempted. Three curves for the non-catalyzed reaction were obtained. See Table III and Figure 3.

TABLE III[*]

Conversion of Material I
at boiling point without added materials.

App B		App C		App D.	
Time	%	Time	%	Time	%
1.25	11.5	1.25	11.5	1.50	16.5
2.50	14.0	3.00	18.6	2.50	24.0
6.25	18.4	4.00	21.1	4.50	26.0
10.50	32.5	5.75	22.6	7.00	28.2
21.25	53.0	16.25	47.7	17.25	43.7
23.25	57.0	20.25	66.3	20.25	54.8
27.75	63.3	21.50	80.7	21.75	63.9
31.00	68.4			23.75	65.0
				26.25	66.5

[*] (Tables III - XIII show the running time in hours and the percent by weight of hexachloroethane formed.)

(b) With added materials.

Using Material I an attempt was made, to find a catalyst. Aluminum chloride seemed the most likely of the materials generally used as catalysts (7). Much difficulty was encountered in its use as it caused charring (cf.experimental) of the tetrachloroethane.

Ten percent of $AlCl_3$ caused such a heavy charring that readings could not be made; prechlorination for several

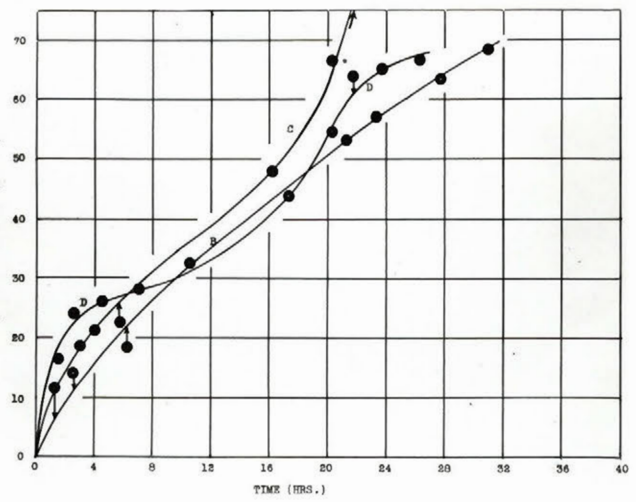

Figure 3

The following key will show the meaning of the symbols used in fig.3-10.

Key

Material I ●
Material II ▲
Material III ■

Material IV ○
Material V △
Material VI □

Mixtures X

hours before adding the catalyst did not prevent this charring.

One half percent of $AlCl_3$ still caused charring but in apparatus B after 11.5 hours 25.6% of hexachloroethane was produced.

One fifth percent of $AlCl_3$, in some cases gave slight charring and in other cases no charring at all. The study was carried on at this $AlCl_3$ concentration. The results obtained are given in Table IV.

Attempts at using $FeCl_3$ (7) showed it to cause even more charring than $AlCl_3$.

Two concentrations of $SnCl_2$ were tried; 0.2% gave no charring but 2% caused some charring that became more pronounced as the reaction proceeded.

Two percent of $NiCl_2$ was tried. It caused no charring.

The results are summarized in Table V (i).

Three concentrations of S_2Cl_2 were used. One fifth percent gave no charring; 2.0% gave no charring (Table V (ii). Twenty percent of S_2Cl_2 reduced the boiling point of the tetrachloroethane to 141°C. The subsequent rise in temperature as the reaction proceeded was taken as an indication of the rate. In seven hours 7.5% conversion was effected.

TABLE IV.

Conversions of Material I
at the boiling point with $AlCl_3$ added.

App C.		App D.		App E.	
Time	%	Time	%	Time	%
No charring		Charring		Charring	
1.00	13.5	3.25	15.1	5.00	13.1
2.00	20.4	10.50	17.0	8.25	16.7
3.50	24.9	20.00	19.0	10.00	18.0
5.25	40.0			22.00	21.0
7.75	54.0				
10.75	63.2				

- -

App C.		App D.		App E.	
Very slight charring		Charring		Charring	
1.25	12.9	1.25	13.5	1.00	9.9
2.50	15.1	2.75	16.4	2.00	21.3
3.50	17.2	3.25	22.7	4.25	23.5
4.75	21.2	4.00	26.1		
5.75	24.7	5.25	27.1		
8.50	28.1	6.00	28.2		
12.75	32.5	7.25	29.3		
23.25	42.8	18.00	35.0		
25.50	46.4	20.00	41.4		
29.75	50.6				
33.50	58.8				
35.75	64.4				

TABLE V

Conversion of Material I
at the boiling point using other added materials.

App B.		App C.		App E.	
Time	%	Time	%	Time	%
(i) 20% $SnCl_2$		0.2% $SnCl_2$		2.0% $NiCl_2$	
3.50	5.3	1.00	14.0	2.00	6.1
5.25	5.3	3.50	25.5	3.25	8.8
8.25	5.3	7.25	31.6	5.25	10.3
		16.25	36.1	7.75	11.0

- -

(ii)

2.0% S_2Cl_2		0.2% S_2Cl_2	
1.00	9.7	2.00	9.7
3.00	13.2	9.25	10.5
4.00	15.5	10.50	13.0
5.75	17.4	21.50	16.4
16.25	29.8	25.00	20.0
20.25	36.8		

VI RESULTS OF CONVERSIONS AT 100°C.

(a) Without added materials.

It was noticed at this time, that rates at 100°C. seemed to be faster than rates at the boiling point, while at room temperature (25°C.) there seemed to be hardly any reaction. Rate studies were therefore made at 100°C.

Tables VI - IX, give the results of these studies in pyrex.

Figures 4 (data in Table VII) and 5 (data in Table VIII) are representative of the type of rate curves obtained.

Table X, shows the result of three runs in the quartz apparatus (G).

Table XI, shows the results obtained in apparatus B,E,F, when packed with finely ground pyrex.

TABLE VI

Conversions at 100°C. in Apparatus B
using various samples of tetrachloroethane
without added materials.

Material II

1.

Time	%
5.25	17.0
10.50	24.6

2.

Time	%
6.25	32.3
11.25	42.5
16.75	44.5

Material IV

1.

Time	%
3.25	24.8
7.00	33.4
19.25	45.0
27.25	53.7
36.50	61.0

2.

Time	%
5.00	42.0
13.25	66.7
17.25	78.9

Material V

Time	%
3.25	27.5
8.50	40.3
13.50	54.4
18.75	63.9

Mixture

38.7% Material II 61.3% Material III

Time	%
6.50	14.0
14.50	18.0
20.50	22.2
25.50	26.3

TABLE VII

Conversions at 100°C. in Apparatus C
using various samples of tetrachloroethane
without added materials.

Material I

1.

Time	%
4.25	19.0
9.25	43.5
11.75	45.0

2.

Time	%
3.00	13.0
6.25	24.8
9.50	33.0
16.75	69.8
21.50	74.6

Material II

1.

Time	%
3.75	26.0
7.00	30.0
12.00	47.4
16.00	61.1
20.50	75.3

2.

Time	%
5.25	31.0
10.50	65.3

3.

Time	%
6.25	35.4
11.25	60.4
16.75	75.2

4.

Time	%
4.25	20.4
9.75	33.4
15.00	53.0
21.50	66.0

5.

Time	%
4.75	21.4
13.25	38.4
17.25	51.6

6.

Time	%
4.25	4.5
10.00	21.0

7.

Time	%
3.25	11.6
8.25	29.0
12.25	33.2
17.25	52.0
22.50	56.5
25.75	62.5

8.

Time	%
4.25	11.0
10.50	26.5
14.50	31.0
18.75	31.8
23.00	33.2
27.25	36.1

9.

Time	%
5.25	17.6
10.00	26.5
14.50	27.2
22.75	33.4
26.75	47.5

10.

Time	%
5.50	24.8
11.00	24.8
15.50	39.5
20.50	40.0
25.00	54.0
30.25	56.1

Material III

1.

Time	%
4.00	6.4
11.75	12.0
16.25	20.5
24.00	32.5
29.00	47.6
33.00	59.7
38.25	64.3

2.

Time	%
5.50	20.0
10.00	31.6
15.00	65.3
18.25	76.4

3.

Time	%
4.00	27.1
8.25	53.8
13.75	60.8
19.75	83.7

Material IV

Time	%
5.00	24.9
10.25	35.0
16.50	51.3
21.00	64.2

Material V

Time	%
3.50	49.3
8.50	73.6

Mixture 19.1% II
80.9% III

Time	%
6.75	26.4
16.00	46.1
22.25	59.4
29.50	71.3

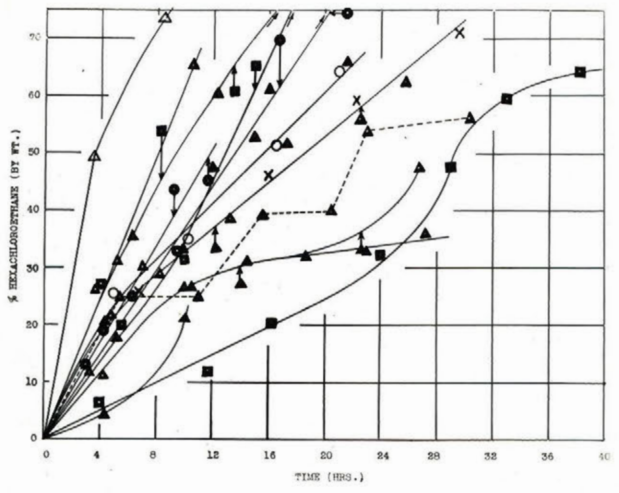

Figure 4

Conversions at 100 C. in Apparatus C using various samples of tetrachloroethane without added materials.

TABLE VIII

Conversions at 100°C. in Apparatus D
using various samples of tetrachloroethane
without added materials.

Material II

1.

Time	%
4.00	28.6
7.75	49.3
11.00	57.1
17.75	74.5
23.00	82.5

2.

Time	%
6.25	14.3
11.50	28.0
21.25	33.2
27.50	42.0
31.25	47.4

3.

Time	%
3.25	25.7
8.25	45.3
12.25	45.9
17.25	53.8
22.50	58.0
25.75	64.3

4.

Time	%
4.25	26.0
9.75	38.6
15.00	52.0
21.50	57.5

5.

Time	%
4.25	17.4
10.50	30.8
14.50	39.5
18.75	44.6
23.00	52.0
27.25	54.8

6.

Time	%
5.25	20.4
10.00	34.8
14.50	37.5
22.75	44.8
26.75	67.5

7.

Time	%
4.75	32.0
13.25	51.6
17.25	65.3

8.

Time	%
5.50	18.9
11.00	21.4
15.50	32.0
20.50	33.7
25.00	40.9
30.25	40.9

9.

Time	%
4.25	10.9
10.00	25.8

Material III.

1.

Time	%
5.25	12.2
8.75	13.5
13.00	17.5
18.50	27.5
24.75	32.9
29.00	55.8
37.25	67.7

2.

Time	%
5.50	28.6
10.00	35.3
15.00	70.8
18.25	75.3

3.

Time	%
4.00	24.0
8.25	34.6
13.75	45.7
19.75	61.1

Material IV

Time	%
3.50	12.9
7.75	24.0
12.25	35.0

Mixtures

1.

21.2% II
78.8% III

Time	%
3.75	6.4
9.75	11.7
15.25	14.3
19.75	20.6

2.

42.0% II
58.0% III

Time	%
7.75	6.4
15.50	11.7
20.75	14.3
26.00	21.0

3.

40.7% II
59.3% III

Time	%
4.00	3.7
9.00	11.7
14.00	18.4
19.00	25.6

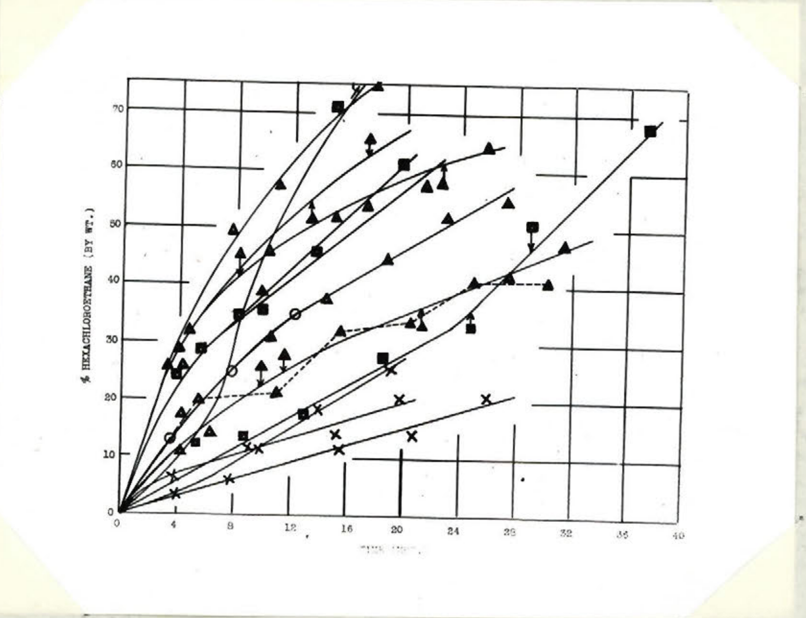

Figure 5

Conversions at 100 C. in Apparatus D using various samples of tetrachloroethane without added materials.

TABLE IX

Conversions at 100°C. in Apparatus E
using various samples of tetrachloroethane
without added materials.

Material I

1.

Time	%
3.25	24.2
11.75	60.7
15.50	69.9
19.25	80.1

Material II

1.

Time	%
5.00	9.6
11.00	25.6
16.75	32.5
21.75	40.9

2.

Time	%
6.25	25.6
11.50	27.0
16.50	37.0
21.25	39.8
27.50	50.1
31.25	64.2

3.

Time	%
3.25	26.1
8.25	43.4
12.25	47.5
17.25	64.6
22.50	65.4
25.75	81.3

4.

Time	%
4.25	29.5
9.75	55.0
15.00	61.5
21.50	68.4

5.

Time	%
4.25	15.5
10.50	29.8
14.50	35.7
18.75	43.0
23.00	45.3
27.25	45.9

6.

Time	%
5.25	15.5
10.00	26.5
14.00	32.4
22.75	40.5
26.75	63.4

7.

Time	%
4.75	31.8
13.25	51.6
17.25	57.8

Mixtures

1.		2.		3.	
19.6% II 80.4% III		19.1% II 80.9% III		38.7% II 61.3% III	
Time	%	Time	%	Time	%
4.50	8.7	3.75	8.7	3.75	9.6
8.00	20.6	9.50	25.0	9.00	23.7
17.25	30.2	14.50	34.4	14.00	39.5
23.75	45.0	19.50	45.0	19.00	52.0
31.25	49.5				
35.75	56.4				

TABLE X

Conversions at 100°C. in Apparatus G (Quartz) using Material II without added materials.

Material II

1.		2.		3.	
Time	%	Time	%	Time	%
4.25	0.0	6.50	17.5	5.25	9.9
5.00	13.1	11.00	33.0	9.75	17.2
22.75	56.0	15.00	37.2	14.75	33.0
26.50	74.5	19.00	44.6	18.00	43.7
		23.25	55.8	22.50	50.4
		30.00	76.7	26.75	75.7

TABLE XI

Conversions in pyrex packed Apparatus at 100°C.

Material II

1. App.E.

Time	%
5.50	26.8
11.00	28.7
15.50	36.6
20.50	38.3
25.00	49.5
30.25	54.0

2. App.F.

Time	%
5.50	29.0
11.00	32.5
15.50	45.9
20.50	54.0
25.00	67.2
30.25	74.3

3. App. E.

Time	%
4.25	4.0
10.00	18.3

4. App. F.

Time	%
4.25	21.0
10.00	54.4

5. App. B.

Time	%
1.00	8.8

Material III

1. App. F.

Time	%
3.75	14.9
8.00	29.4
13.50	40.2
19.50	45.0

(b) With added materials.

At 100°C. attempts were made to catalyze the reaction by adding the following materials:

1. Activated coconut charcoal (7) caused a large drop in the boiling point of the tetrachloroethane. As Yamaguchi (C.A., 29, 4326^5) had observed that charcoal caused dechlorina-

tion of tetrachloroethane at 400°C. it was suspected that some cracking may have been taking place at 100°C.

2. The addition of small quantities of water had no effect on the rate. Larger quantities caused a drop in the boiling point with no change in rate.

3. Benzoyl peroxide caused no increase in rate.

4. $AlCl_3$ addition (0.2%) behaved in much the same manner as at the boiling point. Table XII (i).

5. SO_2 and Cl_2 passed over activated coconut charcoal at 100°C. did not increase the rate. Table XII (ii). The addition of SO_2Cl_2 merely decreased the boiling point with no change in rate.

6. Nickel gauze was added in two rate determinations to see if it corroded or affected the rate, i.e. could nickel be used as a reaction vessel. There was slight corrosion of the nickel but no change in rate. Table XII (iii).

TABLE XII

Conversions at 100°C. using various samples of tetrachloroethane with added materials.

(i) Material I Apparatus C. - 0.2% $AlCl_3$

Time	%	Time	%
Slight charring		No charring	
2.00	11.8	5.75	17.5
7.00	17.2	8.50	29.6
9.75	19.1	12.75	56.1
14.25	21.5	16.00	72.9
24.75	60.0	18.50	77.2
32.75	71.9		

(ii) Material I - SO_2 and Cl_2 passed over activated coconut charcoal at 100°C.

Apparatus D		Apparatus E	
5.75	32.0	6.75	34.4
8.75	47.7	11.50	46.8
12.75	62.9	14.50	54.9
16.25	70.3	22.00	76.8
18.75	73.6		

(iii) Material II - Nickel gauze added.

Apparatus B		Apparatus C.	
5.25	16.6	5.00	21.5
9.75	24.0	9.50	38.7
14.25	36.0	14.25	64.2
20.25	43.4	20.00	79.4

VII RESULTS OF CONVERSIONS FROM PENTACHLOROETHANE

The rate of chlorination of pentachloroethane to hexachloroethane was determined in two cases at 100°C. (Table XIII, Fig. 6).

TABLE XIII

Conversions at 100°C. using Material VI without added materials.

Time	%	Time	%
Apparatus D		Apparatus E	
2.00	6.0	2.00	27.2
4.25	8.4	4.25	40.8
8.75	14.9	8.75	61.3

VIII DISCUSSION OF THERMAL RESULTS

Throughout the course of the work simultaneous or successive rate determinations did not coincide in more than two simultaneous or successive cases. This was believed due to some fault in the experimental set up. In accumulating the above results the following details were considered, but changes did not eliminate this heterogeneity of rates;

(i) The outlet tubes (G) were near the ventilating fan. It was suspected that the fan may have caused a slightly reduced pressure in the system.

(ii) The use of different chlorine cylinders.

(iii) Different position of the reaction vessels in the laboratory (in relation to the windows).

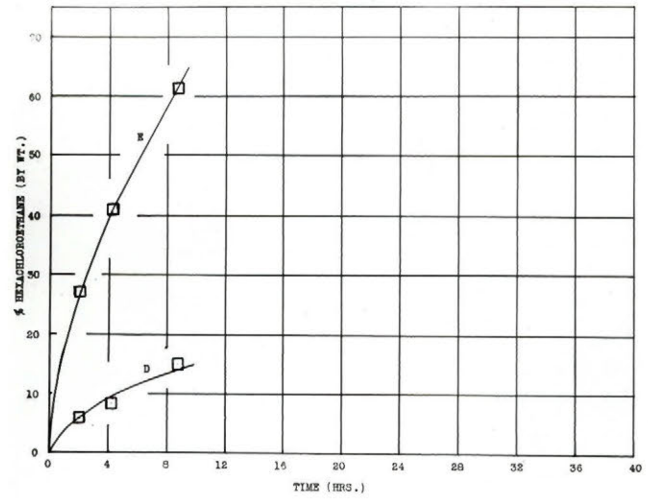

Figure 6.

Conversions at 100°C. using pentachloroethane without added materials.

Curve D - in Apparatus D
Curve E - in Apparatus E

(iv) To see if ultra violet was the effective light an ultra violet sun lamp was turned on Apparatus A containing material II. In 24.0 hours, 72% conversion was effected i.e. 3%/hr. This was only an average rate.

(v) At one time it appeared that Material III (very pure) was slower than the less pure sample (II). The rates found with mixtures eliminated the possibility of there being any trace catalyst in the less pure material.

(vi) The question arose as to whether the reaction might not be taking place in the condenser. A rate determination, in apparatus H eliminated this.

(vii) The length of the neck above the bulb in each apparatus was slightly different. In case the reaction was taking place here at 100°C. in the gas phase, apparatus H was wound and kept at 100°C. during a determination. (The tetrachloroethane was boiled to drive the vapor into the column). Only an average rate was obtained.

(viii) The purity or previous history of the material is not the cause of the discrepancy in rates.

After several rate determinations the hexachloroethane was extracted and weighed. The weight deviated very little from the value found using the calibration curves. This supports the indication (cf. experimental) that very little pentachloroethane was present, and is further supported by Kokatnur's observations (7).

The apparent increase in rate at 100°C. over the rate at the boiling point was not true for all cases.

Tables X and XI, show that the glass surface was not catalyzing the reaction, although, it had appeared that the glass surface may have had a catalyzing effect.

No added material seemed to give a rate faster than the fastest rate obtained without added material.

The same heterogeneity of rates is indicated for the chlorination of pentachloroethane.

It seemed likely that some factor not yet considered was affecting the rate. From data supplied by the Meteorological Bureau Table XIV was drawn up. (the three reaction vessels had been kept in the same water bath and the same chlorine cylinder and same outlet had been used for several runs.)

The table shows the percentage conversion per hour for a number of runs, the portion of the day when the measurements were made, the average hours of sunlight (in tenths of an hour), the average atmospheric pressure (in mm. Hg.) and the daily relative humidity.

TABLE XIV

Relating data from Meteorological Bureau and rates of conversion.

Rate of Conversion/Hr.			Portion of Day	Av. Sun	Pressure	Humidity
C	D	E				
3.6%	7.9%	8.0%	Morning	0.0	762.6	93
3.5	3.9	3.5	Afternoon	0.0	762.4	
1.0	0.2	1.0	Night	0.0	762.0	
3.8	1.6	3.4	Morning	0.1	762.6	89
0.9	0.8	0.1	Night	0.0	757.6	
1.8	1.9	4.9	Morning	0.6	752.5	72
4.8	6.1	7.0	Morning	1.0	763.5	64
2.4	2.3	4.6	Afternoon	1.0	760.5	
3.7	2.6	1.2	Morning	0.4	749.0	71
2.0	0.8	1.1	Afternoon	1.0	752.1	
2.6	4.1	3.7	Morning	0.9	765.3	66
2.5	2.1	2.3	Afternoon	0.7	763.6	
1.1	2.2	1.5	Morning	0.0	758.6	87
0.2	1.2	1.7	Afternoon	0.0	755.0	
0.3	1.7	0.5	Night	0.0	755.0	
0.7	0.7	0.1	Morning	0.9	751.0	70
3.4	3.9	3.0	Morning	0.7	756.5	61
1.9	3.0	2.3	Afternoon	0.9	756.7	
0.2	0.6	1.0	Morning	1.0	763.2	67
0.8	0.6	1.3	Afternoon	0.7	765.2	
3.5	5.7	5.7	Morning	1.0	767.2	58
4.5	3.4	4.9	Morning			
2.0	2.3	2.3	Afternoon			
3.3	3.4	1.6	Morning			
4.5	3.4	4.9	Afternoon			
0.0	0.5	0.3	Night			

Plotting this data showed no relation between humidity and rate, and, as would be expected, no relation between the rate and sunshine, as the sun shone into the laboratory only in the mornings.

There was a slight indication of increase in rate with increase in pressure, but a rate determination with a column of water seven feet high attached to the outlet of apparatus D (increasing the internal pressure by about 1/4 atmos.) gave a rate of conversion of 0.4%/hr. This eliminates pressure changes as the major cause of our rate discrepancies.

When the average rate for the three assemblies of apparatus is listed as in Table XV it is apparent that rates at night are considerably slower than during the day.

These results indicate that light is the cause of the previously mentioned discrepancies in spite of the experiment with the sunlamp or the changing of the positions of the reaction vessels relative to the windows.

Experiments were, therefore, continued to investigate the photochemical chlorination reaction.

TABLE XV

Rates of Conversion of tetrachloroethane
and portion of day during which the conversion occurred.

	Morning	Afternoon	Night *
	6.5%/hr	3.6%/hr	0.7%/hr
	2.9		0.6
	2.9		
	6.0	3.1	
	2.5	1.3*	
	3.5	2.3	
	1.6	1.0*	0.8
	0.5		
	3.4	2.4	
	0.7	0.9*	
	4.9		
	4.2	2.2	
	2.8	4.3	0.3
Average	3.1	2.3	0.6

* Unless the chlorinating period between temperature determinations was entirely after $10^{\underline{00}}$ P.M. the determination was not considered a night determination.

IX CONCLUSIONS FROM THERMAL RESULTS

1. Chlorinating tetrachloroethane in the liquid phase in diffused daylight results in a heterogeneity of rates.
2. Added materials do not give a rate faster than the fastest rate obtained without added material.
3. Rates at night are much slower than rates during the day - indicating that light may be effective in increasing the reaction rate.

X RESULTS - PHOTOCHEMICAL

(a) To Prove Light Effective

That light is effective in catalyzing the reaction was proven by :

(i) constructing an asbestos tent and placing it over the reaction vessels at different times. Table XVI shows that when the apparatus was covered the rate observed was the same as obtained for runs made at night.

Table XVI

Conversions using Material II when apparatus is alternately exposed to diffuse sunlight and covered by a tent.

Apparatus	Rate of Conversion/hr. Uncovered	Rate of Conversion/hr. Covered
C	3.3 ; 3.1 ; 2.9	0.1 ; 0.4 ; 1.1
D	2.4 ; 1.6 ; 2.6	0.3 ; 0.0 ; 2.5
E	1.8 ; 2.5 ; 2.5	0.3 ; 0.9 ; 0.9
Average	2.5	0.7

One of the alternately uncovered and covered runs is shown by the dotted curve in each of figures 4 and 5.

(ii) By allowing the reaction to proceed for about 48 hours in the dark and then turning on seven

500 watt incandescent lamps.

This light combination caused a tremendous increase in rate as compared with the fastest rate obtained in diffused daylight (compare Tables XV, XVI, XVII).

TABLE XVII

Rate of conversion of Material II in the dark and under the influence of seven 500 watt lamps.

Time	% Conversion/hr.			Average Rate/hr.
	App.C	App.D	App.E	
7.00	16.6	15.4	13.4	
13.50	17.5	15.4	16.5	
21.50	21.2	22.0	22.0	
28.50	25.6	24.3	23.7	0.6 %/hr. (dark rate)
35.50	27.8	24.9	24.3	
42.50	29.5	25.6	24.9	
49.50	33.7	30.4	27.0	(Lights turned on)
51.50	87.2	66.6	62.3	20.8 %/hr. (rate when illuminated)

Apparatus C seems to have had a faster rate than the other two when the lights were on. It will be noticed in section VI that apparatus C showed some rates considerably faster than apparatus D and E rates. This may have been due to the greater surface to volume ratio of apparatus C.

If light is effective in catalyzing the reaction in only the first few millimeters of liquid, it would be expected that the greater the surface exposed to the light the faster should be the reaction. This would explain why in some of the rates previously observed the walls seemed to have an effect that was not emphasized by packing the vessel with glass.

Some light and temperature combinations were then tried to get an idea of the rate-temperature relation and how altering intensity of the light affected the rates. These results are shown in Table XVIII.

(b) The Light Absorbed

A spectrograph was used in an attempt to find which wave lengths of light were absorbed i.e. which wave lengths were effective in speeding up the reaction.

The plates showed a continuous spectrum from 6000A° to 2850A° . In light of later work, it did not seem necessary to study above 6000A° .

Since pyrex vessels were used the effective light must be transmitted by pyrex. The pyrex vessels used transmitted light to 3150A°. Pyrex is reported to have an extinction coefficient of 10.6 at 3000A° (3).

Tetra-, penta- and a 50-50 solution of tetra- and hexachloroethane were all transparent to light in the region 6000-3150A° . Hamai (6) reports di-, tri, tetra-, penta-, and hexachloroethane transparent to Hg 4360A° and 3650A° light, but the presence of Cl_2 makes them opaque to these

TABLE XVIII.

Rates of conversion obtained at various light intensities and temperatures.

Apparatus	Rate per hour									
	In the Dark			One 500 w. Lamp.		Seven 500 w. Lamps.				
	100°C.			100°C.		100°C.		43.2°C.	at B.Pt.	At B.Pt.*
C	1.4%	0.0%	0.0%	14.6%	14.1%	22.0%	26.5%	20.7%	3.3%	24.0
D	0.1	3.0	2.0	27.7	15.1	--	18.4	--	1.0	8.2(?)
E	2.0	0.0	0.0	19.7	--	24.5	19.6	17.9	9.0	5.9(?)
Average	0.9%			18.2%		22.2%		19.3%	4.4%	

* In this case the vessels were boiled using a direct flame in contrast to using an oil bath in the case previous to it.

(?) These rates are doubtful, it is suspected that the chlorine flow into these two vessels stopped during the run.

wave lengths.

In this work addition of Cl_2 to the above two liquids and the solution rendered them opaque to light in the region 4600-3150A° i.e. from blue light to the limit of the ultra violet obtainable.

Gibson and Bayliss (4) report the extinction coefficient of chlorine gas at 18° C. to change with wave lengths as follows:

λ A°	ϵ	λ A°	ϵ
4275	2.3	2666	2.7
3862	9.4	2802	7.9
3741	18.2	2883	15.7
3640	29.0	3011	33.3
3573	37.5	3074	44.7
3484	50.6	3174	58.2
3346	64.3	3274	64.3

They report that as the temperature is increased the absorption at the maximum is decreased but the region of continuous absorption is increased.

Since the run with the ultraviolet lamp did not increase the rate it was suspected that light from 4600A°-4000A° was the most effective. Especially as the Hg 4360A° line appears to be the one most used for chlorinations and brominations (1,8,10,11). (Poor intensity might explain the failure of the sun lamp to accelerate the reaction.)

(c) The Depth of Penetration of the Effective Light

In part (a) of section IX it was indicated the effective light was not penetrating the whole of the solution. It was also indicated that the intensity of the light made very little difference in the rate, and, that there was a very small temperature coefficient. It would appear from part (b) that blue and violet was the effective light.

Apparatus I was used to establish or contradict these indications. A light chamber was constructed so the whole bottom of the flask could be illuminated while in a water bath. A Corning filter (#586) transmitting near ultraviolet (3900 to 3300A°) in conjunction with a photo cell and galvanometer were used to keep a check on the intensity of the light during the runs. It was believed that this range would roughly represent the light absorbed by the chlorine solution.

The results obtained using a 500 watt tungsten filament lamp at 75° and 100° C. and a 200 watt tungsten filament incandescent lamp at 100°C. for both tetra- and pentachloroethane are given in tables XIX-XXII and shown in figures 7-10.

In these tables the first column always shows the thickness of the liquid in the flask in mm. All rates are recorded as percent conversion by weight in one-half an hour. Each determination generally lasted one-half an hour. A run of fifteen minutes duration was used when 0.5 mm. layers were employed. When pentachloroethane was being studied the rate of conversion in half an hour had to be obtained from runs as short as five minutes. This had to be done because beyond 50-60% conversion the reacting mixture becomes solid, invalidating the determination and increasing the sampling error. The last column in the tables shows the value of the rate of conversion in half an hour for each thickness of liquid as read from the smooth curve. For this reason, these values may be a little different from the experimental values.

Table XIX (fig.7) records the results obtained at $75 \pm 2^{\circ}$C. with a 500 watt lamp. Using material II, a spread of values, with every now and then a fast run, was observed. When material III was used the results coincided with the averages of the slower rates obtained with material II. It is probable that some impurity in material II occasioned the fast rates.

TABLE XIX

Conversions using a 500 Watt Lamp
at 75 ± 2°C.

(i)

t(mm.)	Percent Conversion							
	Material II					Average	Material III	Value from smooth curv
0.5	55.6	57.2				55.7	54.4	58
1.0	51.2	47.6	45.0	45.6	50.8	47.9	47.0	48
1.5	41.6	38.4	41.1	35.0	42.6	39.9	---	39
2.0	34.1	29.5	34.1	30.4		32.2	32.8	33
2.5	24.1	23.4	32.2	26.0		26.4	---	28
3.0	25.3					25.3	24.7	24
5.0	----------------					---	16.8	17

- -

(ii)

t(mm.)	Fast Runs				
0.5	81.6	87.6	75.0	83.0	81.8
1.0	65.5				65.6
1.5	56.0				56.0
2.0	---------------				----
2.5	50.3	47.6	42.7	53.6	48.5
3.0	47.5	35.4	34.9		39.3
5.0	24.4	28.6			26.5

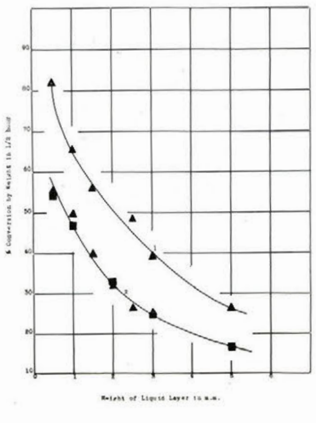

Figure 7

Conversions using 500 Watt Lamp
at 75 ± 2°C.

Curve 1 - Fast Runs - Material II
Curve 2 - Average Runs - Material II & III

Table XX shows the results with material III at 100°C. using a 500 watt bulb. From table XIX and XX the average temperate coefficient between 75° and 100° can be obtained. (Fig. 8 compares the average rates obtained at 75°C. with those obtained at 100°C.)

TABLE XX

Conversions using 500 Watt Lamp
at 100°C.

t(mm.)	Percent Conversion		
	Material III		Value from smooth curve
0.5	(115.0)	90.0	90
1.0	57.6	54.5	58
1.5	50.4		48
2.0	35.9		40
2.5	35.2		35
3.0	31.4		31
5.0	22.2		22

TABLE XXI

Conversions using a 200 Watt Lamp
at 100° C.

t(mm.)	Percent Conversion					
	Material V			Material III		Value from smooth curve
0.5	(118)	32.0	37.0	66.4	($\sim$60)	66
1.0	55.8	17.6		46.5	44.2	47
1.5	54.7			37.9		38
2.0	44.3			31.4		31
2.5	----			----		27
3.0	----			23.4		23
5.0	31.3	32.7		14.7		15

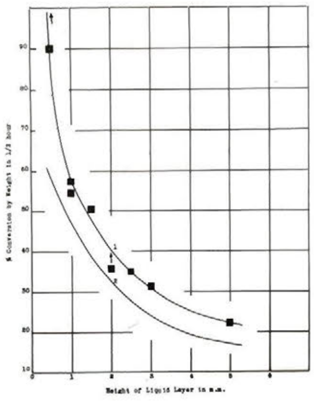

Figure 8

Conversions using a 500 Watt Lamp

Curve 1 - Rates at 100° C.
Curve 2 - Rates at 75° C.

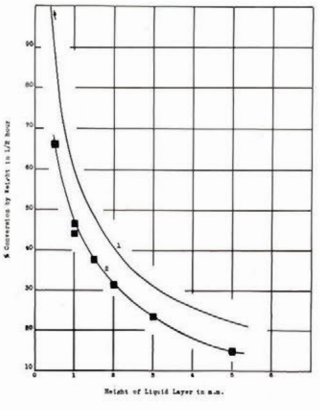

Figure 9

Conversions at 100° C.

Curve 1 - using 500 Watt Lamp.
Curve 2 - using 200 Watt Lamp.

As a matter of curiosity material V was used in attempting to determine the rates at 100°C. with the 200 watt lamp. Again scattered results were obtained, so, material III was reverted to in establishing rates under these conditions. These results are shown in table XXI. Figure 9 shows the drop in rate occasioned by using the smaller lamp.

It seemed of interest to see how the rate of conversion of pentachloroethane compared with tetrachloroethane. The results of determinations at several thicknesses are shown in table XXII. These values are only approximate as the rate is so fast that accurate determinations are difficult. Figure 10 compares the rates obtained for tetra- and pentachloroethane at the same light intensity and temperature.

TABLE XXII

Conversions using a 200 Watt Lamp
at 100° C.

t(mm)	Percent Conversion Material VI	Value from smooth curve
0.5	($\sim$ 240)($\sim$ 140)	190
1.0	82.5	84
1.5	----	77
2.0	70.6	71
2.5	----	66
3.0	62.4	62
5.0	52.6	53

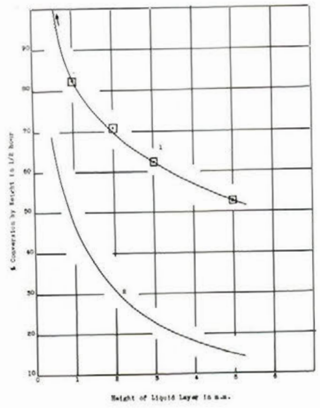

Figure 10

Conversions using a 200 Watt Lamp
at 100° C.

Curve 1 - Conversion of Pentachloroethane.
Curve 2 - Conversion of Tetrachloroethane.

XI DISCUSSION OF PHOTOCHEMICAL RESULTS

From the data in tables XIX and XX (figure 8) temperature coefficients (between 75° C. and 100° C.) may be calculated for a constant light source (Table XXIII).

TABLE XXIII

Temperature Coefficient at Constant Light Intensity.

t_{mm}	$\frac{R_{T+10}}{R_T}$
0.5	1.17
1.0	1.08
1.5	1.09
2.0	1.08
2.5	1.09
3.0	1.11
5.0	1.10
Average	1.10

These values are of the same order as temperature coefficients calculated for other similar light sensitized chlorinations, eg., 1.16 (8) 1.13, 1.21 (10), support the data in Table XVIII.

From tables XX and XXI and figure 9 it is seen that the rate is greater when the source of light is more intense.

According to wattage ratio the ratio of rates with each lamp should be $\frac{500}{200} = 2.5$.

The 500 watt lamp gave a deflection on the galvonometer of 4.3 units while the 200 watt lamp gave a deflection of 2.5 units. These deflections indicate that the intensity of the light in the range where chlorine absorption occurs was not 2.5 times as strong in the 500 watt lamp but only $\frac{4.3}{2.5} = 1.7$ times as strong.

Calculations of ratios of the rates with the 500 watt lamp and 200 watt lamp (at 100°) gives us the data in table XXIV.

TABLE XXIV

Ratio of rates at different light intensities at constant temperature.

t_{mm}	$\frac{R_{500\ W}}{R_{200\ W}}$
0.5	1.4
1.0	1.2
1.5	1.3
2.0	1.3
2.5	1.3
3.0	1.3
5.0	1.5
Average	1.3

Even though the galvonometer deflections do not represent all the band of light absorbed by the chlorine, it would be expected that the ratio of the intensities would be more nearly identical. A rather astonishing coincidence is found when the ratio of the square root of the intensities is taken:

$$\frac{\sqrt{4.3}}{\sqrt{2.5}} = \frac{2.1}{1.6} = 1.3 = \frac{R_{500\ W}}{R_{200\ W}}$$

i.e. it seems that rate $\propto (I)^{\frac{1}{2}}$.

Essentially the same observation has been made in the chlorination of tetrachloroethylene (8). However, no definite conclusion can be drawn from the use of only two intensities.

Table XXV shows that pentachloroethane is converted to hexachloroethane at a rate approximately 2.5 times as fast as tetrachloroethane, i.e. if the reaction goes through pentachloroethane the pentachloroethane conversion is not a retarding feature of the reaction. (Table XXV is arranged from data of Tables XXI and XXII.)

TABLE XXV

Ratio of rate of conversion of penta- and tetrachloroethane at constant light intensity and temperature.

t(mm)	$\frac{R_{penta-}}{R_{tetra-}}$
0.5	2.9
1.0	1.8
1.5	2.0
2.0	2.3
2.5	2.4
3.0	2.7
5.0	3.5
Average	2.5

Another feature that offers interesting speculation is the rate obtained in each 0.5 mm. layer of liquid (assuming the layers of liquid do not mix) as the volume of the liquid is increased. These rates are shown in table XXVI for the temperatures and lamps used.

TABLE XXVI

Rate of conversion of tetrachloroethane in each 0.5 mm. layer.

Layer	Percent Conversion in each layer		
	500 W. 75°C.	500 W. 100°C.	200 W. 100°C.
0.0-0.5	58	90	66
0.5-1.0	17	13	14
1.0-1.5	7	9	7
1.5-2.0	4	4	3
2.0-2.5	2	3	2
2.5-3.0	1	2	1

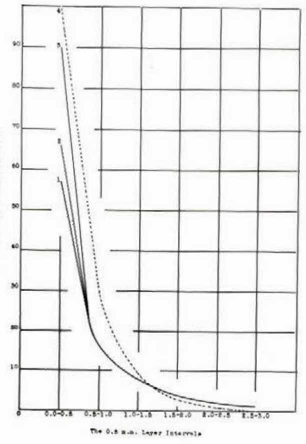

Figure 11

Rate of Conversion of
tetrachloroethane in each 0.5 mm. layer.

Curve 1 - Rate in layers at 75°C using 500 watt lamp
Curve 2 - Rate in layers at 100°C using 200 watt lamp
Curve 3 - Rate in layers at 100°C using 500 watt lamp
Curve 4 - Ideal rates falling off, if light at maximum absorption is effective, and 100% conversion is obtained in first layer.

A sample calculation at 75°C. with 500 watt lamp:

Percent conversion with 1.5 mm. liquid = 39

Percent conversion with 2.0 mm. liquid = 33

If no reaction took place in the 1.5-2.0 mm. layer the conversion in 1.5 mm. would have merely been decreased by dilution due to the added 0.5 mm. of liquid.

Decreased rate expected due to dilution = 3/4 x 39 = 29% in $\frac{1}{2}$ hour.

But, since 33% in $\frac{1}{2}$ hour was the conversion obtained, the conversion in the 1.5-2.0 mm. layer = 33-29 = 4% in $\frac{1}{2}$ hour.

Data of Table XXVI is shown graphically in fig.11. Here, only the difference in the 0.0-0.5 mm. layer is shown. The other values are not sufficiently different, i.e. it would seem that increased intensity is only effective in increasing the rate in a very thin layer.

It is of interest to include (Table XXVII) a few calculations showing by what fraction the original intensity is reduced in passing through layers of tetrachloroethane, 0.5 mm. thick, saturated with chlorine at 100°C.

To do this:

(i) Beer's Law is used $I = I_0 10^{-\epsilon cd}$.

where I = intensity of the transmitted light

I_0 = intensity of the incident light

ϵ = the extinction coefficient

Where c = concentration of the material absorbing the light (cf. part III)

d = thickness of the absorbing material in cm.

(ii) It is assumed that the values of ϵ for chlorine gas (4) for different wave lengths are valid for chlorine in tetrachloroethane solution.

TABLE XVII

Fraction by which light intensity at different wave lengths is reduced on passing through each 0.5 mm. layer.

λ	ϵ	I/I_0
3346	64.3	0.306
3484	50.6	0.394
3573	37.5	0.501
3640	29.0	0.579
3741	18.2	0.715
3862	9.4	0.841
4275	2.3	0.959

Comparing the decrease in rate with increasing thickness (Table XXVI and Figure 11) with these fractions showing how the light decreases on passing through each 0.5 mm. layer it would appear that the light about the region of maximum absorption of chlorine (λ = 3200-3400A^{o} is the most effective for this reaction.

Curve 4, fig. 11 shows how the rate should drop off if this were the effective light, if the rate varied as the intensity and if a rate of 100% conversion in a half an hour were assumed for the 0.0-0.5 mm. layer.

It is well known that light at λ 4360A° has sufficient energy to break the chlorine bond.

Ultra violet is indicated to be more effective than visible, which might be taken to indicate that after the chlorine bond is broken the chlorine atom must be activated.

Since light at λ 4360A° is active in chlorine additions (1,8) it might be that light of greater energy would be necessary for substitutions.

XII CONCLUSIONS FROM PHOTOCHEMICAL RESULTS

1. Light is a most effective means of increasing the rate of conversion of tetrachloroethane to hexachloroethane in the liquid phase.

2. Light exerts its greatest effect only in the first few millimeters of liquid nearest the light source.

3. Calculations from known values of the extinction coefficient for chlorine gas indicate that ultraviolet light in the region where chlorine has maximum absorption (λ = 3200-3400A°) is the most effective. This indicates that light which not only breaks the chlorine bond but activates the chlorine atom may be used to obtain maximum rates.

4. If the rate varies as the first power of the intensity of the incident light, to double the intensity should double the rate. If, as indicated, the rate varies as the square root of the intensity, doubling the intensity increases the rate by a smaller factor.

5. The reaction has a small temperature coefficient of about 1.10 for 10° change of temperature.

6. Obviously a great deal more work could be done to arrive at conclusions of theoretical importance. It is not considered, however, that this would aid materially in the construction of a commercial plant. These results are offered only as an aid to design a plant for the chlorination of tetrachloroethane in the liquid phase on a commercial scale.

XIII SUMMARY

1. The thermal reaction is not satisfactory for commercial development. The dark reaction is very slow.

2. Photochemical chlorination in the liquid phase may be made to give satisfactory rates.

3. The characteristics of the photochemical change, some of which may favor, others hinder technical development, are briefly:

   (a) Small temperature coefficient.

   (b) Reaction proceeds rapidly only in thin layers.

   (c) Indications that the rate $\propto (I)^{\frac{1}{2}}$.

BIBLIOGRAPHY

1. Dickinson, H.G. & Carrico, J.L.: J. Am. Chem. Soc.; 56, 1473-80 (1934).

2. Egloff, G., Schadd, R.E. & Lowry, C.D.: Chem. Rev.; 8, 1- 80 , (1931).

3. Farkas, A. & Melville, H.W.: Experimental Methods in Gas Reactions; McMillan & Co., 1939. Chap.IV.

4. Gibson, G,E. & Bayliss, N.S.: Phys. Rev.; 44, 188-192 (1933).

5. Hamai, S.: Bull. Chem. Soc. Japan; 9,542-8 (1934).

6. Hamai, S.: Bull. Chem. Soc. Japan; 10, 43-50 (1935).

7. Kokatnur, V.R.: J. Am. Chem. Soc.; 41,120-4 (1919).

8. Leermakers, J.A. & Dickinson, R.G.: J. Am. Chem. Soc.; 54, 4648-57 (1932).

9. Miller, G.E.: Ind. Eng. Chem.: 17,1182-3 (1925).

10. Muller, K.L. & Schumacher, H.J.: Z.Physik.Chem.;
    B-35, 285-97 (1937).
    B-35, 455-62 (1937).

11. Willard, J. & Daniels, F.: J.Am. Chem. Soc.; 57, 2240-5 (1935).

A STUDY OF HEAT EVOLUTION DURING THE SORPTION OF GASES BY CHARCOAL

by

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Submitted to the Faculty of Graduate
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II. A STUDY OF HEAT EVOLUTION DURING THE SORPTION OF GASES BY CHARCOAL.

The purpose of this study was to explore the possibility of finding a gas or mixture of gases which when sorbed on gas mask charcoals will involve sufficient heat to render the gas mask ineffective.

The results, using high concentrations of a number of gases and gas mixtures that were believed to create the most heat when sorbed on a charcoal, showed that these gases and gas mixtures under field conditions would not create sufficient heat on a charcoal to render a gas mask ineffective.

III. A NEW METHOD OF STUDYING SORPTION IN A FLOW SYSTEM AND SOME EXPERIMENTAL VALUES FOR THE SORPTION OF BUTANE.

An apparatus has been put into operation which permits a continuous study of temperature rise and other data at various rates of air flow, moisture contents of air and charcoal, concentrations of the sorbate to be studied, and at various depths of the charcoal bed.

Several studies using this apparatus are suggested.

A new measure of service time that can be easily determined is suggested.

A STUDY OF HEAT EVOLUTION DURING THE SORPTION OF GASES BY CHARCOAL.

Purpose.

To explore the possibility of finding a gas or mixture of gases which when sorbed on gas mask charcoals will evolve sufficient heat to render the gas mask ineffective.

Introduction.

The data, recorded in the literature, on the sorption of gases by activated charcoal shows that the heat evolved in some cases is relatively large. In the case of oxygen, for example, the heat of sorption on "Norit" rises from 70,000 calories at 18°C. to 115,000 or 116,000 at 200°C. and to the astounding value of 224,000 calories at 450°C. (2,5).

Besides being a function of temperature the heat evolved will depend on the chemical character of the sorbate and the nature and history of the sorbent. Gaudechon (3) and Gurwitsch (4) found that the greatest heat effects are produced in the sorption of especially reactive substances. The sorption of such substances is often accompanied by a decomposition process, e.g. ethylene dichloride and sulphuryl chloride (6, p.61). Arsine on charcoal is believed to decompose into arsenic and atomic hydrogen.

In the case of impregnated charcoals chemical combination of the sorbate with the impregnation may occur with the evolution of heat. Unfortunately, there are few data in the literature on this point. The moisture content of the charcoal may also determine the nature of the sorption process, the sorbing power of the charcoal and its activity as a catalyst for decomposition. This is well illustrated by the behaviour of phosgene on wet charcoal (1,7). Here the amount of sorption is a function of the wetness of the charcoal and hydrolysis to carbon dioxide and hydrogen chloride occurs.

It is apparent from the foregoing that for certain favourable cases, a high heat of sorption accompanied possibly by a heat of decomposition or a heat of reaction or both could result in a large overall heat evolution. Since adiabatic conditions prevail in the interior of the charcoal this effect may be extraordinarily pronounced.

Arsine is well adapted to such a study; it is toxic, decomposes on carbon, and experiments in this department have shown it to have a large heat of sorption on gas mask charcoals. The heat evolution has been reported to be great enough to cause the charcoal to smoke, Consequently arsine and some reactive fluorides were considered suitable for a preliminary investigation.

Experimental

The apparatus consisted of a cell 1.5 cm. radius and 5 cm. in height, provided with two thermocouples inserted into the centre of the charcoal at 1 and 4 cm. levels. Air was metored through the cell by means of a "Hyvac" of controlled pumping capacity. The gas was introduced into the air stream from a burette by mercury displacement. The flow of mercury was regulated by a scratched stop cock.

Where the nature of the air is not specified in the results, unconditioned room air was used.

A copper impregnated charcoal was the adsorbent in all experiments except those with chlorine, ethane and acetylene, where an unimpregnated charcoal was used. For all but one case the charcoals contained approximately 15% moisture.

Arsine and brominetrifluoride were prepared in this department, all other gases were obtained from commercial firms.

Results.

Results are shown in Table I.

It should be noted that during a run maximum temperature is reached before admission of gas is discontinued and only after most of the water has been driven off. If at the end of a run the air stream is not shut off the charcoal cools rapidly and falls below room temperature

Table I

Gas or Gas Mixture	Ratio of Gases in Mixture	Gas Conc. in air stream	Rate of air flow	Approx. Maximum Temp. reached.	Remarks
AsH_3		1:50	2 l./min.	80°C.	For this gas and all others, moisture was driven off the charcoal and condensed on the glass tubing below the cell. The heating effect appears to be more marked after the water is driven off.
BF_3		1:50	2 l./min.	60°C.	Partial hydrolysis in moist air and on the charcoal. HF passes right through the charcoal.
$AsH_3:BF_3$	1:1	1:50	2 l./min.	90°C.	Partial hydrolysis of the BF_3.
H_2S		1:50	2 l./min.	65°C.	
$AsH_3:H_2S$	1:1	1:50	2 l./min.	90°C.	AsH_3 and H_2S reacted in gas reservoir.
BrF_3		1:50	2 l./min.	40°C.	
$AsH_3:BrF_3$	1:1	2:3		80°C.	A gas-air mixture was passed over the carbon at the rate of 50 c.c./minute.
$COCl_2$		1:50	2 l./min.	70°C.	
$COCl_2:BF_3$	1:1	1:50	2 l./min.	80°C.	Partial hydrolysis of the BF_3.

Table I (cont'd)

Gas or Gas Mixture	Ratio of Gases in mixture	Gas Conc. in air stream	Rate of air flow	Approx. Maximum Temp. reached	Remarks
$COCl_2:H_2S$	1:1	1:50	2 l./min.	90°C.	
SO_2		1:50	2 l./min.	70°C.	
$SO_2:COCl_2$	1:1	1:50	2 l./min.	80°C.	
$SO_2:BF_3$	1:1	1:50	2 l./min.	60°C.	Partial hydrolysis of the BF_3.
N_2O		1:1		30°C.	The gas air mixture was passed over the carbon at the rate of 50 cc./minute.
$N_2O:COCl_2$	1:1	1:50	2 l./min.	65°C.	
Cl_2		1:50	2 l./min.	40°C.	Dry air used on unimpregnated charcoal.
C_2H_2		1:50	2 l./min.	26°C.	" "
C_2H_6		1:50	2 l./min.	29°C.	" "
C_2H_6		1:50	2 l./min.	39°C.	On unimpregnated charcoal dried for 6 hrs. at 140°C.
H2O			2 l./min.	40°C.	" The air stream bubbled through water before entering cell.

Table II

Run #24
Unimpregnated charcoal dried at 140°C. for 6 hours.
Rate of air flow = 2 l./min.
Ethane concentration = 1:50
Room Temperature = 26°C.

Time (min)	Temp. of charcoal	
0	26°C.	
2	39	
3	33	
6	28	
11	26	
14	26	Ethane shut off
15	22	
17	21	
20	23	
26	24	
29	26	
33	26	

due to desorption. This is shown for ethane in Table II.

A more detailed analysis of the thermal effects was made during the runs with chlorine ethane and acetylene. Here an unimpregnated charcoal was used. (Runs were conducted with dry and wet charcoals and dry and wet air). It would not be profitable to give all these in detail; the results obtained showed that where the equilibrium value of the moisture in the charcoal is greater than the moisture content of the air stream desorption of water occurs. This desorption is so pronounced as to diminish markedly the temperature rise and for weakly sorbed materials, e.g. ethane and acetylene, the temperature may fall below the initial value. A typical run showing this is given in Table III.

Table III

Run #18
Unimpregnated Charcoal
Rate of Air Flow = 21./min.
Acetylene concentration = 1:50
Room Temperature = 23°C.

Time (min)	Temp. of Charcoal
0	23°C.
1	24
2	26
2½	22
3	21
6	20
8	19

Discussion.

The maximum temperature values in the tables were generally smaller than anticipated. Bromine trifluoride is perhaps exceptional in that, although exceedingly reactive, relatively small heat was developed.

It must be remembered, however, that the experiments with ethane, acetylene and chlorine show that the values recorded in Table I are peculiar to and conditioned by the nature of the experimental method. Here, two factors prevent a large temperature rise:

1. The charcoal used was wet; since water has a remarkably high heat of adsorption (approx. 11,000 cals.) and, hence of desorption, a very large portion of the heat developed is utilized in desorbing water. This is verified by the adsorption of ethane on wet and dry charcoal. In the former case the maximum heat attained was three degrees above the initial temperature; in the latter, thirteen degrees above the initial temperature.

2. In a dynamic flow system the air stream exerts a large cooling effect. This is illustrated by the fact that a maximum temperature is reached before the introduction of the gas is discontinued and by the very rapid cooling of the charcoal under the influence of the air stream above.

It is quite probable that for a static system with a dry charcoal the temperature rise would be considerably higher. Unfortunately, such conditions do not prevail in practice and it seems unlikely that the charcoal temperature could be raised above 100°C. This condition appears particularly valid because gas concentrations used were approximately one hundred times greater than under field conditions.

McBain (6, p.58 et sq.), discussing the activation of charcoals, points out that charcoal does not decompose appreciably in a stream of air at about 350 C. consequently the heat developed can at most, serve to desorb other gases present. In practice the temperature rise, hence the desorption, would probably be small.

The possibility exists, of course, that other gases may be found which have more suitable characteristics than those investigated. Other methods of investigation e.g. the use of pyrotechnical materials might also prove fruitful.

Conclusion

The possibility of using gas or gas mixture to create sufficient heat on a charcoal to render a gas mask ineffective has been examined and the results indicate that the method is not feasible under field conditions.

REFERENCES

1. Barden and Scarletescu, Bull.Soc.Chim., 6, 46,(1939).
2. Garner, W.E. and McKie, D., of Chem. Soc. 1927, 2451.
3. Gaudechon, H. Compt. read., 157, 209, (1913)
4. Gurwitsch, L.G. J. Russ. Phys-Chem. Soc. 47, 805, (1915).
5. Keyes, F.C. and Marshall, M., J. Am.Chem. Soc. 49,156 (1929).
6. McBain J.W., The Sorption of Gases by Solids, Routledge and Sons, London (1932)
7. Neilsen, J., Z.ges. Scheiss-Spreng, 136, 27 (1932).

A NEW METHOD OF STUDYING SORPTION IN A FLOW SYSTEM AND SOME EXPERIMENTAL VALUES FOR THE SORPTION OF BUTANE

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A NEW METHOD OF STUDYING SORPTION IN A FLOW SYSTEM AND SOME EXPERIMENTAL VALUES FOR THE SORPTION OF BUTANE

Introduction

Preliminary work on the temperature effects during sorption in a flow system has been reported (3). It was obvious that reliable data could be obtained only under carefully controlled conditions and that correlation of heat data with other sorption measurements was essential.

An apparatus has therefore been designed and put into operation which permits a study of temperature rise and other data at various rates of air flow, moisture contents of air and charcoal, concentrations of the sorbate to be studied, and at various depths of the charcoal bed.

The apparatus is designed to follow continuously the amount of sorption, the temperature rise at various points in the charcoal bed, and to collect samples of the sorbate passing out of the charcoal bed.

Experimental

Details of the apparatus are shown in Figures 1 and 2.

Referring to Figure 1, air is introduced at A from a compressor through a 45 l. ballast volume at approximately the desired rate. B, represents a series of soda-lime tubes to remove carbon dioxide from the air. The air is dried by three calcium chloride tubes (C) and brought to the correct moisture level (4) in a series of sulphuric acid bubblers (D). A scratched stopcock (E_1) permits closer control of the volume of air admitted to the cell. The rate of air flow is measured by the calibrated butylphthallate flowmeter, G. H leads to a calcium chloride tube used to check the moisture content of the air and is used only before and after a determination. During a run the air is carried directly to the cell at I, the gas being admitted to the air shortly before it reaches the cell.

The sorbate is admitted from the cylinder at P, passes through the purification train represented by O and goes to a 26.28 l. storage volume at N. By maintaining a pressure greater than atmospheric in N (measured on the mercury manometer, M) and careful regulation of the scratched

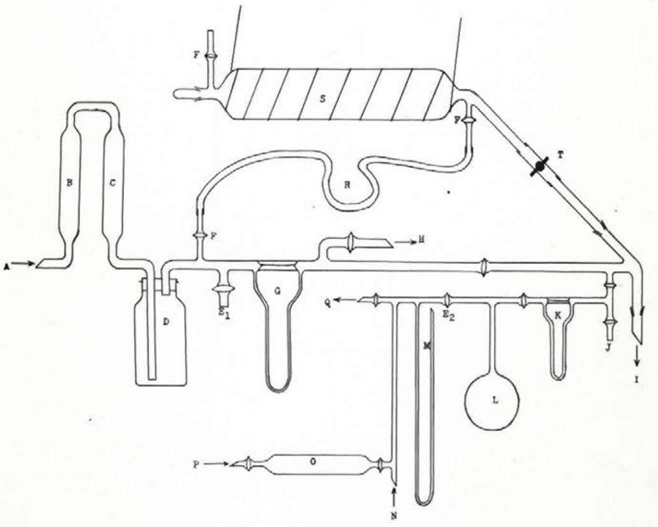

Figure 1.

Diagram of Sorption System.

stopcock (E_2) the sorbate can be admitted into the air stream at any desired rate. L acts as a buffer volume and K is a calibrated butylphthallate manometer. The blow-off J permits regulation of the sorbate flow to the desired value before introducing it into the air stream. Q goes to a Cenco Hy-vac.

The charcoal is stored in the volume, S. Prior to use it is heated to 400 ± 10 C. for 12 hours in a stream of dry, carbon dioxide-free air, then allowed to cool to room temperature and attain equilibrium with air of the desired moisture content for another 12 hours. The screw clamp and rubber tubing at T allows for the delivery of the required amount of charcoal into the cell without letting it come into contact with anything but air of the desired moisture content. Packing should be a constant factor since this arrangement always delivers the charcoal from a constant height. The stopcocks (F) on the conditioner are kept closed except when conditioning of charcoal is taking place. R is a piece of rubber tubing to permit the conditioner to be moved.

The sorption cell is shown in Figure 2. It consists of a piece of glass tubing of 4 cm. inside diameter and 21 cm. long. A brass cap is fastened to the top of the tube with DeKhotinsky cement. Through the centre of the cap is a brass tube 1.5 cm. in inside diameter and 7 cm. long.

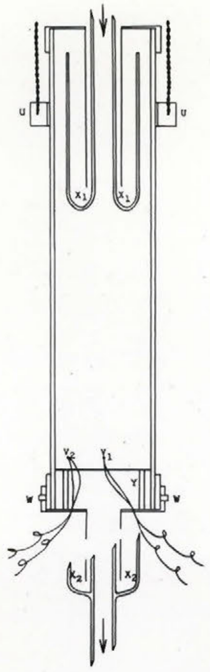

Figure 2.

Diagram of Sorption Cell.

The walls of this tube are 0.25 mm. thick. The bottom is closed by a similar cap, the only differences being that the brass tube extends out of rather than into the cell and the cap is attached to a brass ring by a semi-screw arrangement of projections (W) in the brass ring and slits in the cap. By this means the cap can be drawn tightly against the bottom of the tube. The brass ring is fastened to the glass tubing with Dekhotinsky cement. Thus a sample of used charcoal can be readily removed from the cell.

The charcoal rests on a piece of metal gauze of the type generally used in gas masks. This is attached to a short length of glass tubing arranged to let the air flow freely on passing out of the cell.

The cell is marked in centimeters so that the depth of the charcoal bed can be varied from one to six centimeters.

The cell is suspended from the arm of a balance by two light chains attached to pivots in a ring (U) that clamps around the cell. To allow the Cell to move freely the brass tubes dip into cups (X_1,X_2) filled with butylphthallate attached to the inlet tube (I, Figure 1) and to an outlet tube.

The accuracy of a weighing is about ±0.005 gm.

V_1 and V_2 are thermocouples; V_1 is in the centre of the cell and V_2 1.5 cm. away from it. Both are arranged to measure the temperatures in the middle of the last centimeter layer of the charcoal bed. The thermocouple wires are B & S #28 gauge and are coiled loosely so as to not interfere with the weighing.

Evacuated gas pipettes of about 600 cc. volume are attached to a "T" in the outlet tube. A capillary tube allows the pipettes to be filled at a rate less than the rate of the air stream, therefore only air from the air stream can be drawn into the bulb.

In commencing this work butane was chosen as a suitable sorbate for study. It was analyzed by combustion; the analysis detecting less than 0.01% butane. As butane is very pure it was only passed through $CaCl_2$ dryers in the purification train.

The charcoal used was unimpregnated and had been in contact with a dry carbon dioxide-free air stream for 12 hours prior to use, after being heated to 400°C. for 12 hours in a dry carbon dioxide-free air.

The air stream used during these preliminary determinations was free of carbon dioxide and contained only 0.004% water vapor (by volume). The rate of air flow was 2.5 litres per minute.

The accuracy anticipated in this arrangement of apparatus was ±5%, as it is very difficult to attain much greater accuracy when studying colloidal systems.

(NOTE: When referring to charcoal in the cell, the term '1 cm. bed' refers to a depth of 1 cm. of charcoal in the cell, '2 cm. bed' refers to a depth of 2 cm. of charcoal in the cell, and so on; while the 'first centimeter layer' refers to the layer of charcoal lying between 0 and 1 cm. in the cell, the 'second centimeter layer' refers to the layer lying between 1 and 2 cm. in the cell, and so on.)

A Sample Experiment.

To facilitate understanding of this apparatus the record of a sample experiment is as follows:

Dry, carbon dioxide-free air is passed through the cell to remove any traces of moisture that may have collected in the tubing and cell. The air stream is then passed through a weighed calcium chloride tube at H at the required rate for a definite length of time, to check its moisture content.

The cell is weighed empty with the air stream cut off. The air stream is started and the required amount of charcoal is delivered. The charcoal weight is obtained while having momentarily diverted the air stream through H. The air is again passed through the cell and the cell is balanced in the presence of the air stream. The zero readings on the thermocouples obtained.

The rate of flow of butane is then regulated using the blow-off (J). At the appropriate moment the butane flow is changed to pass through the cell, the pressure on the manometer (M) is read and the first sampling bulb is opened to the issuing air stream.

Weight readings are taken at five minute intervals except in the case of a one centimeter charcoal bed. Temperature readings are taken more often. Samples of the issuing gas are taken whenever the time is felt to be appropriate. (It is interesting to note here that the appropriate time for taking gas samples can be fortold reasonably well from the value of the thermocouple reading.)

When the experiment is finished the final pressure on M is read and the increment in weight of the charcoal is taken without the gas-air stream passing over the charcoal as a check on the readings taken in the presence of the air stream. Maximum difference ih these two sets of weighings is about ±0.02 gms.

It must be realized that both butane and air flow will vary to a certain extent. A sample of data for a determination is as follows (details of the combustions are omitted, and the temperature readings have been converted to degrees, as the millivolt readings would have no meaning to the reader):

Experimental Conditions

Room Temperature = 24.2°C.
Atmospheric Pressure = 76.0 cm. Hg.
Rate of Air Flow = 2.5 l./min(approx) =(1.70 on flowmeter scale)

Weight of $CaCl_2$ tube after passing air through for 15 min. = 49.4952

Weight of $CaCl_2$ tube before = 49.4942
Increment due to moisture = 0.0010 gms.

Volume of moisture present $= \frac{0.0010}{18.0} \times 24{,}500 = 1.4$ cc.

Volume of air passed $= 2500 \times 15 = 37500$ cc.

% moisture (by volume) $= \frac{1.4 \times 100}{37{,}500} = \sim 0.004\%$

Rate of Butane Flow ≈ 50 cc./min.(approx) = (14.8 on flowmeter scale)

Volume of Butane Used -

Manometer Readings	Left arm	Right arm	P(cm.Hg.)
Initial	76.1	46.2	29.9 + P(atmos.)
After 55 min.	72.4	50.9	21.5 + P(atmos.)
	Decrease in Pressure		8.4 (cm. Hg.)

Volume of Butane used $= \frac{8.4}{76.0} \times 26.28 \times 10^3 = 2905$ cc.

Actual Flow Rate $= \frac{2905\text{cc.}}{55} = 52.8$ cc./min.

Depth of dry, unimpregnated charcoal bed 4 cm.

Weight of charcoal and cell = 31.36
Weight of cell = 4.62
Weight of charcoal = 26.74 gms.
Weight of charcoal, cell and Butane sorbed = 35.03
Weight of Butane sorbed = 3.67 gms.

Time (min.)	Weight (gms.)	V_1(°C.)	V_2(°C.)	Bulb taken off and composition
0	31.83	25	25	Bulb 1 opened to air stream) at 1 min
3				Bulb 2 off) comp. = 0.02 % Butane
5	32.35	26	26	
8		30	29	
10	32.92	33	32	Bulb 2 opened to air stream)at 11 min
13		37	35	Bulb 2 off) comp.= 0.03 % Butane
15	33.48	40	38	
18		42	41	
20	34.02	45	43	
22		45	44	Bulb 3 opened to air stream)at 23 min
25	34.47	45	43	Bulb 3 off) comp.= 0.12 % Butane
30	34.85	45	41	
32		44	49	Bulb 4 opened to air stream)at 33 min
35	35.15	42	37	Bulb 4 off) comp.= 0.17% Butane
40	35.33	36	32	Bulb 5 opened to air stream)at 41 min
43		32	30	Bulb 5 off) comp.= 1.60% Butane
45	35.40	30	29	
50	35.46	28	28	
55	35.48	27	26	Bulb 6 opened to air stream)at 56 min
58				Bulb 6 off) comp.= 1.75 % Butane
60	35.48	26	26	
65	35.48	25	25	

Results

In Table I the temperature rise, as measured in the centre of each centimeter layer, is shown as a function of time. The bracketed figure shows the temperature at the outer thermocouple. Figure 3 shows the temperature-time curves for the centre thermocouple and in the centre of each centimeter layer. Temperature values were read to the nearest degree.

The results showing the weight increment in the respective charcoal beds and the flow rates are given in Table II and shown in Figure 4.

The time at which maximum temperature rise occurs in the last layer of each bed (calculated from Figure 3) in relation to the shape of the weight time curves is shown by the arrows in Figure 4.

Since the depth of the charcoal bed cannot be adjusted to give exactly the same weight of charcoal per centimeter depth, it is of interest to calculate $\frac{X}{m}$ for the various charcoal beds. This with volume of butane admitted per gram of charcoal, is given in Table III (Figure 5).

By subtracting the volume of sorbate taken up per gram of charcoal from the total amount of gas admitted per gram of charcoal at any definite time we get the amount of

Table I

Temperature rise in the centre of various charcoal layers as a function of time.

Layer

1st cm.		2nd cm.		3rd cm.		4th cm.		5th cm.	
Time (min.)	Temp. rise (°C)	Time (min.)	Temp. rise (°C)	Time (min.)	Temp. rise (°C)	Time (min.)	Temp. rise (°C)	Time (min.)	Temp. rise (°C)
1	7(6)	3	6(5)	3	2(2)	5	2(1)	3	0(0)
2	10	5	9(8)	5	5(4)	8	6(5)	5	1
3	11(11)	7	14(13)	7	9(7)	10	9(7)	7	2
5	11(12)	10	17(16)	8	11(9)	13	13(11)	8	4(3)
6	10(11)	13	18(17)	10	13(12)	15	15(13)	10	7(5)
8	8(9)	15	19(15)	12	17(15)	18	18(16)	12	8(7)
10	7(7)	18	17(12)	15	19(18)	20	20(18)	15	11(10)
13	4(4)	20	11(8)	18	20	22	20(19)	18	14(13)
15	3(3)	22	10	20	20(17)	25	21(19)	20	16(14)
18	2(2)	25	7(5)	25	18(13)	30	20(16)	23	17(16)
20	1(1)	30	3(3)	30	13(8)	32	19(15)	25	18(18)
23	1(1)	35	1(1)	35	8(5)	35	18(12)	28	19(19)
25	1(1)	40	1(1)	40	4(3)	40	12(7)	30	19(19)
30	> 0	45	> 0	45	2(2)	43	8(6)	33	19(18)
				50	1(1)	45	5(4)	35	19(16)
				55	> 0	50	3(3)	38	18(13)
						55	2(2)	40	16(12)
						60	1(1)	45	14(9)
						65	> 0	50	12(8)
								55	10(6)
								60	7(4)
								65	3(2)
								70	2(1)
								75	1(1)
								80	> 0

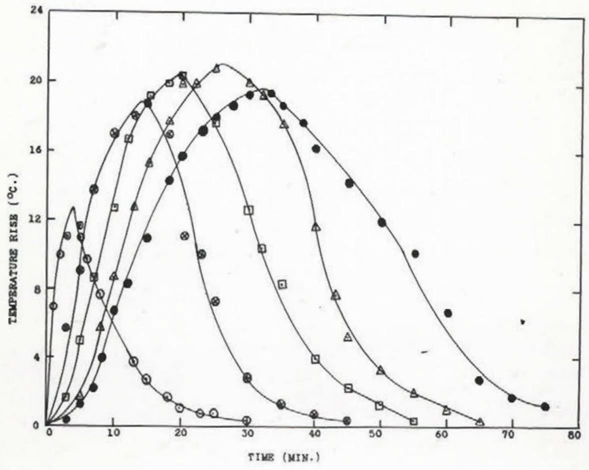

Figure 3.

Temperature rise in the centre of various charcoal layers during sorption of butane.

⊙ In 1st. cm. layer
⊗ In 2nd. cm. layer
▣ In 3rd. cm. layer
△ In 4th. cm. layer
● In 5th. cm. layer.

Table II

Increase in weight in various charcoal beds with time.

Average Rate of Butane flow for series = 50.4 cc./min.

	Rate of Butane flow for each experiment				
	45.5 cc. min.	48.3 cc. min.	52.4 cc. min.	52.8 cc. min.	53.0 cc. min
	Weight of charcoal				
	6.76 gms.	14.26 gms.	20.10 gms.	26.74 gms.	33.51 gms.
	Depth of charcoal bed				
	1 cm.	2 cm.	3 cm.	4 cm.	5 cm.
Time	Increment in weight in gms.				
0	0	0	0	0	0
3	0.27	-	-	-	-
5	0.47	0.50	0.54	0.52	0.54
8	0.74	-	-	-	-
10	0.79	1.00	1.07	1.09	1.11
13	0.87	-	-	-	-
15	0.89	1.45	1.57	1.65	1.70
18	0.90	-	-	-	-
20	0.91	1.71	2.07	2.19	2.23
23	0.91	-	-	-	-
25	0.91	1.85	2.37	2.64	2.81
30	0.91	1.87	2.51	3.02	3.31
35		1.89	2.61	3.32	3.76
40		1.89	2.65	3.50	4.11
45		1.89	2.67	3.57	4.29
50			2.67	3.63	4.51
55			2.67	3.65	4.61
60				3.65	4.66
65				3.65	4.71
70					4.72
75					4.74
80					4.74

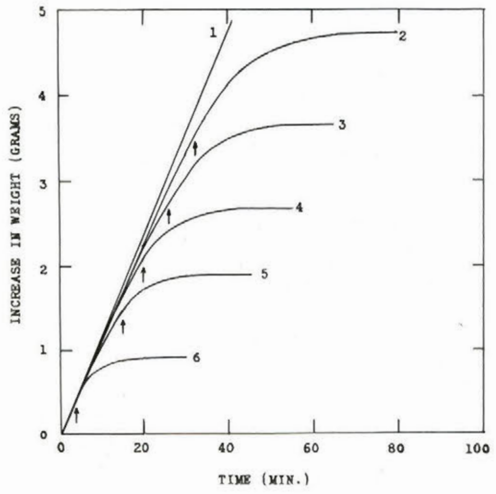

Figure 4.

Showing Increase in Weight in various charcoal beds with time

Curve 1 - Increment in weight for total sorption of butane,

Curves 2,3,4,5,6 show increments in weight in 5,4,3,2,1 cm. charcoal beds respectively.

Arrows indicate time of Maximum Temperature Rise in the last layer of the respective beds.

Table III

Variation of $\frac{x}{m}$ with time for various charcoal beds during sorption of butane.

	Volume of Butane admitted per gm. of charcoal/minute				
	6.7	3.4	2.6	2.0	1.6
	Depth of charcoal bed.				
	1 cm.	2 cm.	3 cm.	4 cm.	5 cm.
Time	Volume of Butane sorbed per gram.				
0	0	0	0	0	0
3	16.7	-	-	-	-
5	28.3	14.8	12.0	8.2	6.8
8	46.1	-	-	-	-
10	49.2	29.5	23.8	17.2	14.0
13	54.2	-	-	-	-
15	55.4	42.8	35.0	26.0	21.4
18	56.1	-	-	-	-
20	56.7	50.5	46.1	34.5	28.0
23	56.7	-	-	-	-
25	56.7	54.6	51.8	41.6	35.6
30	56.7	55.2	55.8	47.6	41.6
35		55.8	56.9	52.3	47.2
40		55.8	57.4	55.1	51.6
45		55.8	57.6	55.7	53.9
50			57.6	56.2	56.6
55			57.6	56.3	57.9
60				56.3	58.6
65				56.3	59.2
70					59.3
75					59.6
80					59.6

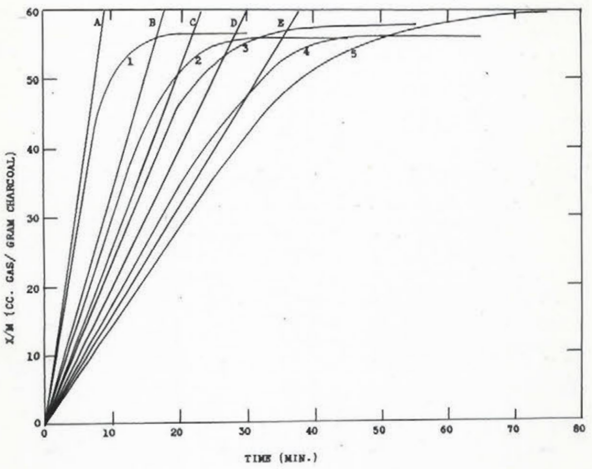

Figure 5.

Variation in $\frac{x}{m}$ with time for sorption of butane by charcoal.

A,B,C,D,E; volume of butane admitted per gm. of charcoal in 1,2,3,4,5 cm. layers respectively.

1,2,3,4,5; $\frac{x}{m}$ for the 1,2,3,4,5 cm. beds respectively.

Table IV

Showing the volume of sorbate that has leaked through various charcoal beds during constant time intervals (on the basis of 1 gm. of charcoal per bed.)

Time(min.)

	5	10	15	20	25	30
Bed.	Volume of butane not sorbed by charcoal (in cc.)					
1 cm.	5.2	17.8	45.1	78.3	110.8	144.3
2 cm.	2.2	4.5	8.2	17.5	30.4	46.8
3 cm.	1.0	2.2	4.0	5.9	13.2	22.2
4 cm.	1.8	2.8	4.0	5.5	8.4	12.4
5 cm.	1.2	2.0	2.6	4.0	4.4	6.4

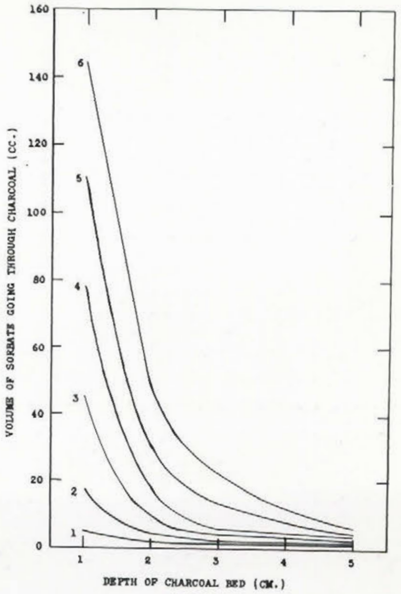

Figure 6.

Showing the volume of sorbate passing through respective charcoal beds (on the basis of one gram) for the time intervals noted.

Curves 1,2,3,4,5,6 show volume of butane passing through charcoal in 5, 10, 15, 20, 25, 30 minute periods respectively.

Table V

Variation in butane with time.

Time Interval (min.)	Depth of charcoal bed.				
	1 cm.	2 cm.	3 cm.	4 cm.	5 cm.
	(a) Percent sorbed (on basis of total gas flow rate).				
0-5	1.65	1.76	1.90	1.77)	1.90)
5-10	1.12	1.76	1.86	2.00)av.=	2.00)
10-15	0.35	1.58	1.75	1.90)1.89	2.07)av.=
15-20	0.07	0.91	1.75	1.90)	1.86)1.97
20-25	0.00	0.14	1.05	1.58	2.04)
25-30	0.00	0.07	0.49	1.33	1.75
30-35		0.07	0.35	1.05	1.58
35-40		0.00	0.14	0.63	1.23
40-45		0.00	0.07	0.25	0.63
45-50			0.00	0.21	0.77
50-55			0.00	0.07	0.35
55-60				0.00	0.18
60-65				0.00	0.18
65-70					0.04
70-75					0.08
75-80					0.00

(b) Percent sorbate in issuing stream (on basis of total gas flow rate).

Bulb	Time Interval (min.),follows percent value,in brackets.-				
1	0.03(0- 2)	0.02(0- 2)	0.02(0- 2)	0.02(0- 2)	0.02(6- 8)
2	0.27(5- 6)	0.03(7- 9)	0.03(10-12)	0.03(10-12)	0.03(14-16)
3	1.12(10-11)	0.95(15-17)	0.65(20-22)	0.12(22-24)	0.22(29-31)
4	1.48(15-17)	1.28(22-24)	1.32(27-29)	1.17(32-34)	1.13(40-44)
5	1.49(20-22)	1.51(31-33)	1.82(35-37)	1.60(40-42)	1.58(54-56)
6		1.52(37-39)	1.81(45-47)	1.75(55-57)	1.87(69-71)

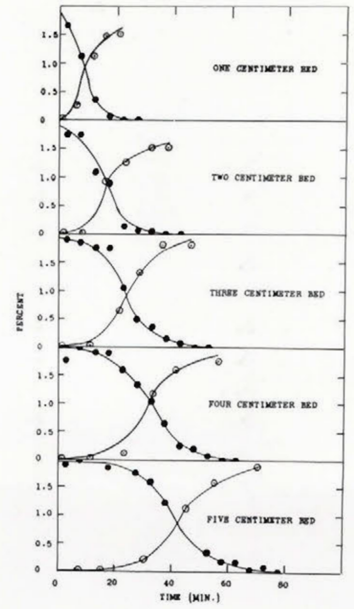

Figure 7.

Variation in sorption of butane with time and depth charcoal bed.

- ● Percent sorbed (on basis of total gas flow rate).
- ⊙ Percent in the issuing stream (on basis of total gas flow rate).

sorbate passing through from one bed and that should be sorbed by the next layer in that time period,on a comparative basis (i.e. per gram of charcoal). This is shown in Table IV and Figure 6.

In Table V and Figure 7 the percent of butane (calculated on the basis of the total gas flow) retained by the charcoal and the percent of butane found in the issuing gas stream are shown as functions of time.

Discussion

It can be seen from figures three and four that the attainment of maximum temperature with increasing charcoal layers is a linear function of time.

The maximum temperature attained appears to increase with the increase in charcoal layer, to reach a maximum temperature value in the fourth centimeter layer and to fall off in the fifth centimeter layer. The increase in the value of the maximum temperature with increase in layer might be expected as the air passing through the first layers is warmed by the heat already generated in these layers, and some of this heat will be transferred to the lower layers. The decrease in the fifth centimeter layer might be explained by assuming since there is some sorption going on in the lower layers while maximum temperature is being attained in the higher layers, therefore the sorption in the last layer is spread over a greater period of time and there is more opportunity for dissipation of the heat. However, from the shape of the time-temperature curve it seems more likely that the rate of air flow increased accidentally during a portion of this determination causing a greater dissipation of heat. Further investigation of this is anticipated.

From Figure 4 it is apparent that the maximum temperature occurs prior to time of maximum sorption. It will be interesting to study the temperature rise at various rates of air flow, various concentrations of the gas in the air stream, and various moisture contents of air and charcoal.

In Figures 4 and 5, we can see that, at first, sorption is directly dependent on the rate of sorbate flow and after some sorption occurs the rate depends on the amount of sorbate already sorbed on the charcoal.

The maximum values of $\frac{x}{m}$ from the data in Table III shows agreement within experimental error. The average value of the maximum $\frac{x}{m}$ is 56.4 cc. per gram.

The value of the data in Table III can be seen more readily, when the data are treated as in Figure 6(Table IV). Here, we can see that some of the butane goes through even a five centimeter charcoal bed almost immediately. This would correspond to zero "service time" by any empirical test of sufficient sensitivity, and it might lead to the conclusion that a thin bed is ineffective.

Authorities suggest conducting a dynamic study to a point where the issuing stream is identical in composition with the entering one (1,2).

It is often rather difficult to determine the exact point at which the composition of the issuing stream is identical with the incoming stream. However, a glance at Figure 7 will show that the point where the amount of sorbate taken from the air stream is equal to the amount of sorbate in the issuing stream can be definitely determined. The ratio of the times at which the curves cross is almost equal to the ratio of the depth of the charcoal i.e. 1:2:3:4:5.

Since the curves are symmetrical the value of using this point is as great as the value of using that point where the composition of the issuing stream is the same as the incoming stream, and, it is more easily determined. Moreover, the time at which any concentration of gas commences to come through the charcoal can be easily determined by interpolation on either of the pair of curves.

It is tenatively suggested, therefore, that the point where the concentrations are equal would provide a truly satisfactory measure of service time for theoretical studies.

It will be very interesting to study the amount of sorption at different air flow rates, keeping the concentration of the sorbate in the air stream constant. Such a study might indicate whether diffusion of the gas molecules from the air stream to the surface of the charcoal is the governing factor in sorption in a flow system.

A study of sorption at a constant rate of air flow and varying the concentration (i.e. partial pressure) of the sorbate should show the relation of sorption in a flow system to the partial pressure of the sorbate.

Summary

1. A new sorption apparatus has been designed and shown to be practical.

2. This apparatus is arranged to follow continuously:

(a) The temperature rise at various points in the charcoal bed.

(b) The increase in weight due to the sorption of some sorbate.

(c) The composition of the issuing air stream.

3. The apparatus arranges for control of the following variables;

(a) Depth of the charcoal bed.

(b) Moisture content of the entering air stream.

(c) Moisture content of the charcoal.

(d) Rate of air flow.

(e) Concentration of sorbate in the air stream.

4. The following studies are anticipated:

(a) Temperature rise in charcoal under various conditions.

(b) Relation of sorption and diffusion of sorbate from air stream.

(c) Relation of sorption and partial pressure of sorbate in the air stream.

5. A new measure of service time that can be easily

determined is suggested.

6. Some values for the sorption of butane by an unimpregnated charcoal are recorded.

References.

1. Gregg, S.J.: The Adsorption of Gases by Solids, Methuen & Co., 1933.

2. McBain, J.W.: The Sorption of Gases by Solids, Routledge & Sons, 1932.

3. Pearce, J.A. and Rabinovitch, B.S.: (See Previous Report).

4. Wilson, R.E.: J. Ind. Eng. Chem.: 13, 326(1921).

CONTRIBUTION TO KNOWLEDGE

1. A new calorimeter has been designed incorporating several new features, not recorded in the literature, that should increase the accuracy of the results and decrease the difficulties in manipulation.

2. "$Na_2SiO_3.9H_2O$" behaves in water as if H_2SiO_3 were a dibasic acid.

3. Information has been obtained that could be used in designing a plant to convert tetrachloroethane to hexachloroethane in the liquid phase.

4. From a study of temperature rise in charcoals during sorption, it seems unlikely that gases or gas mixtures under field conditions would create sufficient heat to render a gas mask ineffective.

5. A new apparatus for studying sorption in a flow system has been designed and found to be practical. A new measure of service time is suggested.

GENERAL INDEX

Abstracts

Foreword

Work was commenced at McGill under the direction of Dr. J.H. Mennie. Urgent war problems prevented completion of this work.

All war projects were carried out under the direction of Dr. C.A. Winkler.

Studentships awarded by the National Research Council for the sessions 1939-40 and 1940-41 made this work possible.