THE MECHANISM OF THE SORPTION OF GASES BY CHARCOAL
AND
OTHER RESEARCH IN CHEMICAL WARFARE

A thesis

by

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Ph.D. CHEMISTRY

John Carstairs Arnell

The Mechanism of the Sorption of Gases by Charcoal
and
Other Research in Chemical Warfare

From service time and sorption gradient studies on sulfur dioxide and carbon tetrachloride, it was found that: (1) the equilibrium sorption weight could be represented by the Langmuir Adsorption Isotherm; (2) the "critical length" was a linear function of the initial concentration; (3) the length of the sorption gradient and the dead length varied as the logarithm of the initial concentration; (4) the weight of gas sorbed at any point in the charcoal bed increased with time according to:

$$x = K e^{-k/t}$$

and (5) the initial sorption of the gas by the first layers of the charcoal bed followed the relation:

$$x = W_s (1 - e^{-bt}).$$

Studies on the amines showed that the service time - bed length plot was not linear throughout its length.

Chloropicrin could be removed from charcoal with 90% efficiency by refluxing with commercial pentane.

In the fluorination of sulfur, diluting the fluorine with nitrogen and cooling the reaction tube gave higher yields of disulfur decafluoride and the lower fluorides and a lower yield of sulfur hexafluoride.

INTRODUCTION

The study of the sorption of a gas from a stream of air by activated charcoal was first undertaken during the last World War. When the respirator, which had a canister filled with activated charcoal for removing any toxic substance from the air, was introduced as the defence weapon against poisonous gas, some method of estimating the protective power of the charcoal was required. This method had to be relatively simple and quick to carry out and yet it had to be trustworthy, as the life of the wearer of a respirator depended on the ability of the charcoal to be efficient in the removal of the toxic substance from the air. The procedure developed consisted of passing a mixture of the toxic material and air through a charcoal bed and testing the effluent air with a sensitive chemical test for the presence of the gas. The length of time necessary for the appearance of gas in the effluent air was known as the service time or breakdown time. In all the early work, these were routine tests using the standard charcoal bed as put into a service canister, the charcoal being tested against several gases to insure that it gave protection against the different types of gas likely to be encountered in the field. Such tests were all of a purely empirical nature and were known as proofing tests.

The first approach to laboratory study came when a standard laboratory test was found to be desirable. Such a test was developed and the results of the test could be substituted in an empirical formula to give a value known as the volume activity. The volume activity gave a means of comparing the adsorptive powers of two different charcoals. The volume activity of a charcoal was determined by passing carbon tetrachloride, under specific conditions, mixed with air through a known volume of dried charcoal until the first traces of gas appeared in the effluent gas. The appearance of the gas was detected by passing the effluent air through a pyrolyzer and then bubbling the air through a potassium iodide-starch solution. If any carbon tetrachloride was present, it would break down to give free chlorine in the pyrolyzer and this would produce the characteristic blue colour in the solution. The volume activity was calculated from the formula:

$$\text{Volume activity} = \frac{\text{Increase in weight of charcoal} \times 100}{\text{Volume of charcoal used}}$$

More recent work in Canada has involved the study of proofing tests on a laboratory scale under comparable conditions to determine whether the same service time was given by a charcoal bed of small cross section as that obtained using service canisters. There has also been a considerable amount of laboratory proofing carried out on new compounds, that have shown toxic properties. But again all this work has been empirical.

In all the previously mentioned work, the concentrations of the gas in the air stream have been of the order fifty to hundred times as high as that found in the field under actual fighting conditions. This was done so that the service time would be short (ranging from a half to three hours) instead of perhaps running into days, if the proofing were done under field conditions. If the service time from the proofing test was satisfactory, it was considered that the service time under field conditions would also be satisfactory, because it was assumed that the service time varied roughly as the inverse of the concentration of gas in the entering air stream.

Since 1925 there have been many workers, who have attempted to work out a formula that, by substitution of known physical constants of the gas, the charcoal and the apparatus, would predict the service time.

The first observation that was made concerning the service time, and the only one on which all the workers agreed, was that at service time the charcoal bed appeared to have an unused residual activity. This resulted from a determination of the service times for different volumes of charcoal bed. When the service times were plotted against the volumes, a straight line was obtained which extrapolated to give a positive volume, Qh, at zero service time. From this plot, the formula for the service time was worked out:

$$T = k_o(V-Qh). \quad . \quad . \quad . \quad . \qquad (i)$$

where V is the total volume of the charcoal bed, Q the cross sectional area of the bed, k_o a constant, and h the "dead length". The "dead length" was defined as the length of bed which appeared to be inactive. However it was usually considered to be purely a mathematical term, which gave a measure of the residual activity of the charcoal bed remaining at service time.

The constant k_o in equation (i) has a definite physical meaning, as it works out to:

$$k_o = \frac{k}{vC_o} \quad . \quad . \quad . \quad . \quad . \qquad (ii)$$

where v is the rate of flow of the air stream (vol. of flow /unit time), C_o the concentration of gas in the air stream (weight/liter of air), and k the maximum amount of gas taken up/cc. of charcoal at equilibrium with the gas concentration, C.

In a recent report (1), Hinshelwood, working from purely theoretical considerations, obtained a similar formula for the service time:

$$T = \frac{N_o}{C_oL}(\lambda - \lambda_c) \quad . \quad . \quad . \quad . \qquad (iii)$$

where C_o is the concentration of the gas in the entering air stream, L the linear flow rate, N_0 the number of active centers/cc. of charcoal, λ the total length of the charcoal bed, and λ_c the "critical length". The "critical length" was defined as the distance that a detectable amount of gas travelled through the bed before being removed from the air.

Once equation (i) was established, the various workers worked out formulae on different theoretical grounds to express the residual activity. Mecklenberg (2) visualized the charcoal bed, after gas had been passing for some time, as divided into three parts:

(a) A length next the front surface saturated with the gas,

(b) A "working" length in which the gas was being taken up, and

(c) A length not yet reached by the gas.

He considered the "working" length and assumed that the gas was being taken up by the charcoal by condensation in the capillaries of the charcoal and also assumed that the gas diffused out of the air stream and into the capillaries with a velocity similar to that given by Nernst for a heterogeneous reaction. Using these assumptions he formulated an equation for h:

$$h = \frac{\delta_r}{DF}\left(\frac{kQ}{v}\right)^{n-1}\left[\ln\frac{C_0 - C'}{C_x - C'} - \frac{C_0}{C_0 - C'}\right] \quad . \quad . \quad . \ (iv)$$

where δ_r is a constant relating to the thickness of the layer of gas adhering to the surface of the charcoal, D the diffusion constant of the gas in air, F the surface of the charcoal/cc., kQ the portion of the cross section of the cell not actually filled by charcoal, C_x the concentration of gas in the air stream below which it is not possible to detect the gas, C' the vapour pressure of the liquefied gas in the capillaries expressed in weight of gas/liter of air, and n a constant.

From equation (iv), Mecklenberg was able to predict that the "dead length", h, was:

(a) inversely proportional to the square root of the cross section, Q,

(b) directly proportional to the square root of the rate of flow of the air stream, v,

(c) directly proportional to the diameter of a single charcoal grain, a, and

(d) directly proportional to the logarithm of the initial concentration, C.

He confirmed the last two predictions with experiment. The first two predictions were later confirmed by Engel (3).

Engel attempted to confirm the theory of Mecklenberg, but found large deviations from the laws for the variation of k and L, which Mecklenberg derived from the Nernst equation. This he explained as due to the fact that Mecklenberg's theory was valid only for capillary condensation, while in reality many processes (adsorption, etc.) proceed side by side. He also found with chlorine, phosgene and cholorpicrin, that chloropicrin, with the highest molecular weight, was sorbed the best, and chlorine, with the lowest, was sorbed the least. In addition the sorption ran parallel with the boiling points, so he pointed out that apparently vapour pressure lowering in the capillaries played a part.

Shilow, Lepin and Wosnessensky (4) determined the amount of chlorine sorbed by different sections of a charcoal bed under different experimental conditions. They attempted to give the "dead length" a physical meaning by the introduction of two empirical constants and wrote:

$$h = \frac{\tau}{\partial} \quad . \quad . \quad . \quad . \quad . \quad . \quad (v)$$

where τ is the initial loss of time of protective action, and ∂ the coefficient of protective action.

They also carried out three series of experiments with chlorine concentrations varying from 0.66% to 1.36% and verified the equation:

$$C_o \times T = \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad (vi)$$

where C_o is the initial concentration and T the service time.

Dubinin (5) expressed the service time in a different form:

$$T = \phi L - \tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (vii)$$

where ϕ is the coefficient of protective action, L the bed depth, and τ the protective time loss due to the very rapid penetration of the gas at the start of a run. He also derived a formula almost identical to that of Mecklenberg and correlated the results of Mecklenberg (2) and Shilow et al. (4).

Dubinin, Parshin and Pupuirev (6) investigated the service time of the first sections of a charcoal bed, using chlorine as the sorbing gas. They found that even with bed lengths shorter than the "dead length" there was some protective action. As a result they pointed out that the "dead length" was purely a mathematical fiction, because the protective action of the"dead length" might sometimes constitute as much as 10% of the service time of a whole bed.

Mecklenberg (7) applied the data of Shilow et al. (4) to his equations for service time as a function of:

(a) the diameter and length of charcoal bed,

(b) the velocity and initial concentration of the gas-air mixture,

(c) the capacity and specific surface of the charcoal, and

(d) the vapour pressure of the absorbate in the capillaries of the charcoal.

In each case the equations were confirmed by the experimental data. In the course of discussing his equations, Mecklenberg pointed out that at the beginning of a run there would be no liquid in the capillaries of the charcoal and in consequence, the term C' in his equation would be zero. This would change the concentration term in the equation to

$$\left(\ln \frac{C_o}{C_x} - 1\right)$$

As the gas sorbed, C' would increase up to its maximum, C_o.

This would show up in the service time-bed length plot. Instead of a straight line extrapolating to a value h, as given in equation (i), the service time would decrease linearly as the bed length decreased until at some point the values would curve in towards the origin. This meant that the bed length, for which the service time was zero, was considerably less than the "dead length". Both Shilow et al. and Mecklenberg confirmed this. He also investigated the dependence of the absorption capacity, k (equation ii), on the initial concentration of the gas in the air stream. He found that the relationship was given by the equation of the Freundlich adsorption Isotherm:

$$k = aC_o^b \quad . \quad . \quad . \quad . \quad . \qquad \text{(viii)}$$

where a and b are constants. For chlorine, Mecklenberg found that a = 8.38 and b = 0.164.

Syrkin and Kondraschow (8) investigated the sorption velocities of the vapours of carbon disulfide, pyridine, isobutyl alcohol and dimethyl ethyl carbinol by the dynamic method over a temperature range from 10°C to 100°C. They found that the amount sorbed by the whole bed was related to time by the equation:

$$\log \frac{A}{A - c} = 0.434\ KT \quad . \quad . \quad . \qquad \text{(ix)}$$

where A is the maximum sorption, c the amount sorbed in time T and K a constant. K was found to vary with temperature, according to the formula:

$$\tau = \left(\frac{K_{T_2}}{K_{T_1}} \right)^{\frac{10}{T_2 - T_1}} \quad . \quad . \quad . \quad . \quad . \quad . (x)$$

In this work, the apparatus was so arranged that only part of the gas was sorbed from the air stream, the remainder passing out with the effluent air.

Izmailov and Sigalovskaya (9) studied the sorption of the vapours of benzene, n-heptane, phenol, naphthalene and carbon disulfide in an air stream by a charcoal bed and found that they were all sorbed by a mechanism of capillary condensation, as predicted by Kubelka (10) from studies on a static system. They also noted that the thickness of the sorbate in the capillaries at service time was the same for all the substances studied.

Walter Ruff(11) carried out a study of dynamic sorption by a charcoal bed of acetic acid and phenol dissolved in water. The liquid was allowed to filter through the charcoal bed and a series of taps permitted withdrawal of samples at various depths of the bed. The adsorption isotherms obtained agreed with the Freundlich equation. The equations developed by Shilow (4), Mecklenberg (2,7) and Dubinin (5,6) for the sorption in the gaseous phase were found to hold for the aqueous solutions studied. In the same way the lawa governing sorption in the gaseous phase were found to be also valid for the liquid phase. Differences observed in sorption in the gaseous and liquid phases were explained by the slower diffusion rate in the latter case.

Allmand (12) developed an equation for the "dead length":

$$h = \frac{Q - \ln \gamma_B}{k_o} \left(\frac{V}{A} \right)^{1/2} d \quad . \quad . \quad . \quad . \quad . \quad (xi)$$

where Q is a coefficient peculiar to charcoal and vapour, γ_B the fraction of the entering concentration of the vapour transmitted at service time, V the volume of air flow per unit time, A the cross section of the charcoal bed, d the average diameter of a charcoal granule, and K_o a constant, which is equal to $(\ell/T)^{1/2}$. The derivation of this equation was not given but the relations between the "dead length" and :

(a) the cross section of the bed,

(b) the rate of flow of the air stream,

(c) the diameter of a charcoal granule, and

(d) the initial concentration,

were identical to those predicted by Mecklenberg from equation (iv).

Hinshelwood (1), starting from purely theoretical considerations, developed a theory from which equations could be derived for the various measurable quantities. He developed his theory, first in a simple form for rough comparisons, and followed with a more rigorous mathematical solution of a partial differential equation. In the simple theory, he considered that the concentration of the gas over the charcoal in the bed decreased exponentially with length and increased exponentially with time, viz:

$$c = c_o e^{-\frac{k\ell}{L}} e^{\frac{kbt}{L}} \quad . \quad . \quad . \quad . \quad . \quad (xii)$$

where k is a measure of the rate of sorption, L the linear flow rate, and b the rate of exhaustion of the charcoal. From a consideration of equation (xii), he obtained the equation for the service time given above (iii). He had no "dead length", but called it "critical length" instead, which was defined in a different manner.

In the more detailed theory, he started with the fundamental equation for the removal of a gas in an adsorbing column:

$$-\frac{\partial c}{\partial l} = \frac{1}{L}\left[\frac{\partial x}{\partial t} + \frac{\partial c}{\partial t}\right] \quad . \quad . \quad . \quad . \; (xiii)$$

where L is the linear flow rate, $\partial c/\partial l$ the rate of concentration change of gas in air stream with length, $\partial c/\partial t$ the rate of concentration change with time, and $\partial x/\partial t$ the rate of sorption of the gas by charcoal with time. He made the assumptions that the rate of removal of the gas was proportional to the concentration of the gas in the air stream, c, and to the number of "active centers" per cc. of charcoal, N_o. This gave:

$$\frac{\partial x}{\partial t} = kcN_o = -\frac{\partial N_o}{\partial t} \quad . \quad . \quad . \quad . \; (xiv)$$

He also assumed that an active center was made up of n active centers of unit activity, N_o'. One active center of unit activity was assumed to be destroyed each time a molecule of gas was sorbed by the charcoal. Solving equation (xiii), by substituting equation (xiv), he obtained the equations for critical length (dead length) and service time:

$$\lambda_c = \frac{L}{N_o k} \ln\left(c_o/c' - 1\right) \quad . \quad . \quad . \quad . \quad . \; (xv)$$

APPARATUS AND TECHNIQUE

Two sets of apparatus were constructed, the first for handling gaseous compounds and the second for handling liquids. Later the second apparatus was modified to handle cylinder-stored gas as well. In the first apparatus there were facilities for storing the gas being studied either expanded in a large storage bulb or condensed in liquid air. In the second apparatus the liquid was stored in a carburetter and the gas added to the air stream by passing a slow controlled stream of air over the surface of the liquid and on into the air stream.

The apparati were essentially of four parts:

(1) A system for storing the gas and introducing it into the air stream in the required proportions,

(2) A device to produce an intermittent flow of the gas-air mixture through the charcoal cell to simulate breathing. This type of flow will be henceforth called respiratory flow as opposed to steady flow, which is a continuous flow of the gas-air mixture through the cell,

(3) A charcoal cell, and

(4) A testing cell.

The first apparatus was designed, after a consideration of the earlier service time apparati which had been used at McGill University, to include the following improvements:

(1) The continuous addition of gas to the air stream,

(2) The use of two sorption cells simultaneously,

(3) The measurement of the relative humidity of the air stream, and

(4) A wider variation in the flow rate of the air stream and in the number of pulsations per minute through the charcoal cell, than had been previously possible.

FIRST APPARATUS

Gas Storage System

The system for manipulating the gas is shown in Figure 1. The apparatus had the female part of a ₮ 10/30 ground glass joint open to the air. This could be closed off from the apparatus by means of a glass stopcock. At this same end of the apparatus there was a line which led to a Cenco Hyvac pump through a second glass stopcock. The gas, which was being admitted, was led through a glass trap (C), the bottom section of which was attached to the apparatus by means of a large ground glass joint. This section could be shut off from the remainder of the apparatus by a stopcock. The gas storage section consisted of a large (10 l.) storage bulb (A) for gaseous storage and a bulb (B) for storing the gas as a solid in liquid air. Gas pressures inside the apparatus could be read on the mercury manometer (M). The final part of this system was for the introduction of the gas into the air stream continuously and in any desired amount. This consisted of two calibrated burettes (16 mm. O.D.) having a three way stopcock (T4, T5) at the top of each and a two way stopcock (T6, T7) at the bottom. From the bottom of each burette there was a small glass tube which ran up along the side of the burette to at least the height of the three way stopcocks. Above the burettes was a mercury reservoir, from which mercury was led through a three way stopcock (T1).

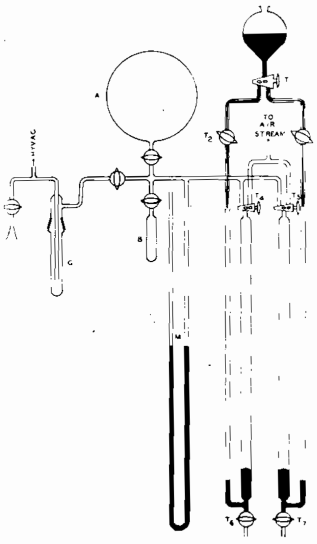


Figure 1.

The two resulting lines led through two stopcocks (T2, T3) and the tubes ended in fine tips just inside the side tubes of the burettes, so that mercury when allowed to run out either of these tubes, fell in a fine spray down the corresponding tube and in consequence raised the mercury level of the burette. The stopcocks (T2, T3) had fine scratches part way around their barrels to give a very fine adjustment of the mercury flow. One side of the stopcocks (T4, T5), leading from the burettes, was connected to the gas storage system and the other led through a common tube into the air stream.

Gases were introduced into the apparatus either from a trap fitted with the male part of a $\$$ 10/30 ground glass joint containing the gas frozen in liquid air or a piece of vacuum rubber tubing could be attached to a gas cylinder and the opposite end fitted with the male part of a $\$$ 10/30 ground glass joint. In either case, the procedure of introducing the gas into the apparatus was the same:-the trap or the rubber tube was fitted into the ground glass joint on the apparatus and all the stopcocks opened except the two leading into the burette. The whole system was then evacuated and a vacuum flask containing liquid air was put around the small bulb (B). Once all the air had been removed from the apparatus, the stopcock on the vacuum line was closed. The gas was then allowed to distil over into the cooled bulb (B). The trap with the removable bottom acted as a protection for the Hyvac pump, liquid air being put around it to trap out any stray gas. It could also be used for removing a fraction, if the gas was to be purified by distillation, or for the removal of all the gas from the system. For long term storage, the gas could be expanded into the large bulb (A).

To fill the burettes with gas, they were first filled with mercury. The liquid gas was removed from around bulb (B) and the pressure inside the apparatus allowed to come to atmospheric. The stopcock T4 was opened to the gas system and the mercury was drained out through stopcock T6 at a rate equal to its displacement by the vaporization of the gas.

The method of introducing the gas into the air stream was as follows:

The scratched stopcocks (T2, T3) were adjusted to deliver mercury into the side tubes of the burettes at a rate that would displace the required number of cc. of gas per minute. The three way stopcock at the top of one of the burettes was opened to the air stream and stopcock (T1) was opened in such a way as to let mercury run into that burette and as the mercury ran into the burette the gas was forced out into the air stream at a constant rate. The pressure of the gas in the burette during a run was about 3 cm. of mercury less than atmospheric, as the pressure of the air stream was reduced by that amount due to the resistance of the flow-meter, etc. Two burettes were used so that the emptied burette could be re-filled with gas without interrupting a run.

Air Stream System

Figure 2 is a diagrammatic sketch of the first part of the system. The air stream was drawn through the system by a Cenco Hyvac pump, the rate of flow being adjusted by means of a stopcock open to the air between the pump and the system. The air entered the apparatus through a flowmeter (F). This was standard Venturi principle flowmeter and was constructed in the form of a U-tube, with one arm of small diameter tubing and the other of large diameter tubing. This was to eliminate the necessity of having to read both oil surfaces, as with this type of flowmeter the variation in the height of the oil in the large diameter tube is negligible over the full range of levels in the small tube. A capillary tube joined the two arms of the flowmeter together and the air was led through it. The flowmeter was filled with Hyvac oil, having a specific gravity of 0.891, and was calibrated by allowing water to run out of a large volume, to which the flowmeter was connected, at different known rates. The air was then drawn through three bubblers (C) filled with diluted sulfuric acid to give it the desired relative humidity (13). The relative humidity was checked by a dry and wet bulb hygrometer built into the apparatus. The dry bulb was put before the wet bulb, so that any slight evaporation that might take place would not affect the readings. By means of the three way stopcock (T1), the hygrometer could be by-passed if an experiment was to be carried out under anhydrous conditions. Immediately after the hygrometer, the gas from the burettes entered the air stream directly through a small

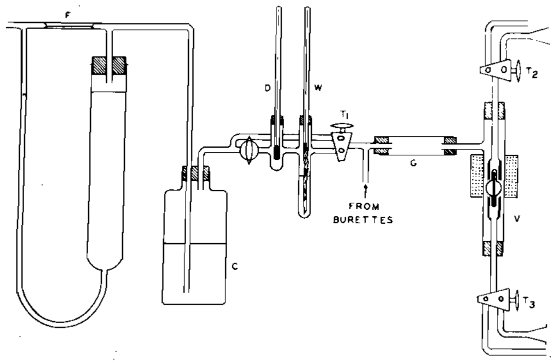


Figure 2.

diameter tube. The gas-air mixture was passed through a large diameter tube (20 mm. O.D.) packed with glass wool (G) to facilitate mixing.

Respiratory Flow Valve

The gas-air mixture was then passed through the device which produced the respiratory flow (V). This consisted of a piece of large diameter tubing (22 mm. O.D.) with a side arm at the upper end for the air inlet. A coil of 560 turns of No. 18 insulated copper wire was wound around the middle of this tube. The length of the finished coil was about three inches and was used as an electromagnet. Inside this tube was a glassvalve made from a short length of tubing in the middle of which a bulb had been blown with an outside diameter of 16 mm. An iron nail was put inside the valve and the two ends sealed up. The valve seats were made of glass tubing of 2 mm. wall thickness (13 mm. O.D.) and were ground with a steel ball of approximately the same size as the glass valve. When the seat had been shaped, the valve was ground in using fine emery powder. The two valve seats were connected to glass tubes which led out through rubber stoppers at either end of the large diameter tube.

The operation of the valve was such that when a direct current was passed through the coil, the valve was raised due to the resulting magnetic field. This shut off the gas-air mixture to the upper lead-off tube. When the current was shut off, the valve dropped and shut off the lower lead-off tube. The make and break of the current was controlled by a brush made of aluminium and attached to a rotating wheel by means of a piece of spring steel. The wheel was driven by an electric motor and suitably geared down with pulleys. In addition a rheostat was connected in the motor circuit so that the speed of the motor could be varied to give different numbers of respiratory pulsations per minute. A piece of sheet aluminium was placed parallel to the rotating wheel, in such a position that the brush was in contact with it during exactly one half of each revolution. The magnet circuit was connected through the wheel and plate, so that when the brush was in contact with the plate, a current was flowing through the electromagnet and the valve was in its raised position. With this device the time interval when the circuit was closed was equal to that when it was open and in consequence the same amount of gas passed through each of the lead-offs with each pulsation.

The gas-air lead-offs led through three way stopcocks (T2, T3). On one of the two resulting tubes was the female section of a ₮ 10/30 ground glass joint, to which the charcoal cell was attached. The other tube served as a by-pass around the charcoal cell.

Charcoal Cells

The charcoal cells consisted of glass tubes with the male part of a ₮ 10/30 ground glass joint on a side arm about an inch from the top of the tube. The bottom of the tube narrowed down to a piece of standard 8 cm. O.D. diameter tubing such as was used throughout the apparatus. The cell was about 15 cm. long and the top end was closed with a rubber stopper. As a support for the charcoal bed, a piece of perforated brass plate was cemented with de Khotinsky cement~~ed~~ to the end of a short piece of glass tubing. This was put into the tube with the brass uppermost and served as a good base on which to build the charcoal bed. The diameter of the cell was 1.26 cm. This was calculated from the following considerations.

Standard gas mask canisters were used for all sorption work at Ottawa and therefore with smaller apparati as described here, it was necessary to keep the rate of flow of the air stream and the cross-sectional area of the charcoal cells in the same proportions in order to produce comparable results.

The depth of the charcoal bed for a service time on any gas was standardized at 5.0 cm., which is the same as that of a service canister. It might be noted here that the gas mask canister has the top surface of the charcoal curved upwards towards the outside. This is to remove any possibility of the gas channeling up the charcoal-metal surface. In the experiments described below, as the cells were of small diameter, the top surface was flat. No evidence of channeling was ever observed.

In order to obtain comparable results from sorption cells of different cross sectiohs, the flow rate must be such as to give the same space velocity through each cell. The formula relating the three factors is:

$$F = SA$$

where F is the flow rate, S the space velocity and A the cross sectional area of the sorption cell. From this, the formula relating the flow rates and cross sectional areas of two cells at a constant space velocity is:

$$\frac{F_1}{F_2} = \frac{A_1}{A_2}$$

where the subscripts represent the two cells.

The standard canister has a cross-sectional area of 80 sq. cm. and the routine service times are done in Ottawa with a flowrate of 16 litres per minute through the charcoal bed. In the apparatus described here, a flow rate of 500 cc. /min. was used. But as this was through two cells alternately, only 250 cc./min. went through one cell. Applying the above formula:-

$$\text{Required area} = \frac{250 \times 80}{16000} = 1.25 \text{ sq. cm.}$$

Therefore the required diameter of the charcoal cell was:

$$d = 2\sqrt{\frac{A}{\pi}} = 2\sqrt{\frac{1.25}{3.14}} = 1.26 \text{ cm.}$$

The method of packing the charcoal in the cells was standardized. At the beginning of the work, the charcoal was put in little by little and after each addition, the wall of the cell was tapped with some object such as a heavy pencil, which tended to pack the charcoal particles closer together. It was found that the results from this type of packing did not check very well. This led to the following method: A glass tube that would just fit easily into the cell was cut off about three inches longer than the length of the cell and one end was closed by cementing a piece of wire gauze over it and covering the wire gauze with de Khotinsky cement. To pack the cell, one centimeter of charcoal was put in the cell and the glass plunger dropped from two centimeters above the charcoal ten times. This procedure was carried out with each succeeding centimeter of charcoal until after the final layer of charcoal was put in and then the bed was tapped twenty times. For a ten centimeter bed, however, the charcoal was put in two centimeters at a time and the plunger dropped fifteen times after each addition except the last, when it was dropped twenty-five times. This method of packing gave very close checks and was considered an improvement because the personal element was removed.

After the first experiments, which were carried out using gaseous amines, it was decided to follow the distribution of sorbed gas through the charcoal bed and a new type of cell was constructed. It was made in removable sections, each section containing a depth of 1 cm. of charcoal. With this type of cell, the amount of charcoal in each section could be determined before a run by weighing and the amount of gas sorbed was given by the difference between the final and initial weight of each section.

A thick-walled bakelite tube, 1.25 cm. inside diameter was cut into sections of about 1.3 cm. length. An inside thread was cut on one end of a section and an outside thread on the other. The ends were threaded in such a manner that the sections could be screwed together with a close fit. A disk of copper gauze was cemented into the bottom of each section. When the cell was assembled, the distance between successive disks was 1 cm. End pieces were threaded to fit each end of a cell and were made with small tubes for rubber tubing connections.

It was found that the bakelite was too brittle to stand constant usage as the threads stripped easily. Therefore, another cell was constructed in the same manner from heavy-walled brass tubing. These sections had an inside diameter of 1.65 cm. and a depth of 1 cm., this diameter being calculated for a flow rate of 500 cc./min. through each cell. The charcoal was held in these cells by cementing in the perforated brass discs with a solution of Gelva in acetone.

When either of these cells was used, an empty section was put in at each end to give a free space above and below the charcoal, so that the small tubes, which carry the influent and gas-air mixture, would be removed from the immediate vicinity of the charcoal surface.

When these cells were first used, they were simply screwed together, but it was found that, due to the partial vacuum inside, air leaked in through the joints. Coating the complete cells with paraffin eliminated this trouble but it was very difficult to remove all the wax after a run, and when analytical methods of determining the amount of sorbed gas had been tried and found unreliable, it was considered that the wax would prove an indeterminate error, when the amount of sorbed gas was determined by weighing, and this method was discarded. The next system tried consisted of putting a glass tube, of slightly larger diameter than the cells, over the cells and closing the ends with rubber corks, which were then waxed. This method was used throughout the sulfur dioxide work and proved to be quite satisfactory, where Congo Red paper was used as the test paper. However, when the carbon tetrachloride experiments were started, it was found that a blue colour always developed in the potassium iodide starch solution, which was used as the indicator, after about 60 minutes running, regardless of concentration. This was finally traced to the fact that a amall amount of the gas-air mixture was leaking out the threads at the top of the bed and down between the cell and the glass tube and in again at the bottom. From a consideration of the length of time it took to develop the blue coloration, the amount of indicator solution used and its sensitivity, the concentration of the gas leak was calculated to be of the order of one part of carbon tetrachloride to two million parts of air or a partial pressure of about 0.0004 mm. of mercury. After this leak was discovered, gaskets were cut of thin sheet rubber and put on each section and no more trouble was experienced. The cells were always weighed with the gaskets on. This difficulty was not experienced with the Congo Red paper, as the test sensitivity was not sufficient to detect leaks of this magnitude.

Testing Cells

The testing apparatus for the hydrocarbons consisted of an electrically heated pyrolyzing furnace, made by filling a quartz tube with copper oxide in the wire form, and an absorption bottle through which the carbon dioxide, formed in the furnace, bubbled. Several solutions were tried in the absorption bottle to find the most effective test for the carbon dioxide produced by pyrolysis. A saturated solution of calcium hydroxide was found to be too insensitive, while a saturated solution of barium hydroxide was too sensitive, showing turbidity after standing in the air for a very short time. A solution of one part of saturated barium hydroxide in five parts of water was found to be the most suitable concentration. During the hydrocarbon experiments, a potassium hydroxide scrubber was put in series with the sulfuric acid bubblers to remove the carbon dioxide from the air entering the apparatus.

Indicator papers were used in the amine and sulfur dioxide work. The test cell consisted of a short piece of 16 mm. O.D. glass tubing with a side arm on which was a stopcock through which the gas to be tested was led in and at the bottom of the cell was a three way stopcock, so that the cell could be by-passed when it was necessary to change the test papers. A rubber stopper with a wire hook on it served to close the top of the cell and to hold the test paper in front of the opening in the side so that the influent gas from the charcoal bed would strike it.

All the glass tubing in the apparatus, with the exception of those parts which have been described in detail, had an outside diameter of 6 mm. The stopcocks were 2 mm. bore except on the gas-air lead offs from the respiratory valve and on the test cells, which were 3 mm. bore. A diagram of the whole apparatus, as set up with a sulfur dioxide cylinder and the sectionalized cells is shown in Figure 3.

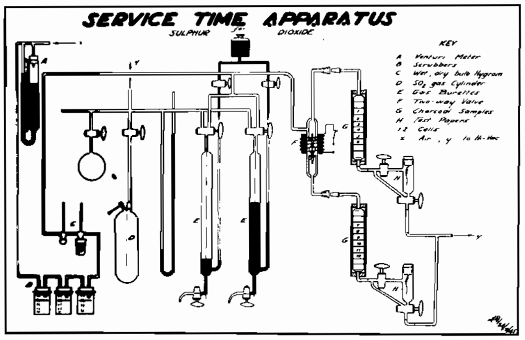

SERVICE TIME APPARATUS
SULPHUR for DIOXIDE
KEY
A Venturi Meter
B Scrubbers
C Wet, dry bulb Hygrom
D SO_2 gas Cylinder
E Gas Burettes
F Two-way Valve
G Charcoal Samples
H Test Papers
12 Cells
x Air, y to Hi-Vac
A
B
C
D
E
E
F
G
G
H
H
x
y
y

Figure 3.

SECOND APPARATUS

Figure 4 shows the apparatus in diagrammatic form.

The air entered the apparatus at 2 and passed through the flowmeter (J) This flowmeter, similar to that used on the first apparatus, works on the Venturi principle. A constriction was interposed in the tube along which the air was flowing and the difference in pressure on either side of the constriction gave a measure of the rate of flow. The constrictions on the various flowmeters used were all made of capillary tubing, ranging from 1 mm. bore for flow rates of 1000 cc./min. to thermometer capillary for flow rates of 25 cc./min. The body of the flowmeter (the left hand side of J in Fig. 4) was made of large diameter glass tubing (about 3 cm.), while the gauge glass was made of 5 mm. diameter tubing. Due to this difference of diameter, the liquid level in the body of the flowmeter could be considered as constant and the pressure drop measured entirely by the liquid level in the gauge glass. The flowmeter liquid was Stanolax, which is mineral oil sold by Imperial Oil Limited. This was dyed red by adding a small amount of an oil soluble red dye.

The air stream was dried by passing it through two towers (K) filled with granular calcium chloride. On emergence from the second drying tower, the air stream was divided into two parts. The subsidiary air stream, the flow of which was controlled by a pinch cock, passed through the second flowmeter (J) and then by a warming coil of copper (G) to the

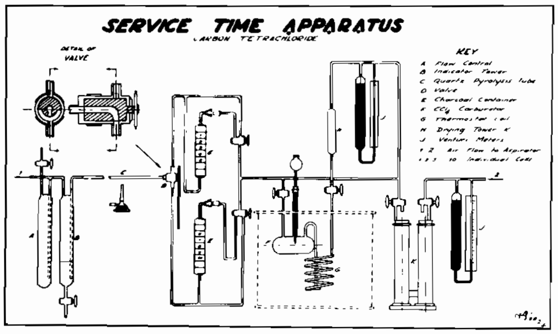

SERVICE TIME APPARATUS
CARBON TETRACHLORIDE
DETAIL OF VALVE
KEY
A Flow Control
B Indicator Tower
C Quartz Pyrolysis Tube
D Valve
E Charcoal Container
F CCl_4 Carburetor
G Thermostat Coil
H Drying Tower K
J Venturi Meters
1 2 Air Flow to Aspirator
1 2 3 10 Individual Cells
A
B
C
D
E
F
G
H
J
K
1
2

Figure 4.

carburetter (F). Just at the point where the air stream was divided, there was a piece of 1 mm. capillary tubing inserted into the main flow tube. This served to produce a large enough pressure drop along the main flow tube that an air flow up to 60 cc./min. could be passed through the carburetter system.

The carburetter was a horizontal cylindrical vessel measuring about 3 inches long by 1 inch in diameter, with three vertical tubes, as shown in diagram. The centre tube was about half-inch bore and was fitted with a cork and a separatory funnel which served as a reservoir for the carbon tetrachloride; the stem of the funnel was drawn out to a fine jet which was used to indicate the correct level of carbon tetrachloride in the carburetter. The two side tubes were about 10 mm. bore and one of them was bent to connect up with the copper coil, the other leading into the main air stream. The copper coil and carburetter were suspended in a thermostat maintained at a constant temperature. This temperature was varied from room temperature to 30° C.

The subsidiary air stream, saturated with carbon tetrachloride vapour met the main air stream again before the stream was divided to go to the two charcoal cells (E). The charcoal cells were the brass unit cells previously described and were connected to the apparatus in the same way as in the First Apparatus. After the air-gas stream split, there were three-way stopcocks, so that the charcoal cells could be by-passed if necessary. The charcoal cells were connected to the apparatus by means of ground-glass joints and rubber tubing. The effluent air stream from the two cells was led to the two sides of the respiratory flow valve (D).

The details of the valve are shown in the insert in Figure 4. It was a two-way brass stopcock with half the passage through the rotating part blocked off and a hole drilled up through the centre of the rotator to join the part of the passage still open. On the surface of the rotator, a passage was cut half-way around at the level of the intake ports. The object of this was that as the rotator revolves, one of the two ports was always open and air was drawn through each port for half a revolution, thus producing a pulsating flow. The lower end of the stopcock was capped with a brass screw cap with a protruding tube, which acted as the delivery tube to the quartz pyrolysis tube. The lower end of the stopcock was threaded so that the cap could be screwed on to give an air-tight connection. The upper end of the stopcock had a toothed wheel soldered to it. A chain connected this wheel to a similar one on a reduction gear, which in turn was connected by a belt to an electric motor, which produced the rotation. The valve made about twenty revolutions per minute.

The air stream, on emerging from the respiratory flow valve, was led through a quartz pyrolyzing tube (C) of about

12 mm. bore. This was heated by a Meker burner to a cherry-red heat. Here any carbon tetrachloride in the air stream was pyrolyzed and free chlorine liberated. The chlorine was then detected when the air bubbled through the potassium iodide - starch solution in the scrubber (B), by the blue colour formed when the free iodine released reacted with the starch. The scrubber had a side arm with a stopcock on it for filling it with the test solution and a draw-off tube, closed with a stopcock, for drawing off the spent solution. The air was then led through a second bulb (A), which had a stopcock at the top. This stopcock was used to control the flow of air through the apparatus. The outlet tube was connected to a water pump, which produced the air flow through the apparatus. Later this was replaced by a Cenco Hyvac pump, when it was found that the changes in water pressure in the main caused large variations in the air flow.

The mode of operation of the apparatus was as follows:

Once past the carburetter, the gas-air mixture was drawn along the main air line. The respiratory flow valve then pulled alternately on the two charcoal cells and thus produced an intermittent flow through each of the cells.

In the later work on the concentration gradients in the charcoal bed, when conditions of steady flow were being studied, only one charcoal cell was used and the respiratory flow valve was disconnected.

The apparatus was modified to handle cylinder gases for the corresponding sulfur dioxide work. The sulfur dioxide cylinder was connected to a large expansion volume and the gas was led through a Venturi flowmeter, similar to those previously described, into the main air line at the same point at which the gas from the carburetter entered. The rate of gas flow was controlled by a stopcock, with two scratches part way around the barrel. There was a mercury escape valve connected to the expansion volume, so that the pressure of the gas could not exceed about 3 cm. above atmospheric. When sulfur dioxide was being used, the carburetter system was shut off and the pyrolysis tube disconnected, a test cell similar to that used in the First Apparatus replacing it. Congo red paper was again used as the test paper.

EXPERIMENT AND RESULTS

1. The Sorption of Hydrocarbons and Amines

Before the experiments on the hydrocarbons were started, it was decided to measure the humidity of the air stream to determine the accuracy of the sulfuric acid bubblers, mentioned previously, and also to check the hygrometer. To do this, three calcium chloride drying tubes were put in series and the air stream drawn through the system of bubblers, hygrometer and drying tubes for an hour, the moisture being absorbed by the drying tubes.

The specific gravity of the sulfuric acid was determined using a pycnometer and found to be 1.251. From the tables (13), this represented a humidity of 69.5% at 25 C.

Table I gives the results of the run.

TABLE I

Time	Flowmeter	Air Flow	Hygrometer Wet Bulb	Hygrometer Dry Bulb	Humidity
0 min.	25.2 cm.	1670 cc/min	20°C	24°C	70%
10	25.0	1665			
20	25.9	1700			
30	25.7	1690			
40	25.7	1690	19.5°C	23.5°C	70%
50	26.2	1715			
60	26.4	1725			

Average 1695 cc/min

The calcium chloride tubes were weighed before and after the run and showed a gain of weight of 1.440 grams, which was taken to represent all the moisture in the air, as only the first tube showed any appreciable gain in weight.

Total air passed through the drying tubes:

$$1695 \times 60 = 101700 \text{ cc.}$$

Grams of water in 101.7.1 of saturated air:

$$\frac{0.001279 \times 453.6 \times 10.17 \times 10^4}{2.832 \times 10^4} = 2.037 \text{ gm.}$$

Therefore humidity of the air (% sat.) $= \frac{1.440}{2.037} = 70.7\%$

The three values of the humidity checked within a little more than 1% and this was considered to be quite accurate enough for experiment.

The following experiments were carried out in an attempt to determine the relationship between the boiling points and service times of the various members of a homologous series and, in the case of the amines, to determine also the effect of molecular complexity on the service time.

The following hydrocarbon gases were used:

Ethane
Butane
Propylene

Two sets of check experiments were carried out on each of the above gases with a bed depth of 5 cm. of charcoal. In each case it was found that little or no gas was sorbed by the charcoal bed before enough gas had been passed to give a test and the service time was zero for the test used.

As the hydrocarbons were unsatisfactory for experimental study, the primary amines were used instead. Dimethyl and trimethyl amine were used for determining the effect of complicating the molecular structure on the service time. In all the preliminary experiments, a 5 cm. charcoal bed was used and later the effect of changing the bed depth on the service time, under constant conditions of concentration, humidity, and air flow, was investigated. Ammonia was studied at the same time.

The service times obtained for the five amines and ammonia for different depths of charcoal bed are tabulated in Table II and these values have been plotted on the graph in Figure 5.

TABLE II

Bed Depth	NH_3	CH_3NH_2	$C_2H_5NH_2$	$C_3H_7NH_2$	$(CH_3)_2NH$	$(CH_3)_3N$
2 cm	--	0.4 min.	--	--	--	--
2.5	--	1.0	--	--	--	--
3	3.3 min.	2.1	5.0 min.	--	--	6.5 min.
4	5.6	4.4	7.0	--	--	12.5
5	8.5	8.5	10.0	12.3 min.	17.5 min.	19.5
6	12.0	--	15.0	--	--	26.5
7	--	13.0	--	--	--	--
10	--	21.3	--	--	--	--

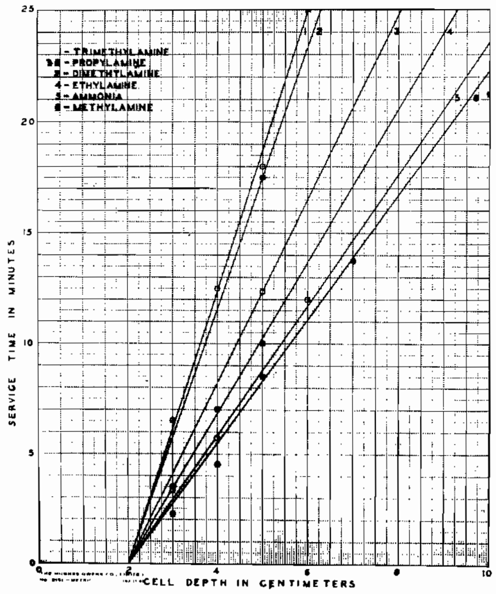

1 - TRIMETHYLAMINE
2 - PROPYLAMINE
3 - DIMETHYLAMINE
4 - ETHYLAMINE
5 - AMMONIA
6 - METHYLAMINE
1
2
3
4
5
6
SERVICE TIME IN MINUTES
0
5
10
15
20
25
0
2
4
6
8
10
CELL DEPTH IN CENTIMETERS

Figure 5.

The conditions of all the experiments reported in this section were:

Air Flow	500 cc/min
Gas Flow	5 cc/min
Respiratory flow rate	20/min
Relative humidity of air	60%
Charcoal (unimpregnated)	A-87 (18% moisture)

and were carried out in the First Apparatus using the glass charcoal cells. Two test papers were used - moist congo red paper and moist phenolphthalein paper - with the latter proving to be a little more effective. The actual sensitivity of the papers was not determined, but from comparative tests, the papers appeared to be quite sensitive.

In Table III, the boiling points and service times for the different compounds are given at a cell depth of 5 cm.

TABLE III

Compound	Boiling Point	Service Time
Ammonia	-33.4 C	8.5 min.
Methylamine	- 6.5 [1]	8.5
Ethylamine	16.6	10.0
Propylamine	48.7	12.3
Dimethylamine	7.4 [2]	17.5
Trimethylamine	3.5 [3]	19.5

Ammonia was not expected to be comparable with any of the other compounds, as it was the only inorganic compound. The primary amines formed three adjacent members of a homologous series and here it can be seen that the service time bears a roughly linear relation to the boiling points. Also the service time increases with increasing molecular complexity, but no simple relation can be established because the boiling point is changing at the same time, with dimethylamine having the highest boiling point.

From the first consideration of the results plotted in Figure 5, it appeared that all the compounds under the conditions of the experiments had a zero service time for a bed depth of 2 cm.

In an attempt to determine whether the action of the apparently inert 2 cm. of charcoal was a mechanical or a surface effect, experiments were carried out with 2 cm. of sawdust in one case, and 2 cm. of powdered coal, in another, on top of 3 cm. of charcoal. The gas used in these experiments was ethylamine. The service times were the same as for 3 cm. of charcoal alone, and, in consequence, as these substances were completely inert, the effect must be a surface action and due to some sort of concentration gradient in the charcoal.

A closer examination of these results shows, however, that the service time is not a linear relation of bed depth, but is greater than predicted by a linear relation for short beds. Further consideration of this point has been left until the Discussion section of this thesis.

2. The Distribution of Sorbed Gas in a Charcoal Bed

Sorption of Ammonia

As a result of the study of the sorption of the amines, the conclusion was reached that in a dynamic system, such as used in determining service times, the gas was sorbed mostly at the beginning of the charcoal bed and that the last centimeters took up little or no gas.

In an attempt to prove this, the distribution of sorbed ammonia through a charcoal bed was studied. This work was carried out in the First Apparatus, under the same conditions as the amines, using the sectionalized Bakelite cells. An ammonia-air mixture of 1:100 was passed through the cells until service time, wet congo red papers, acidified with dilute hydrochloric acid, being used as test papers.

In the first experiments, at service time the cell was taken apart and the contents of each section placed in a beaker of distilled water. After standing for two hours the solutions were titrated with 0.01 N. hydrochloric acid, using methyl red as the indicator. It was found that the same values were obtained if the solution was decanted from the charcoal before titration or if the charcoal was allowed to remain in the beaker during titration.

The results of these runs indicated that the ammonia was sorbed mostly in that part of the charcoal bed with which the ammonia-air mixture first came in contact and there was a decrease throughout the bed until the amount sorbed in the final section was barely detectable.

The actual values of these experiments are not given, because the results could only be treated qualitatively due to the following factors:

(1) Ammonia was only sorbed to a small degree.

(2) The charcoal gave a basic solution in water necessitating a corrective factor which was larger than the ammonia value in many cases and as the cells were not filled by weight, there was a large error in this corrective factor.

(3) The end point obtained in the titration was indistinct due to small suspended charcoal particles and here again a large error was introduced when small amounts of ammonia were present.

It was found that when the amount of ammonia sorbed was determined, by weighing the sections before and after a run, the final sections lost considerable weight. This appeared to be due to the displacement of moisture from the charcoal. An attempt was then made to study the sorption of ammonia under anhydrous conditions, using oven-dried charcoal and air dried by bubbling through concentrated sulfuric acid, so that the amount of ammonia sorbed in each section could be determined directly by weighing, with no error being introduced by water displacement.

Under anhydrous conditions the ammonia passed through the charcoal almost instantly, giving no service time. This seemed to indicate that ammonia was taken up by dissolving in the water present in the charcoal and not by any sorption mechanism.

Sorption of Sulfur Dioxide

Experiments were carried out on sulfur dioxide in the First Apparatus, using the previously described sectionalized brass cells, under anhydrous conditions. The air stream was dried by bubbling through a train of three scrubbers, each containing concentrated sulfuric acid. The charcoal, A-87, was dried by prolonged heating in an oven at 110°C.

The first series of runs was made with a gas concentration of 1:200 with the air flow such as to correspond to 16 litres a minute through a canister. The time of gas flow was varied from 10 min. up to 51 min., which was the service time, in order to determine the spread of the gas through the charcoal bed. The amount of gas sorbed in each section of a cell was obtained by weighing the section, full of charcoal, before and after a run. The weight of gas in each of the five sections of the cell is listed with the time of gas passage in Table IV.

TABLE IV

Time of Gas Flow in minutes	Cell No.	Weight of gas adsorbed in milligrams 1	2	3	4	5
10		46	9	2	0	0
15		64	22	4	0	0
20		78	40	1	0	0
25		83	51	8	2	0
30		92	64	19	2	0
35		94	76	29	2	0
40		92	77	50	13	0
45		93	91	65	21	1
51 (service time)		94	89	86	33	5

In Figure 6 the integral sorptions of the gas have been plotted against the depth. That is, the weight of gas in the first cell is plotted against a depth of one centimeter, the weight of gas in the first two cells is plotted against a depth of two centimeters and so on. This shows the distribution of the weight increase in the cell with depth, and the various curves show this distribution at time intervals up to the service time.

In Figure 7 the weight of gas sorbed in each cell is plotted against the depth. The curves obtained correspond to the derivative at any point of the curves obtained in Figure 6 and show the gradient of the weight of gas sorbed through the cell.

The second series of runs was made with a gas concentration of 1:200 while the rate of air flow was varied to correspond to flow rates from 8 litres a minute to 24 litres a minute through a canister. The times were varied as the rate was varied so that the same amount of gas was passed into the charcoal bed. This was done to show any change in the distribution of the gas at different flow rates but at the same concentration. The weights of gas in each of the cells is listed with the time of gas flow and the rate of air flow in Table V.

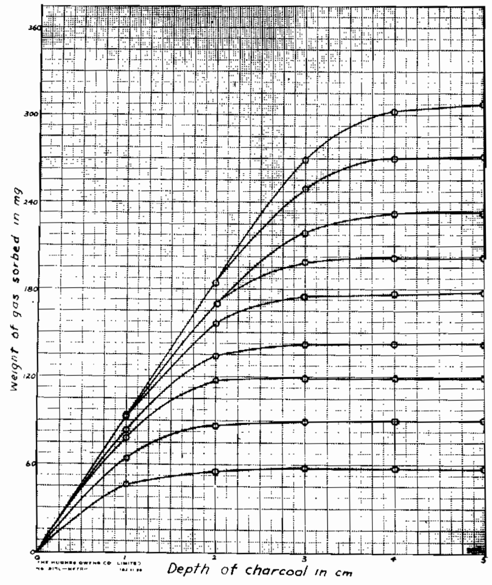

Weight of gas sorbed in mg
360
300
240
180
120
60
0
1
2
3
4
5
Depth of charcoal in cm
THE HUGHES OWENS CO. LIMITED

Figure 6.

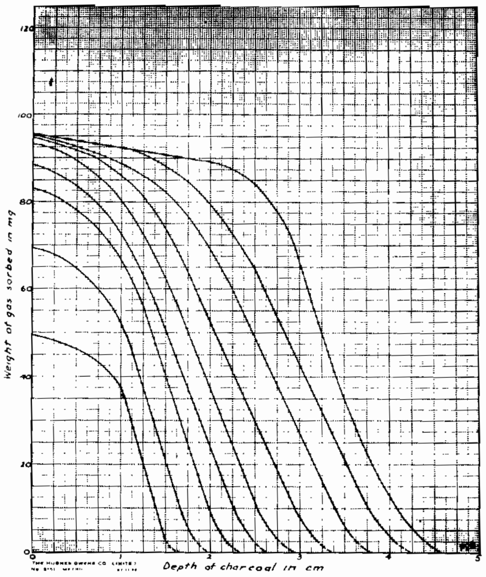

120
100
80
60
40
20
0
Weight of gas sorbed in mg
0
1
2
3
4
5
Depth of charcoal in cm
THE HUGHES OWENS CO. LIMITED

Figure 7.

TABLE V

Rate of Air Flow cc/min.	Time of Flow in minutes	Weight of gas adsorbed in milligrams 1	2	3	4	5
500	90	106	94	63	14	0
1000	45	93	91	65	21	1
1500	30	89	78	61	34	9

Figure 8 gives the integral sorption of the gas and Figure 9 gives the weight of g as sorbed with depth and shows the gradients of the weight of gas sorbed at the different rates. From these curves, it can be clearly seen that an increase in flow rate of air through a charcoal bed decreases the sorbing power/unit weight of the charcoal in the bed and so decreases the efficiency, but the effect is not marked.

The third series of runs was made at a constant rate of air flow and at different gas concentrations. The times of the runs were varied as the gas concentrations were varied, so that the same amount of gas was passed through the charcoal bed in each run. This was done in order to determine whether the amount of gas sorbed per gram decreased as the partial pressure of the gas in the air stream decreased, as predicted by Langmuir's Adsorption Isotherm. In some of the runs, additional brass sections were put into the cells, in order to show the distribution of all the gas passed through the cell. The results obtained are listed in Table VI:

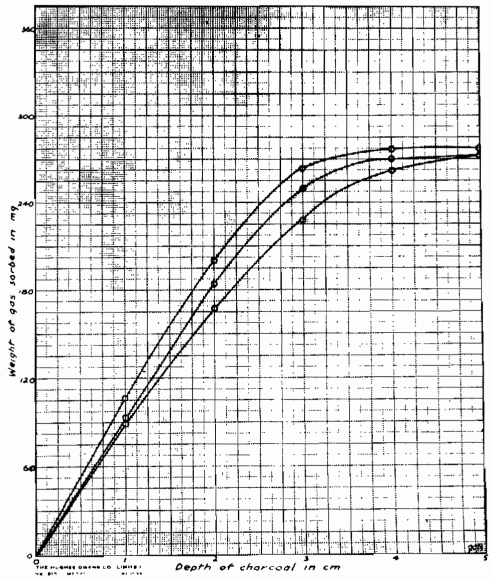

360
300
240
180
120
60
0
Weight of gas sorbed in mg.
0
1
2
3
4
5
Depth of charcoal in cm
THE HUGHES OWENS CO. LIMITED

Figure 8.

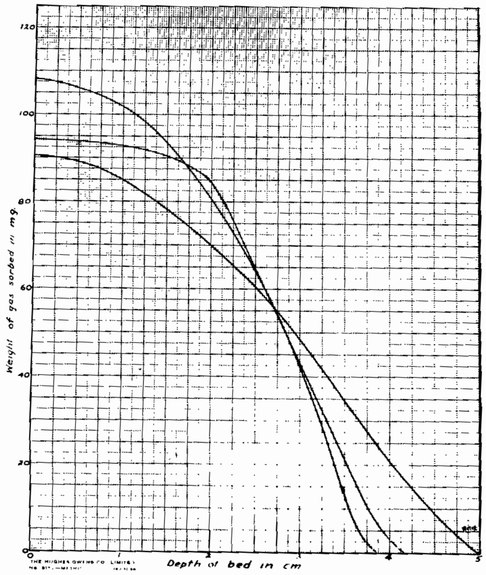

120
100
80
60
40
20
0
Weight of gas sorbed in mg.
0
1
2
3
4
5
Depth of bed in cm
THE HUGHES OWENS CO. LIMITED

Figure 9.

TABLE VI

Gas-Air Ratio	Time of Flow in minutes	Weight of gas sorbed in milligrams 1	2	3	4	5	6	7
1:200	45	93	91	65	21	1	-	-
1:400	90	82	75	62	49	13	-	-
1:800	180	61	59	53	51	30	17	7
1:2300	530	59	49	43	42	36	31	14

Figure 10 gives the integral sorption of the gas and Figure 11 gives the weight of gas sorbed with depth. From these results and the curves it can be seen that the first section, at least, has just about reached its equilibrium value. When these equilibrium values at different concentrations were compared, it was noticed that the amount of gas, capable of being sorbed per gram of charcoal, decreased as the partial pressure of the gas in the air stream decreased. It was thought that this decrease might follow the Langmuir Adsorption Isotherm and the experiments reported under Section 3 were carried out to follow up this observation.

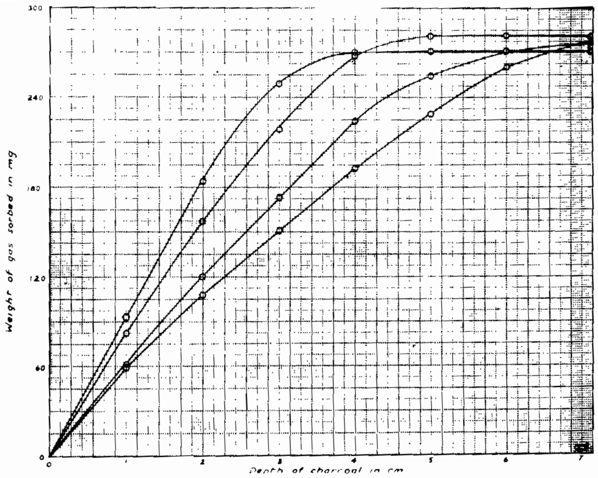

300
240
180
120
60
0
Weight of gas sorbed in mg
0
1
2
3
4
5
6
7
Depth of charcoal in cm

Figure 10.

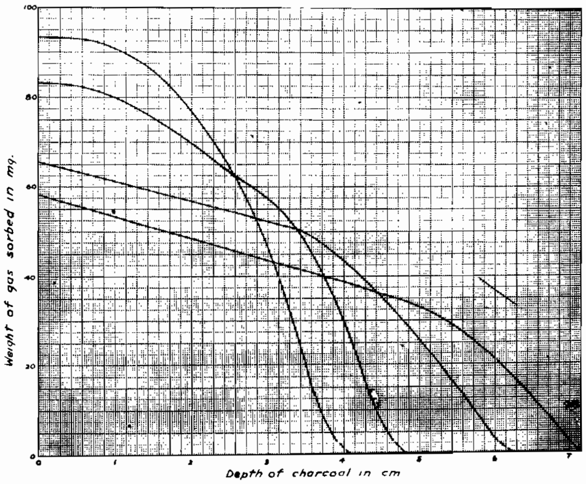

100
80
60
40
20
0
Weight of gas sorbed in mg.
0
1
2
3
4
5
6
7
Depth of charcoal in cm

Figure 11.

Resistance of Charcoal Bed to Air Flow

The study of sorption of the amines led to the conclusion that in a dynamic system, such as used in determining service times, the gas was sorbed mostly at the beginning of the charcoal bed and that the last two centimeters took up little or no gas. This means that with a depth of charcoal of about 5 cm. as in a canister, only 60% of the charcoal is used in sorbing the poison gas. If the same amount of charcoal were packed in a container having double the height and half the cross sectional area and the last two centimeters of charcoal again sorbed no gas, the amount of charcoal that took up gas would be increased to 80%.

The experiments on sulfur dioxide, described above, showed that the distribution of sorbed gas through the charcoal bed changed very little when the rate of flow of the gas-air mixture was doubled. As doubling the rate of flow is comparable to halving the cross sectional area of the cell, a long narrow cell should be more efficient.

However it was found that to change the shape of the charcoal bed by doubling its depth would greatly increase the resistance to the flow of air through the charcoal. A manometer, filled with oil of density .891 gm./cc. was built across the sorption cell and the resistance to the air stream determined for various depths of charcoal, at different flow rates. The results are tabulated in Table VII where the numbers represent the pressure drop in centimeters of oil of density

.891 gm./cc. and are the difference between the total pressure drop across the charcoal-filled cell and that across the empty cell. Table VII is represented graphically in Figure 12 in which pressure is plotted against depth of charcoal. Curves A, B, C, and D, are for flow rates of 235, 470, 700 and 935 cc. per minute respectively, corresponding to flow rates of 8, 16, 24, 32 litres for a canister.

It is apparent that as the depth of charcoal is increased above 4 or 5 cm. the resistance to the flow of air through the charcoal increases rapidly . This effect is more pronounced as the rate of flow is increased. It is, therefore, concluded that any added efficiency in sorption to be gained by increasing the depth of the charcoal bed might be outweighed by the disadvantage of more difficult breathing due to the greater resistance of the charcoal bed, especially in the case of rapid breathing under exertion where the flow rate is greatly increased.

TABLE VII

Pressure Drop Across Depth of Charcoal Expressed in Centimeters of Oil of Density .891

Rate of Flow	Equivalent Flow for Canister	Depth of Charcoal			
		2.3 cm.	4.3 cm.	6.6 cm.	7.9 cm.
235 cc./min.	8 l./min.	0.0	0.6	1.2	1.8
470 "	16 "	0.2	1.3	2.2	3.0
700 "	24 "	0.1	0.9	2.8	4.3
935 "	32 "	0.1	1.4	3.7	6.0

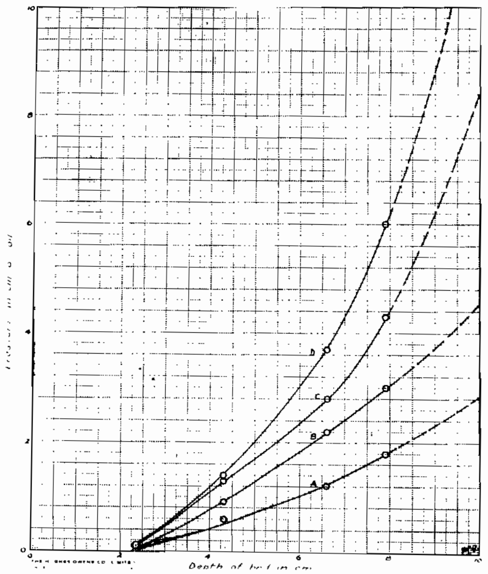


Figure 12.

3. The Dynamic Adsorption Isotherm

All the experimental work was carried out at a flow rate of 1000 cc. of air per minute, fed alternately through two cells with the rate of alternation varying between 16 and 20 per minute. In all cases, the cells were made up of five brass sections filled with charcoal, giving a charcoal bed of 5 cm. The charcoal used was A-87 and each sample was dried at 110°C for a period exceeding 24 hours before exposure to the gas-air mixture. In the experiments on both sulfur dioxide and carbon tetrachloride, the service times were determined over a wide range of concentrations. At the service time of each concentration, the weight of gas sorbed in each section was determined by weighing the cell sections before and after the run. The results are listed in Table VIII and Table X, where:

C is the concentration of gas in the entering air stream,

P_p is the partial pressure of gas in the air stream,

W_1, W_2, etc. are the weights of gas sorbed in the sections at service time,

T_s is the service time, and

$P_p \times T_s$ is the product of the partial pressure and the service time.

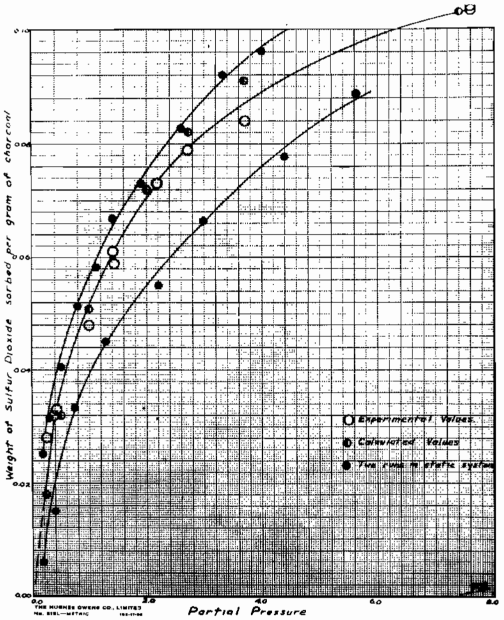
Sulfur Dioxide

The results of the runs are given in Table VIII:

TABLE VIII

C	P_p	W_1	W_2	W_3	W_4	W_5	T_s	P_p x T_s
1/100	7.60	0.124	0.118	0.082	0.044	0.010	26.5	202
1/100	7.60	0.125	0.117	0.090	0.045	0.005	27	205
1/194	3.94	0.094	0.091	0.086	0.031	0.010	45	176
1/198	3.85	0.096	0.099	0.067	0.026	0.008	45	173
1/202	3.76	0.103	0.099	0.068	0.027	0.010	44	168
1/280	2.72	0.095	0.087	0.076	0.039	0.009	64	172
1/350	2.18	0.088	0.085	0.068	0.036	0.011	75	162
1/540	1.42	0.071	0.069	0.065	0.039	0.011	104	148
1/540	1.41	0.073	0.072	0.061	0.035	0.009	101	143
1/760	1.00	0.057	0.056	0.047	0.029	0.011	115	115
1/1820	0.42	0.041	0.042	0.035	0.014	0.002	182	76
1/1960	0.39	0.039	0.037	0.033	0.019	0.004	193	75
1/2980	0.254	0.034	0.029	0.025	0.010	0.004	236	60

In Figure 13 the weight of gas sorbed per gram of charcoal in the first section of each cell has been plotted against the partial pressure. The weight of gas sorbed in a section has been converted into grams of gas sorbed per gram of charcoal by dividing by 1.20. This constant was the average of ten values of the weight of charcoal in a cell section. The maximum error due to filling was found to be about 4%. The curve obtained in Figure 13 could be expressed



0.10
0.08
0.06
0.04
0.02
0.00
Weight of Sulfur Dioxide sorbed per gram of charcoal
0.0
2.0
4.0
6.0
8.0
Partial Pressure
Experimental Values.
Calculated Values
Two runs in static system
THE HUGHES OWENS CO. LIMITED
No. 515L—METRIC

Figure 13.

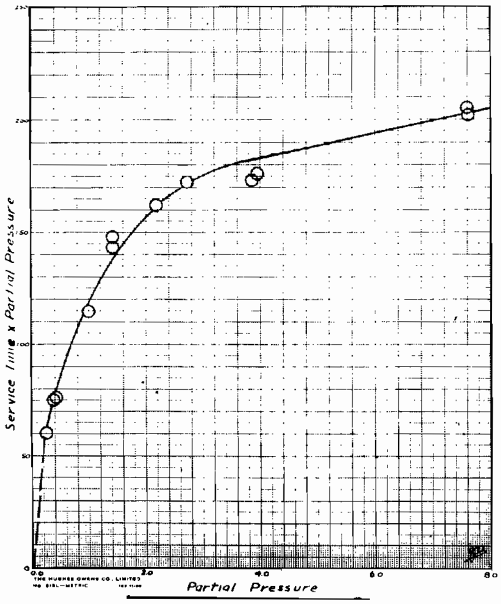

Service Time x Partial Pressure
250
200
150
100
50
0
0.0
2.0
4.0
6.0
8.0
Partial Pressure
THE HUGHES OWENS CO. LIMITED

Figure 14

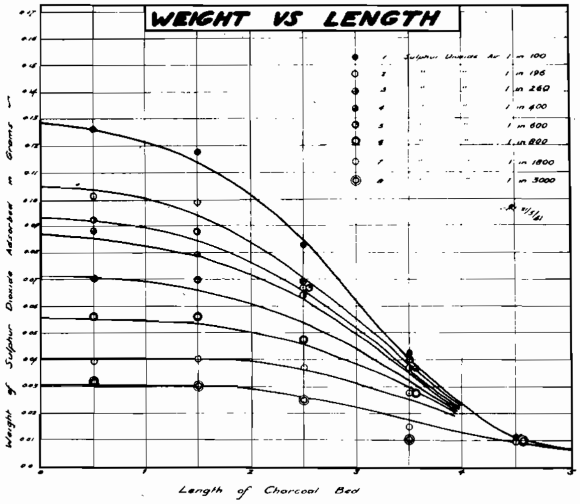

WEIGHT VS LENGTH
1 Sulphur Dioxide Air 1 in 100
2 " " 1 in 196
3 " " 1 in 260
4 " " 1 in 400
5 " " 1 in 600
6 " " 1 in 800
7 " " 1 in 1800
8 " " 1 in 3000
21/5/41
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.0
0
1
2
3
4
5
Weight of Sulphur Dioxide Adsorbed in Grams
Length of Charcoal Bed

Figure 15

TABLE IX

Section No.		1	2	3	4	5
	W_i	36.642	35.771	34.322	30.758	30.571
	W_1	36.744	35.845	34.344	30.761	30.568
First cell	Diff.	0.102	0.072	0.022	0.003	-0.003
	W_2	36.736	35.849	34.360	30.762	30.565
	Diff.	-0.008	0.006	0.016	0.001	-0.003
	W_T	36.711	35.836	34.346	30.781	30.569
	Diff.	-0.025	-0.013	-0.014	0.019	0.004
	W_i	30.341	32.694	36.263	34.892	29.847
	W_1	30.438	32.764	36.284	34.895	29.851
Second cell	Diff.	0.092	0.070	0.021	0.003	0.004
	W_2	30.422	32.770	36.287	34.895	29.854
	Diff.	-0.016	0.006	0.003	0.000	0.003
	W_T	30.396	32.783	36.289	34.910	29.856
	Diff.	-0.026	-0.017	0.002	0.015	0.002

The time at which a test was obtained was 110 minutes. In the second run, only the initial and final weights were obtained.

Section No.		1	2	3	4	5
First Cell.	W_i	36.740	35.827	34.300	30.741	30.580
	W_T	36.811	35.936	34.361	30.757	30.586
Diff.		0.071	0.064	0.061	0.016	0.006
Second Cell.	W_i	30.448	32.781	36.251	34.876	29.832
	W_T	30.514		36.311	34.896	29.832
Diff.		0.066		0.060	0.020	0.000

The service time was 116 minutes.

Carbon Tetrachloride

The results of the runs are given in Table X:

TABLE X

C	P_p	W_1	W_2	W_3	W_4	W_5	T_s	$P_p x T_s$
1/296	2.57	0.458	0.416	0.392	0.238	0.047	140	360
1/390	1.94	0.445	0.432	0.373	0.175	0.027	175	339
1/590	1.28	0.465	0.433	0.388	0.210	0.039	280	358
1/660	1.16	0.443	0.433	0.401	0.255	0.046	295	341
1/1240	0.615	0.434	0.414	0.392	0.257	0.040	590	362
1/1575	0.484	0.430	0.430	0.408	0.220	0.052	745	360
1/2800	0.272	0.375	0.371	0.383	0.265	0.048	1245	338
1/3660	0.208	0.353	0.372	0.352	0.235	0.045	1550	322
1/4560	0.167	0.347	0.334	0.337	0.205	0.030	1770	295
1/8000	0.095	0.270	0.284	0.258	0.148	0.005	2380	226

In Figure 16 have been plotted the weight of gas sorbed per gram of charcoal in the first section of cell against the partial pressure. The weight of gas sorbed in a section has been converted into grams of gas sorbed per gram of charcoal by dividing by 1.26, which was the average of ten values of the weight of charcoal in a cell section. The filling error was again about 4%. The curve obtained in Figure 16 fitted the Langmuir Isotherm equation and had the value:

$$X = \frac{5.26P}{1 + 13.9\ P}$$

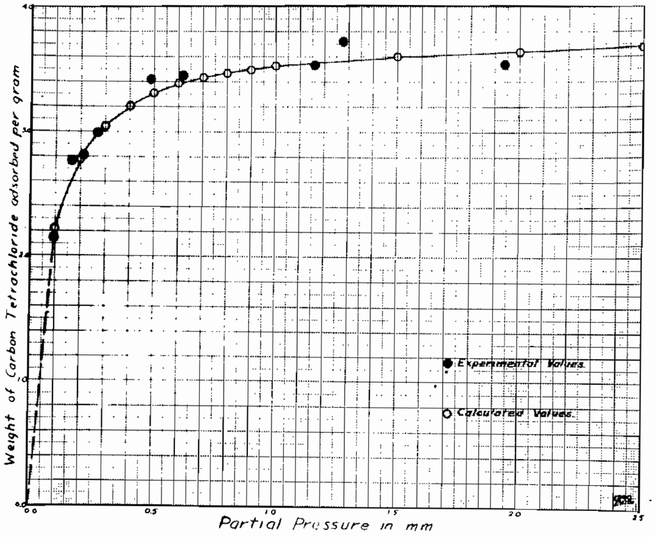

4.0
3.0
2.0
1.0
0.0
0.0
0.5
1.0
1.5
2.0
2.5
Weight of Carbon Tetrachloride adsorbed per gram
Partial Pressure in mm
● Experimental Values.
○ Calculated Values.

Figure 16

where X is the weight of gas sorbed per gram of charcoal and P is the partial pressure. The curve given by the above expression is also plotted in Figure 16 for comparison.

Experimental results for the carbon tetrachloride Isotherm in a static system have also been reported (15). These values have not been plotted in Figure 16 as no comparison could be made between them and the dynamic values listed here. The static values could not be made to fit into the Isotherm formula and the weight of gas sorbed at any partial pressure was less for the static system than for the dynamic. If any difference was observed between the weight of gas sorbed by the static system and the dynamic, it would be expected that the static value would be higher and because of this apparent discrepancy the static results were omitted.

In Figure 17 the product of the partial pressure and the service time has been plotted against the partial pressure. In this case it appears that the assumption that the service time is inversely proportional to the partial pressure holds down to quite low concentrations (1/1500) and then the product of the two terms loses its constancy and starts to fall off in the same manner as for sulfur dioxide.

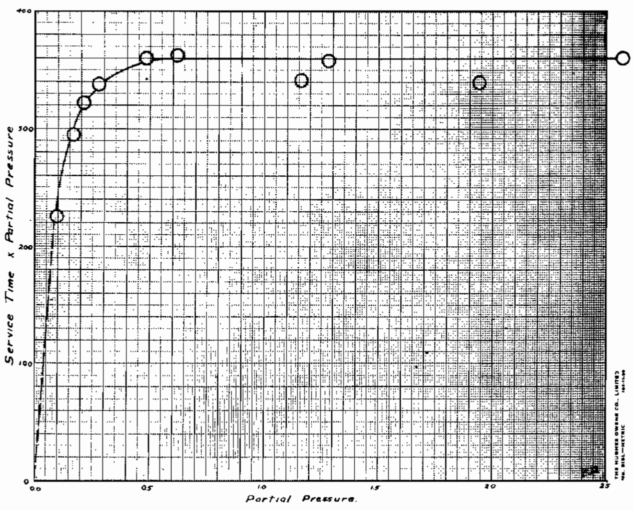

Service Time x Partial Pressure
Partial Pressure.
0
100
200
300
400
0.0
0.5
1.0
1.5
2.0
2.5
THE HUGHES OWENS CO., LIMITED

Figure 17.

4. The Measurement of the Hinshelwood "Critical Depth".

Hinshelwood (1) defined the critical depth of a charcoal bed, i.e. the maximum bed depth at which a service time of zero could be obtained, as the value obtained when the linear portion of the column length-breakdown time curve was extrapolated to zero breakdown time. His theory predicted that the relationship between critical depth and concentration of the gas in the air stream followed the formula:

$$\lambda_c = K \ln (C_o/C'-1)$$

where λ_c is the critical depth, K a constant depending on the rate of flow of the air and the number of active centers per cc. of charcoal, C_o the initial concentration of gas in the air stream, and C' the escaping concentration of gas at service time. In other words the critical depth plotted against the logarithm of the initial concentration should give a straight line, as the value of the escaping concentration is constant for any test used to determine the service time.

The following experiments were carried out to check the above formula, using dried A-87 charcoal, with a flowrate of 1000 cc. of air per minute. The bed was made up using the brass sections. As Hinshelwood had used steady flow, it was used instead of pulsating flow. In Table XI and Table XII are listed the values of the critical length for different concentrations as well as the service times for different bed depths, from which the critical lengths were determined by extrapolation. Table XI are the values obtained for sulfur dioxide and Table XII are those obtained for carbon tetrachloride.

TABLE XI

C	P_p	Service Time 3 cm.	4 cm.	5 cm.	6 cm.	h
1/100	7.60 cm.	--	1.5 min.	3.3 min.	5.0 min.	3.20 cm.
1/150	5.06	--	5.0	9.0	12.8	2.62
1/200	3.80	--	8.0	12.5	17.0	2.35
1/250	3.04	--	10.0	15.5	20.8	2.18
1/330	2.28	5.5	11.5	17.0	22.5	1.99
1/500	1.52	11.5	21.3	30.5	40.0	1.82
1/770	0.99	23.0	41.0	59.0	77.0	1.69

The bed depth-service time curves have not been given as they were all of the same type as the amine curves shown in Figure 5. In Figure 18 the critical depth has been plotted against the concentration of sulfur dioxide in the air stream. This gave a straight line, which was not in accord with Hinshelwood's prediction.

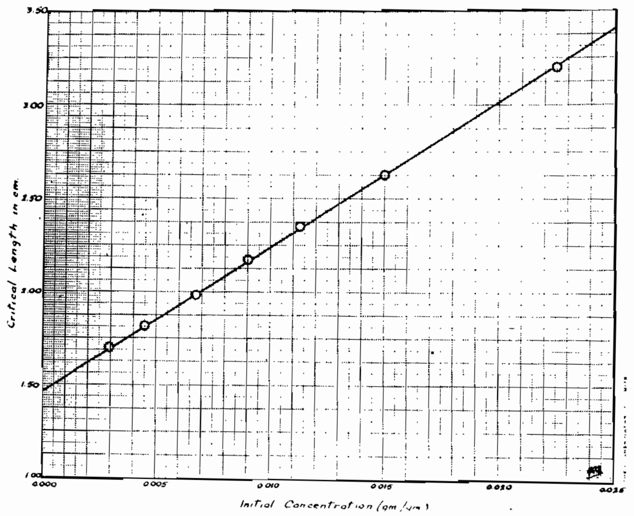

3.50
3.00
2.50
2.00
1.50
1.00
Critical Length in cm.
0.000
0.005
0.010
0.015
0.020
0.025
Initial Concentration (gm./gm.)

Figure 18.

TABLE XII

C	P_p	Service Time 3 cm.	4 cm.	5 cm.	6 cm.	h
1/218	3.50 cm.	15 min.	32 min.	48 min.	65 min.	2.08 cm.
1/345	2.20	26	50	74	96	1.90
1/380	2.00	25	46	70	88.5	1.88
1/600	1.27	45	83	118	153	1.79
1/660	1.15	43	72	107	143	1.77
1/1200	0.67	85	150	215	--	1.70
1/3240	0.24	265	460	--	857	1.65
Pulsating flow						
1/380	2.00	55(27.5)	120(60)	165(82.5)	220(110)	2.0 cm.

The critical depth was determined with a concentration of 1/380 using pulsating flow for comparison with the steady flow results and the results are given at the bottom of Table XII. The figures in brackets are the service times corresponding to steady flow. Comparing the critical depths resulting from the two types of flow at a concentration of 1/380, it appears that the pulsating flow gives a longer critical depth but the service time for any depth is longer. In Figure 19 the critical depth has been plotted against the concentration of carbon tetrachloride in the air stream. This also gave a straight line. Further consideration of this has been left until the Discussion section of this thesis.

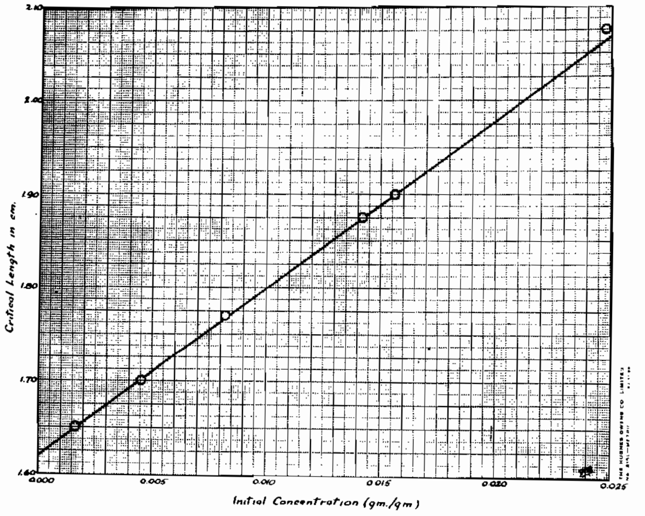

2.10
2.00
1.90
1.80
1.70
1.60
Critical Length in cm.
0.000
0.005
0.010
0.015
0.020
0.025
Initial Concentration (gm./gm)
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Figure 19.

5. The Efficiency of the Carbon Tetrachloride Carburetter

In all the previous work on carbon tetrachloride, carried out in the Second Apparatus, it was assumed that the subsidiary air stream, which passed over the liquid carbon tetrachloride in the carburetter, became saturated with carbon tetrachloride vapour. In other words, the efficiency of the carburetter was assumed to be 100%.

To prove this, two experiments were carried out at different concentrations and the amount of carbon tetrachloride, removed by the subsidiary air stream, was determined by sorbing it in a charcoal cell until a service time was obtained. The gain in weight in the charcoal cell gave the amount of carbon tetrachloride removed. This amount could be converted to cc. removed per minute and compared to that calculated from the rate of flow of the subsidiary air stream and the vapour pressure of the carbon tetrachloride in the carburetter. The results of the two runs are given in Table XIII:

TABLE XIII

	Run No. 1	Run No. 2
Main Air Flow	2000 cc./min.	2000 cc./min.
Subsidiary Air Flow	26.75 cc./min.	10.0 cc./min.
Service Time	21 min.	55 min.
Weight of CCl_4 sorbed	0.685 gm.	0.674 gm.
Rate of CCl_4 sorption	0.0326 gm./min.	0.0122 gm./min.

TABLE XIII (Cont'd.)

	Run No. 1	Run No. 2
	5.06 cc./min.	1.89 cc./min.
Thermostat	30° C.	30° C.
Vapour pressure CCl	143 mm.	143 mm.
Rate of removal	$\frac{143 \times 26.75}{760}$	$\frac{143 \times 10.0}{760}$
	5.04 cc./min.	1.88 cc./min.

From the above calculations, the efficiency of the carburetter is 100%, within the limit of error.

6. The Sorption Gradient in a Charcoal Bed

This work was carried out entirely in the Second Apparatus, using a Canadian silver impregnated charcoal, SBT 95-96, which was dried at 140°C, in an oven for 20 hours. In the sulfur dioxide work, the gas was metered directly into the air stream from a cylinder. In the first group of experiments, the weight of gas sorbed in each section of the cell was determined at service time only for different concentrations under conditions of steady flow. Both carbon tetrachloride and sulfur dioxide were studied. In the second group of experiments, the build-up of the gradient was determined for different concentrations and different rates of flow of the air stream, using a steady flow through the cell. Carbon tetrachloride was first studied, but it was found that the gradient was short and sharp and so sulfur dioxide was used instead, as this has a longer and more gradual falling off in amount sorbed. In the sulfur dioxide experiments, the first three series of runs were carried out keeping the amount of gas constant (i.e. the gas flowmeter was set for a flow rate of 2 cc./min.) while the air flow was changed. The other two runs were carried out changing both the gas flow and the air flow, so that the partial pressure in the gas-air mixture remained constant. The concentration of the gas in the air stream did not halve exactly when the flow rate was doubled because the pressure drop inside the apparatus changed when the flow rate was changed and in consequence a higher rate of flow produced a larger pressure drop in the apparatus. The result of this was that with the same setting on the gas flowmeter, more sulfur dioxide entered the air stream at high flow rates than at lower rates.

The experiments of the first group are listed in Table XIV:

TABLE XIV

C	P_p	W_1	W_2	W_3	W_4	W_5	T_s
Carbon Tetrachloride							
1/375	2.03	0.564	0.563	0.551	0.368	0.074	124
1/675	1.12	0.553	0.553	0.552	0.354	0.080	220
1/1575	0.48	0.510	0.510	0.510	0.433	0.143	515
1/3240	0.235	0.464	0.464	0.464	0.400	0.100	946
Sulfur Dioxide							
1/115	6.61	0.108	0.086	0.070	0.040	0.012	13.5
1/200	3.80	0.078	0.071	0.062	0.036	0.015	19.5

where C is the concentration, P_p the partial pressure, W_1 the weight of gas sorbed in the first section of the cell, W_2 the weight in the second, etc., and T_s the service time. In all these runs the rate of air flow was 1000 cc./min.

The experiments of the second group are listed in Table XV, the last time listed in each series being the service time.

TABLE XV

Time	W_1	W_2	W_3	W_4	W_5
Carbon Tetrachloride					
Subsidiary Air 16 cc./min. Air 1000 cc./min. Concentration 1/340					
10	0.184 gm.	--	--	--	--
20	0.347	0.033 gm.	--	--	--
30	0.418	0.143	0.019 gm.	--	--
40	0.530	0.210	0.022	--	--
50	0.560	0.321	0.069	--	--
60	0.556	0.445	0.117	0.018 gm.	--
70	0.567	0.500	0.199	0.025	--
80	0.567	0.542	0.330	0.065	--
90	0.563	0.542	0.454	0.126	0.016 gm.
100	0.570	0.545	0.521	0.240	0.037
110	0.569	0.560	0.552	0.342	0.071
Sulfur Dioxide					
Gas 2.0 cc./min. Air 500 cc./min. Concentration 1/400					
10	0.030 gm.	0.005 gm.	--	--	--
20	0.050	0.014	0.005 gm.	--	--
30	0.061	0.029	0.012	--	--
40	0.065	0.038	0.019	0.011 gm.	--
50	0.072	0.046	0.024	0.015	0.010 gm.
60	0.079	0.055	0.032	0.015	0.014
70	0.086	0.065	0.042	0.021	0.019
80	0.092	0.077	0.056	0.025	0.018
90	0.099	0.078	0.064	0.041	0.021 Service time - 90 min.

TABLE XV (Cont'd).

Gas 2 cc./min. Air 1000 cc./min. Concentration 1/760

5	0.013 gm.	0.005 gm.	--	--	--
10	0.025	0.012	--	--	--
15	0.038	0.015	--	--	--
20	0.046	0.020	0.005 gm.	--	--
25	0.053	0.029	0.016	--	--
30	0.052	0.034	0.020	--	--
40	0.058	0.040	0.030	0.013 gm.	--
50	0.061	0.050	0.036	0.023	--
60	0.064	0.059	0.047	0.026	0.015 gm.
64	0.073	0.061	0.047	0.032	0.012

Service time - 64 min.

Gas 2 cc./min. Air 2000 cc./min. Concentration 1/1380

15	0.028 gm.	0.019 gm.	0.010 gm.	--	--
20	0.039	0.023	0.018	--	--
25	0.038	0.028	0.020	0.011 gm.	--
30	0.046	0.030	0.022	0.019	--
35	0.046	0.038	0.032	0.019	--
40	0.044	0.042	0.033	0.023	0.017 gm.
45	0.048	0.042	0.038	0.025	0.021
50	0.056	0.047	0.039	0.031	0.024
55	0.057	0.051	0.047	0.030	0.025

Service time - 55 min.

TABLE XV (Cont'd).

Gas 4 cc./min. Air 2000 cc./min. Concentration 1/900

5	0.025 gm.	0.005 gm.	--	--	--
10	0.034	0.023	--	--	--
15	0.040	0.034	0.020 gm.	--	--
20	0.047	0.036	0.028	0.009 gm.	--
25	0.047	0.040	0.034	0.017	0.012 gm.
28	0.044	0.044	0.037	0.024	0.018

Service time - 28 min.

The data listed in Table XV has not been shown in figures here, as the curves are similar in character to those shown in Figure 6 and further consideration of the results has been left until the Discussion.

DISCUSSION

The discussion has been divided into several sections for facility in considering the different aspects of the subject as brought out by experiment.

1. The Dynamic Adsorption Isotherm

The manner in which the weight of gas sorbed by the charcoal at equilibrium with the initial concentration of the gas in the air stream was in complete agreement with the experiments reported by Mecklenberg (2, 7). Mecklenberg found that the constant k in his equation (Equ. iv, Introd.) varied with the initial concentration of the chlorine in the air stream in accordance with the Freundlich Adsorption Isotherm. The Langmuir Adsorption Isotherm, which the sulfur dioxide and carbon tetrachloride experiments, reported in this thesis, were found to follow, is merely a different mathematical expression of the same general form of curve. The constants of the sulfur dioxide and carbon tetrachloride Isotherm equations appeared to be the same as those found to hold for the static systems of the two gases using the same charcoal (15).

This was a significant point because it meant that the constants of the service time equation could be determined using a static system and then the service time predicted from the equation for any experimental conditions by putting in the desired values of the gas concentration, air flow velocity and length of charcoal bed.

Hinshelwood (1) did not take this Isotherm effect into account in his theory, as he assumed that the number of active centers per cc. of charcoal (this was equivalent to the number of molecules sorbed/cc. of charcoal) was a constant, which did not vary with the initial concentration of the gas. This assumption would be true for a catalytic sorption, where an active center would remove a gas molecule by destroying its identity and being destroyed itself in the process. In this type of sorption the gas concentration would have no effect on the activity of the active centers. However, in the experiments being considered here, where dry charcoal has been used, the mechanism of sorption must have been either pure adsorption or some kind of capillary condensation. Either mechanism would represent a reversible type of sorption, where the amount of gas sorbed was determined by the partial pressure of the gas in the air stream and the vapour pressure of the gas sorbed on the charcoal. Hence the amount of gas sorbed would be expected to be a function of the initial concentration of the gas in the air and to follow the Adsorption Isotherm.

From the above, it appeared that the Hinshelwood treatment should be modified to include the Adsorption Isotherm. From Hinshelwood's original assumptions, N_o was the number of active centers per cc. of charcoal and was a constant independent of the initial concentration. If, however, N_o was multiplied by a factor, n, to give N', the number of effective active centers for any specific concentration, this constancy would be removed. From experiment it has been shown that this factor varied with the concentration, n=f(p), where f(p) had the form of the Adsorption Isotherm. Therefore, in the analytical treatment, N', the effective sorbing surface has been substituted for N_o, to give:

$$N' = nN_o = \left(\frac{ap}{1 + bp}\right) N_o \qquad . \qquad . \qquad (xvii)$$

In his elementary theory, Hinshelwood expressed the concentration of the gas over the charcoal at any point in the bed as:

$$c = c_o e^{-\frac{Kl}{L}} \; e^{\frac{Kbt}{L}} \qquad . \qquad . \qquad (xii)$$

where b was the rate at which the active centers were used up, or:

$$b = \frac{c_o L}{N_o} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (xviii)$$

Substitution of equation (xvii) in equation (xviii) gave:

$$b \qquad \frac{c_o L}{N'} \qquad \frac{c_o L}{\left[\frac{ap}{1 + bp}\right] N_o} \qquad . \qquad . \qquad (xix)$$

where N' was the effective sorbing surface for an initial concentration of c_o, which corresponds to a partial pressure of p.

In the Hinshelwood treatment, the relationship between the service time and the partial pressure could be expressed as:

$$T \times p = KN_o = \text{constant} \qquad . \qquad . \qquad (xx)$$

where K was a proportionality constant. When the above modification was introduced, equation (xx) became:

$$T \times p = K \left(\frac{ap}{1 + bp} \right) N_o \qquad . \qquad . \qquad (xxi)$$

It was found in the case of sulfur dioxide, that the total weight of gas sorbed by the whole cell, as well as the weight of gas sorbed in the first section, could be predicted by the Adsorption Isotherm. The denominator of the Isotherm was the same in both cases. The same relation was roughly true for the carbon tetrachloride. Therefore in place of the Isotherm expression in the above equation, the total weight of gas sorbed by the whole cell was used, giving the equation:

$$\frac{T \times p}{W_T} = KN_o = \text{constant} \qquad . \qquad . \qquad (xxii)$$

Table XVI gives the values of the results in Tables VIII and X for sulfur dioxide and carbon tetrachloride.

TABLE XVI

Sulfur dioxide		Carbon tetrachloride	
p	$T \times p/W_T$	p	$T \times p/W_T$
0.254 mm.	293	0.095	118
0.39	285	0.167	113

TABLE XVI (Cont'd)

p	T x p/W_T	p	T x p/W_T
0.42	282	0.208	118
1.00	287	0.272	118
1.41	285	0.484	118
2.18	282	0.615	118
2.72	284	1.16	117
3.71	284	1.28	118
3.85	282	1.94	118
7.60	268	2.57	116

The constancy thus obtained illustrated the value of introducing the correction. The values of the product of the service time and partial pressure without the introduction of the Isotherm modification may be found in Tables VIII and X and in Figures 14 and 17.

2. The Dead Length

The service times of methylamine for different bed depths have been plotted in Figure 20 along with corresponding results reported by Mecklenberg for chloropicrin. From the graph, the two curves were found to be of the same general shape. As outlined in the Introduction, Mecklenberg has shown that his formula accounted for this effect when the increase in the vapour pressure of the gas, condensed in the capillaries, was considered. The vapour pressure increased from zero to an equilibrium value with the initial concentration of the gas in the air stream as the sorption progressed. As the Hinshelwood formulae

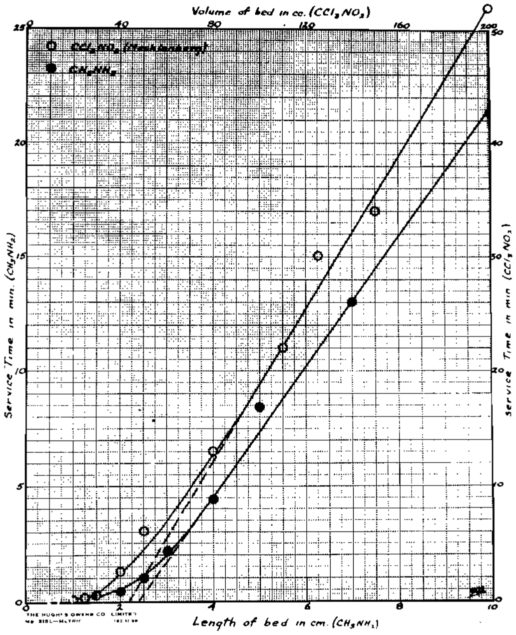
Volume of bed in cc. (CCl_3NO_2)
0
40
80
120
160
200
CCl_3NO_2
CH_3NH_2
Service Time in min. (CH_3NH_2)
0
5
10
15
20
25
Service Time in min (CCl_3NO_2)
0
10
20
30
40
50
Length of bed in cm. (CH_3NH_2)
0
2
4
6
8
10
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Figure 20.

(Equ. iii and xv, Introd.) predicted a linear relation would hold down to a service time of zero, giving, at that point, the critical length of the charcoal, they did not account for this effect.

In the sulfur dioxide and carbon tetrachloride experiments over a concentration range from which the dead lengths have been calculated, the curving effect at low service times was not observed. As the experiments were not continued down to short bed lengths, it could be possible that the region of the curve was never reached.

Mecklenberg listed some values of the dead length as a function of the concentration for chloropicrin. When the dead length was plotted against the chloropicrin concentration, a straight line was obtained. This result was in agreement with the sulfur dioxide and carbon tetrachloride results shown in Figures 18 and 19. In the three cases the value of the dead length was determined by extrapolating the plot of the service time against the bed length to a service time of zero. The Mecklenberg equation predicted that the dead length should vary as the logarithm of the initial concentration, instead of being a linear function. Actually, as shown in Figure 20, extrapolation does not give the true value of the dead length due to the curving of the plot at low service times. However, it was considered possible that the true value of the dead length, i.e. the point at which the curve cut the bed length axis, would, if plotted against the logarithm of the concentration, give a straight line. Such measurements would have very large errors because the service times at the lower end of the curve would only be of the order of a minute or less and a small error in the service time would be greatly magnified in the value of h.

Hinshelwood also predicted that the critical length should vary as the logarithm of the concentration. Experiment has appeared to be in complete disagreement, showing a linear relation. This disagreement could be due to the fact that Hinshelwood gave the critical length a definite physical significance whereas experiment has shown, as in Figure 20, that the critical length or the extrapolated value was merely a mathematical constant that gave the observed value of the service time for long bed lengths (cf. equ. i and iii, Introd.).

From a consideration of the above facts, it was possible to outline, in a general way, the process of a gas being sorbed by a charcoal bed from a stream of air flowing through the bed. The sorption process may be split into two parts:

(1) The building up of the sorption gradient or working length. This is the length of the bed necessary to reduce the concentration of the gas in the air stream from its initial concentration to just below its threshold

value. The threshold value is the concentration which will just give a test with the chemical testing apparatus, used to determine the passage of the gas.

(2) The movement of this gradient, once it is built up, through the charcoal bed with a constant linear velocity.

Consider the process as follows: Suppose the air stream entering the bed is divided into differential amounts, designated by 1, 2, 3, etc. and the charcoal bed divided into differential layers, a, b, c, etc. If now only the differential amount of air, 1, is considered: This amount of air enters layer a of the charcoal bed and an instantaneous equilibrium is set up between the gas in the air and the gas sorbed on the charcoal, as predicted by the Adsorption Isotherm. This will remove a large part of the gas from the air stream. The air then moves on to layer b and the remaining gas immediately comes into an equilibrium between the air and charcoal and some more gas is removed from the air. This process continues until at some layer s_1, the concentration of the gas in the air stream has fallen below the threshold value. When the differential amount of air, 2, enters layer a, only a small amount of gas is taken up by the charcoal to set up a new equilibrium, as this layer already has a large amount of gas on it from the passage of 1. This process continues through the bed until the threshold value is reached at s_2. As the process continues further, the amount of gas taken up by each charcoal layer will gradually decrease for each differential amount of air that passes through the bed and, in consequence, the process of building up the gradient is one of steady change. Finally at some time, t_x, if the bed is long enough, when some differential amount of air, x, enters the bed, layer a becomes saturated and the sorption gradient has reached its full length and stretches through the bed to some layer, s_x, before the gas concentration in the air reaches the threshold value. The next differential amount of air, which enters the bed, will saturate layer b and the threshold value is not reached until one layer past s_x. This latter process represents the movement of the sorption gradient through the bed with a constant linear velocity.

As the shape of the sorption gradient is continually changing during the build-up, the front spur of the gas, (that is the point where the gas concentration in the air stream first drops below the threshold value), will not advance through the bed with a constant velocity. If the first differential amount of the gas-air mixture is considered again, it can be seen that the spur of the gas must move from the face of the bed to the point s_1 during the differential time interval. The velocity of the spur is given by the distance travelled during the time interval divided by the time interval. When the second differential amount of the gas-air mixture moves through the bed, the spur moves a distance $s_2 - s_1$. By the time this gas reaches s_1, its concentration has been considerably lowered in passing over the partially saturated charcoal in that section and in consequence the distance $s_2 - s_1$ must be shorter than the length s_1. This occurs during the same time interval as with amount 1, and as a result the velocity of the spur is less. Using the same deductions until the gradient is built up, it is possible to state that: The spur of gas moves through the charcoal bed with a decreasing velocity reaching a minimum at the moment layer a becomes saturated and this minimum represents the velocity at which the gradient moves through the bed.

This velocity change is shown by the results of the methylamine experiments (Table II) and a series of experiments carried out by Shilov et al.(4) with an initial chlorine concentration of 2.13%. The values used for the methylamine have been taken from the graph shown in Figure 20. In Table XVII, T is the service time for a bed length of L, ΔT and ΔL are the differences between successive time and length values, and V_s is the velocity of the spur as given by the relation $\Delta L/\Delta T$, expressed in cm./min.

TABLE XVII

T	ΔT	L	ΔL	$V_s = \Delta L/\Delta T$
Methylamine				
21.3 min.		10 cm.		
	5.6 min.		2 cm.	0.357
15.7		8		
	5.6		2	0.357

TABLE XVII (Cont'd)

T	ΔT	L	ΔL	$V_s = \Delta L / \Delta T$	
10.1 min.		6 cm.			
	5.5 min.		2 cm.	0.364	
4.4		4			
	2.3		1	0.435	
2.1		3			
	1.1		0.5	0.454	
1.0		2.5			
	0.6		0.5	0.833	
0.4		2			
	0.3		0.5	1.666	
0.1		1.5			
Chlorine					
67.5 min.		80 cm.			
	11.0 min.		10 cm.	0.91	cm./min.
56.5		70			
	11.0		10	0.91	
45.5		60			
	11.5		10	0.87	
34		50			
	11.5		10	0.87	
22.5		40			
	9.6		10	1.02	
12.9		30			
	8.0		10	1.25	
4.9		20			

TABLE XVII (Cont'd)

T	ΔT	L	ΔL	$V_s = \Delta L/\Delta T$
	4.6 min.		10 cm.	2.18
0.3 min		10 cm.		
	0.3		10	33.3
0.0		0		

After the above points were brought out concerning the mechanism of sorption, a closer consideration of the service time-bed length curve yielded many interesting values. A typical curve has been shown diagrammatically in Figure 21. In this curve, AC represents the Hinshelwood critical length, as C is the point at which the straight line section of the curve extrapolates to zero service time. From Figure 21, it can be seen that the length AC has no physical significance and can only be used as a mathematical correction for predicting the service times over the straight line part of the curve. The length AB is the true dead length or the critical length, as it represents the length of charcoal bed that is necessary to reduce the gas concentration to the threshold value, when the first gas is passed through a bed of unused charcoal. The length DE represents the length of the working layer or sorption gradient when it is completely built up, as E is the point at which the straight line relation starts and is consequently the length at which the spur of gas, as well as the sorption gradient starts to move through the bed with a constant velocity. Following from this, the length AD represents the

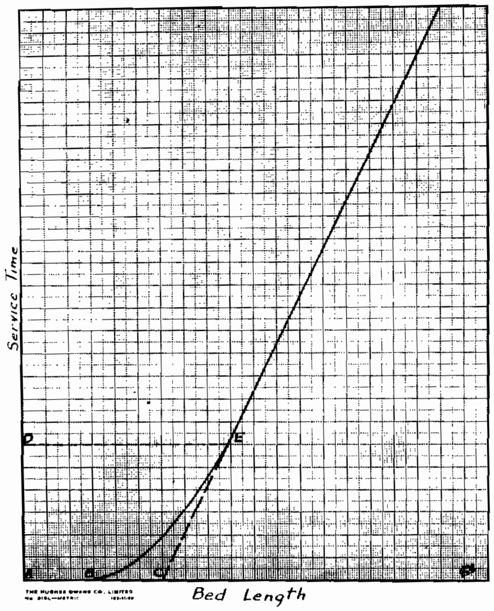

Figure 21.

time necessary to build up the complete sorption gradient.

The sulfur dioxide and carbon tetrachloride series of experiments, as given in Tables IV and XV, on the sorption by a charcoal bed with increasing time have confirmed the above mechanism of sorption. As these different series all gave similar results, only the sulfur dioxide series listed in Table IV has been discussed here in detail. It was first necessary to obtain the sorption gradients for this series. The technique developed to give these gradients was a graphical one and is outlined below.

The integral sorption was first plotted on a large scale diagram. This consisted of plotting the weight of gas sorbed in the first section of the cell against the length of that section (1 cm.), the sum of the weights of gas sorbed in the first two sections of the cell against the length of the two sections (2 cm.), and so on until the total weight of gas sorbed by the cell was plotted against the total length of the cell. A line was then drawn through the plotted points, using a spline, to give the integral sorption curve. The sorption gradient curve was the derivative of this curve. The standard method of graphical differentiation, by using the tangents to the curve at regular intervals throughout its length, was applied to give the sorption gradient curve.

Figure 22 shows the results of this treatment for the sorption of sulfur dioxide at different times, as listed

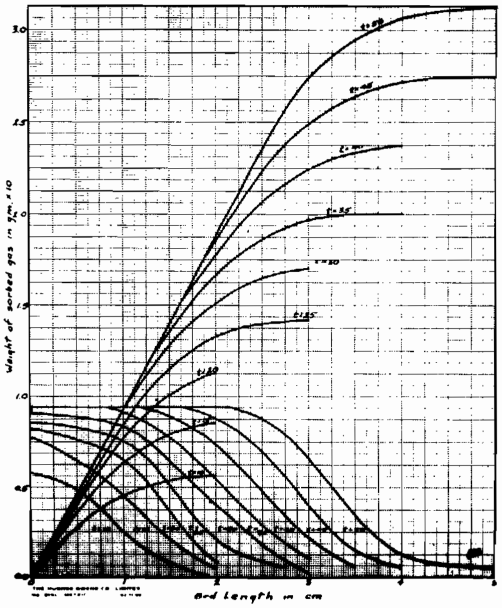
t=50
t=45
t=40
t=35
t=30
t=25
t=20
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
Weight of sorbed gas in gm. x 10
Bed Length in cm

Figure 22.

in Table IV. From Figure 22 it can be seen that the sorption gradients were changing at short times, but at some time between 30 and 35 minutes the gradient was completely formed and as the time increased above this, the gradient retained its shape but was displaced linearly to the right along the length axis. This agrees with the assumption of the sorption process taking place in two parts, the building up of the sorption gradient, followed by the movement of the complete gradient through the bed with a constant linear velocity. The carbon tetrachloride results listed in Table XV gave curves similar to those shown in Figure 22. However, with carbon tetrachloride, the sorption gradient only extended over a length of a little more than 1 cm., while the sulfur dioxide gradient covered nearly 3 cm. This was caused by the high sorptive power of charcoal towards carbon tetrachloride as compared to sulfur dioxide.

Figure 23 shows the differential weight of gas sorbed, (as given in Figure 22), plotted against time at different depths in the bed. The relation between the weight sorbed and the time for very short distances from the surface of the bed appeared to follow an exponential curve and was written as:

$$x = W_s \left(1 - e^{-bt} \right) \quad . \quad . \qquad \text{(xxiii)}$$

where x is the weight of gas sorbed at time t, W_s the equilibrium weight of gas sorbed, and b a constant. This relation was identical to that given by Syrkin and Kondraschow (8)

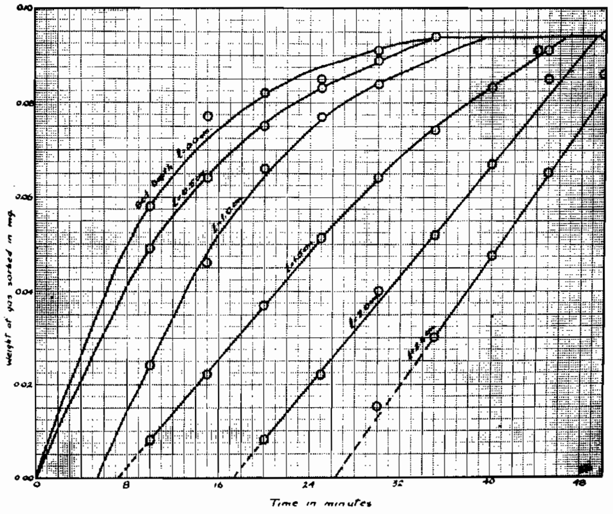
0.10
0.08
0.06
0.04
0.02
0.00
Weight of gas sorbed in mg.
0
8
16
24
32
40
48
Time in minutes
bed depth l=0.0 cm
l=0.5 cm
l=1.0 cm
l=1.5 cm
l=2.0 cm
l=2.5 cm

Figure 23.

for the increase in the weight of a charcoal bed when a gas-air mixture was passed through the bed, only part of the gas being sorbed by the charcoal. However as the distance into the bed increased the exponential curve flattened out, finally becoming a straight line. At all depths larger than this, the relation appeared to be roughly linear. This effect could again be explained by the previous assumptions, for in the length of the charcoal where the gradient was being built up, the sorption of the gas was taking place under changing conditions and, as a result, different curves were obtained at different depths. Once the gradient was built up the sorption was more or less linear and the lines were displaced to the right as the gradient moved through the bed. The reason that some of the curves ran down to give finite times was due to the fact that for bed depths greater than the true dead length (AB in Figure 21), there was a certain length of time before any gas penetrated to that depth.

There was another relation between the weight of gas sorbed and the time of passage of the gas-air stream at constant bed depth. This relation has been shown in Figure 24, where the logarithm of the weight of gas sorbed has been plotted against the reciprocal of the time of passage for different depths in the bed. The values were the same as those used in Figure 23. The values for four depths were plotted and these gave four straight lines which met in a point. This point did not seem to have any particular significance, as it corresponded to a sorbed weight of 0.103 gm. and a time of 57 min., while the equilibrium weight of the charcoal was 0.094 gm. and the service time for a 5 cm. bed was 51 min. However, from Figure 24, the relation was written:

$$x = Ke^{-k/t} \quad . \quad . \quad .. \qquad (xxiv)$$

where x is the weight of gas sorbed at time t, K a constant relating to the equilibrium weight of gas sorbed, and k a second constant which varies with the distance from the top surface of the bed. Preliminary treatment of equation xxiv indicated that k was probably directly proportional to the square root of this length. It has been impossible to date to build up a formula from the above equation to predict the weight of gas sorbed at any depth for any time. Such a formula could be rearranged to predict the service time of any charcoal bed for any experimental conditions.

The length of the gradient for different concentrations of sulfur dioxide has been found by applying the method of graphical differentiation, as outlined above, to the results listed in Table VIII. The dead length was then obtained by measuring the area of the unused part of the charcoal bed with a planimeter and dividing by the equilibrium sorption - weight. This unused portion or residual activity was the area lying between the sorption gradient and the maximum sorption, which was given by a line drawn across the whole bed length through the equilibrium

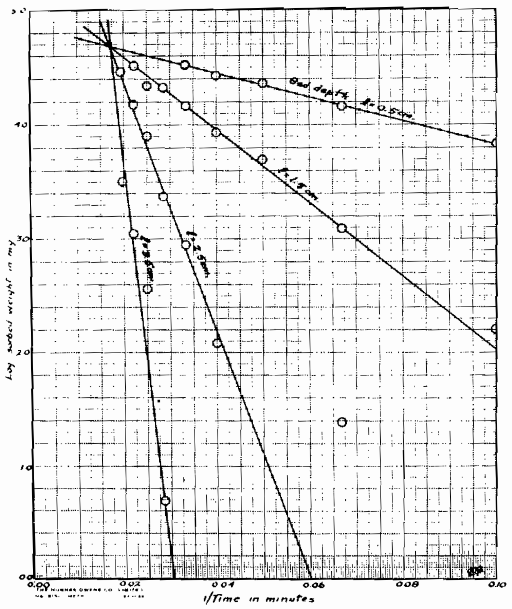
Bed depth, l = 0.5 cm.
l = 1.5 cm.
l = 2.5 cm.
l = 3.5 cm.
Log sorbed weight in mg
5.0
4.0
3.0
2.0
1.0
0.0
0.00
0.02
0.04
0.06
0.08
0.10
1/Time in minutes
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Figure 24.

sorption weight. The values obtained are given in Table XVIII:

TABLE XVIII

c	c_o	W_S	l_g	A	h	A_T	X_T
1/100	0.0133	0.125	4.20	0.240	1.92	0.385	0.380
1/200	0.0066	0.095	3.85	0.170	1.79	0.305	0.305
1/349	0.0038	0.088	3.60	0.148	1.68	0.292	0.288
1/538	0.0025	0.071	3.35	0.104	1.47	0.254	0.253
1/762	0.00175	0.057	3.20	0.084	1.48	0.201	0.201
1/1820	0.00074	0.041	2.85	0.053	1.29	0.152	0.134
1/1960	0.00068	0.038	2.70	0.045	1.20	0.144	0.132

where c is the gas concentration in parts of air, c_o the gas concentration in grams of gas entering bed per minute, W_S the equilibrium sorption weight in grams, l_g the length of the sorption gradient in cm., A the area over the sorption gradient or the residual activity in gm.-cm., h the calculated dead length in cm., A_T the area under the whole sorption curve or the total weight of gas sorbed at service time, and X_T the total weight of gas sorbed at service time, as obtained experimentally.

The values of the length of the sorption gradient and the dead length, when plotted against the logarithm of the initial concentration, gave straight lines, as shown in Figure 25. This was in accord with the theory of Mecklenberg.

The values of the dead length as calculated in Table XVII differed in all respects from those given in

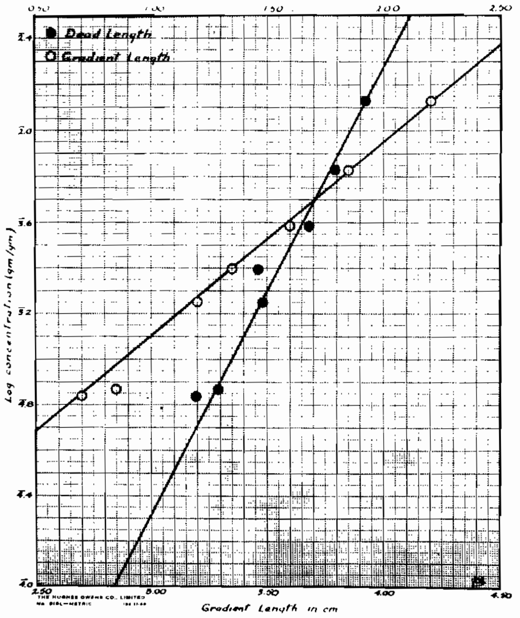● Dead Length
○ Gradient Length
0.50
1.00
1.50
2.00
2.50
$\bar{2}.4$
$\bar{2}.0$
$\bar{3}.6$
$\bar{3}.2$
$\bar{4}.8$
$\bar{4}.4$
$\bar{4}.0$
Log concentration (gm/gm)
2.50
3.00
3.50
4.00
4.50
Gradient Length in cm
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Figure 25.

Table XI, which were obtained by extrapolating the service time-bed length curves. The extrapolated values were always higher for any concentration and showed a linear relation with the concentration instead of the predicted logarithmic relation. There has been no reason to assume that the two sets of measurements corresponded to the same thing. As mentioned earlier in this section, no physical significance could be attached to the extrapolated value and it was assumed to be a mathematical term giving the apparent maximum bed length at which a service time of zero could be obtained. Such a value would not be required to follow the logarithm of the initial concentration, whereas the dead length as given in Table XVIII was actually related to the residual activity and, having a definite physical significance, would be expected to agree with the predictions of the theory, as Mecklenberg assumed the dead length to be a measure of the residual activity.

The above results suggested a simple method of measuring the value of the dead length. An outline of the method follows:

The weight of gas sorbed by a bed of charcoal at service time was measured. The equilibrium sorption weight of the gas at the concentration under study was obtained from the Adsorption Isotherm and the maximum weight of gas, that the above bed was capable of sorbing, calculated by multiplying the equilibrium sorption weight by the bed length.

The difference between the two weights multiplied by the bed length and divided by the maximum sorption weight gave the dead length.

Several trial experiments were carried out but these were only qualitative and there was not sufficient time for a complete investigation.

While several points of theoretical interest have been brought out by the foregoing experiments, the most striking point from a practical view has been the dynamic adsorption isotherm. As previously mentioned, it was generally assumed that the service time varied inversely with the initial concentration of the gas in the air stream (cf. equ. xx). Instead, however, it was found that the isotherm expression entered into the relation and the resulting formula has been given as equation xxi.

This means that the service time of a canister under field conditions will be considerably lower than that predicted by equation xx. As field concentrations may be of the order of 1 part of gas to 20000 parts of air, which corresponds to a partial pressure of about 0.04 mm., the equilibrium sorption weight of the charcoal at this concentration may be reduced to a tenth of the value under proofing conditions. This would mean that the service time of the canister would be reduced to a tenth of the predicted value. However, against most gases, this would still leave the respirator with a fair margin of safety from the defensive point of view. On the other hand from the offensive viewpoint, the lower the concentration of gas that is released, the less gas is necessary to break down the canister. Therefore a gas which is toxic at very low concentrations would be far more effective if released in low concentrations over a long period of time than if the same amount of gas were released at high concentrations for a short time.

APPENDIX I

THE RECOVERY OF CHLOROPICRIN FROM CHARCOAL

INTRODUCTION

From the time that the high sorptive properties of charcoal first became known, charcoal has been widely used for the purification and decolorizing of liquids, the recovery of solvent vapours, and the purification of air by the removal of noxious fumes. After such processes the charcoal has generally been reactivated and the sorbed substances removed by severe heat treatment and/or by the passage of clean air over its surface (16).

A simple system for removing chlorine from charcoal based in theory upon vacuum distillation, was suggested by Melsens (17, 18), who heated the charcoal in one end of a closed bent tube and cooled the other end, the chlorine distilling off the charcoal and condensing in the cooled end of the tube.

Superheated steam has often been used to recover liquids or vapours sorbed on charcoal, the steam being used at temperatures from 100°-150°. Mantell (19) described a complete gasoline recovery plant, and methods for the recovery of ethers (20), alcohols (21), other hydrocarbons (22), volatile vapours (23), and organic halides (24, 25) by steam have all been discussed in the literature. A mixture of alcohol and steam was recommended for butylamine (26) and distillation in the presence of inert gases was suggested to prevent the explosion of certain volatile vapours (27). Anderson and Hinckley (28) studied four methods for recovering gasoline from charcoal and listed them in the order of their efficiency as follows:

(1) Heating with mineral oil,
(2) Heating with glycerol,
(3) Steam distillation, and
(4) Dry heating in vacuo.

The use of hot or boiling liquids having a higher boiling point than the substance to be expelled, and treatment with substances which displace the sorbed substance from the sorbing surface have also been highly recommended (29).

Because of the low inter-solubility of chloropicrin and water (30) it was decided to try steam distillation. Also, since chloropicrin is very soluble in pentane, benzene and kerosene, it was planned to treat with these solvents and determine the recovery on the basis of solubility both at room temperature and the boiling point of the solvent, the chloropicrin to be recovered from the solvent by fractionally distilling the solution.

APPARATUS

For the steam distillation the set-up was as follows:

Approximately 25 gm. charcoal with 6 gm. chloropicrin sorbed on it, were placed in a round bottom three-necked flask with 500 cc. water and boiled. The steam-chloropicrin vapours passed up through a vertical air condenser and were condensed in a Liebig condenser leading downward to the receiver which was constructed as a gravity separator with a stop cock at the bottom for the removal of samples. The chloropicrin, having a density of 1.65, formed the lower layer in the separator and, as the lower portion of the separator was calibrated, the chloropicrin volume could be read off directly. The water, however, ran out through an overflow tube near the top of the separator and was led back to the original distillation flask and thus a steady flow of water circulated through the apparatus. Once the boiling was started the apparatus could be left untended until the chloropicrin ceased to come over. A Bunsen valve at the top of the separator prevented any pressure from building up in the system and all the corks were covered with tin-foil to prevent the chloropicrin from attacking them.

In the reflux apparatus, finally found the most efficient, the solvent was placed in a round bottom flask connected through a ground-glass joint to a wide tube above it. A bulb, blown in this tube, held the charcoal on which the chloropicrin was sorbed. This charcoal was suspended over a thin wire gauze held in place by small constrictions in the glass tube. The tube, in turn, was connected through another ground-glass joint to an ice-cooled coil condenser.

The condensed solvent drained through the charcoal back into the distilling flask but a head was formed in the bulb since the vapours passing up through the charcoal prevented all of the condensed liquid from running back. Thus the liquid solvent was kept in constant contact with the charcoal and the vapours of the solvent were continually bubbling through it. With this design, the suspended charcoal could, on cooling, be drained thoroughly. During a run, any chloropicrin removed by the solvent drained back with the solvent into the large flask and as its boiling point was 112°C. and that of pentane was 35°C., only pure pentane was in contact with the charcoal, except for the small amount of chloropicrin present due to its vapour pressure.

At first the charcoal was suspended in a straight tube without a bulb, but too large a head formed in this tube. A straight Liebig condenser was also used at first, but some of the pentane was lost by evaporation and the ice-cooled coil condenser, later introduced, eliminated this loss.

EXPERIMENT AND TECHNIQUE

Preparation of Samples To simulate the actual condition of the amount of chloropicrin sorbed on the charcoal in a service canister at breakdown, 4 cc. (about 6.3 gm.) of chloropicrin were added slowly to 25 gm. of charcoal (Canadian silver impregnated, SBT 95-96) with constant shaking. The flask containing the chloropicrin and charcoal was then allowed to stand for at least three days to ensure that equilibrium was obtained in the system. This was considered to be long enough as the rate of sorption of chloropicrin by charcoal is very rapid (31, 32).

Steam Distillation Two experiments were carried out:

(1) Tap water was used and the steam distillation continued until chloropicrin stopped coming over.

(2) The water from experiment 1 (i.e. saturated with chloropicrin) was used instead of tap water.

The details of the two experiments are given in Table XIX.

TABLE XIX

	1.	2.
Weight of charcoal	24.980 gm.	25.115 gm.
Weight of sorbed chloropicrin	6.370 gm.	6.250 gm.
Time for maximum recovery	140 min.	295 min.
Volume of chloropicrin recovered	1.61 cc.	1.92 cc.
Weight of chloropicrin recovered	2.66 gm.	3.18 gm.
% Efficiency	42.0 %	50.5 %
Refractive index product (wet)	1.4592	
Refractive index pure chloropicrin	1.4596	

The recovery of chloropicrin by steam distillation with time has been plotted in Figure 26.

Refractive Indices: (n) In order to have an accurate measure of the amount of chloropicrin removed by the solvent in the reflux or standing treatment, sample solutions containing up to 10% by weight of chloropicrin in benzene, kerosene and pentane were made up and their refractive indices determined at 25.0°C. The solvent was first weighed in stoppered weighing bottles. The chloropicrin was then added to it and the solution weighed again. The samples were kept in ice water to prevent any loss due to the evaporation of the solvent.

The Refractive index readings, given in Tables

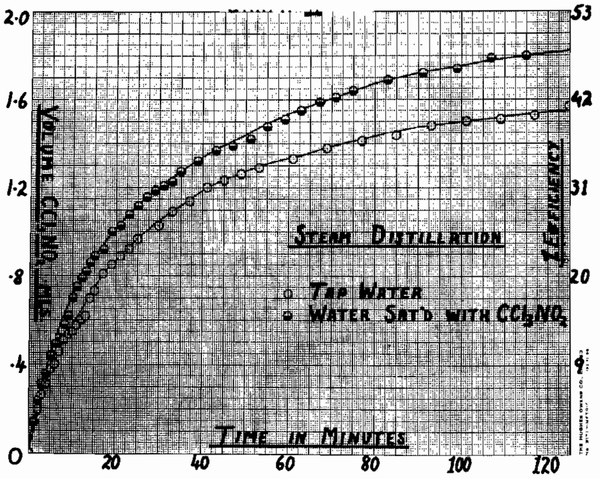
2·0
1·6
1·2
·8
·4
0
53
42
31
20
9
VOLUME CCl_3NO_2 MLS
% EFFICIENCY
STEAM DISTILLATION
○ TAP WATER
● WATER SAT'D WITH CCl_3NO_2
TIME IN MINUTES
20
40
60
80
100
120
THE HUGHES OWENS CO.

Figure 26.

XX, XXI and XXII, are mean values.

TABLE XX

Benzene - Chloropicrin

Wt. CCl_3NO_2	Wt. Benzene	% CCl_3NO_2 by wt.	n
0.000 gm.	4.60 gm.	0.00%	1.4969
0.033	4.40	0.75	1.4968
0.074	4.32	1.69	1.4968
0.082	4.46	1.85	1.4964
0.066	4.40	1.50	1.4964
0.115	4.44	2.60	1.4961
0.165	4.57	3.60	1.4961
0.198	4.55	4.35	1.4960
0.245	4.34	5.36	1.4960
0.247	4.62	5.35	1.4959
0.280	4.62	6.05	1.4954
0.330	4.85	6.80	1.4953
0.363	4.70	7.70	1.4952
0.403	4.39	8.40	1.4950
0.495	4.95	10.00	1.4947

TABLE XXI

Pentane A - Chloropicrin

Wt. CCl_3NO_2	Wt. Pentane A	% CCl_3NO_2 by wt.	n
0.000 gm.	3.09 gm.	0.00%	1.3548
0.044	3.106	1.40	1.3556

TABLE XXI (Cont'd)

Wt. CCl_3NO_2	Wt. Pentane A	% CCl_3NO_2 by wt.	n
0.067 gm.	3.079 gm.	2.11%	1.3558
0.159	4.094	3.75	1.3596
0.158	3.099	4.86	1.3571
0.188	3.086	5.75	1.3578
0.233	3.114	6.97	1.3582
0.259	3.085	7.75	1.3588
0.334	3.069	9.82	1.3595
0.362	3.093	10.47	1.3600

TABLE XXII

Pentane B - Chloropicrin

Wt. CCl_3NO_2	Wt. Pentane B	% CCl_3NO_2 by wt.	n
0.00 gm.	4.00 gm.	0.00%	1.3560
0.073	3.155	2.30	1.3572
0.184	3.138	5.85	1.3589
0.319	3.155	10.10	1.3609

The refractive indices of the three mixtures have been plotted against the weight percent of chloropicrin in Figure 27.

In some of the following experiments pentane B was used as well as pentane A. Pentane A was Commercial Pentane 30° - 40°C. of the Viking Petroleum Co. Pentane B

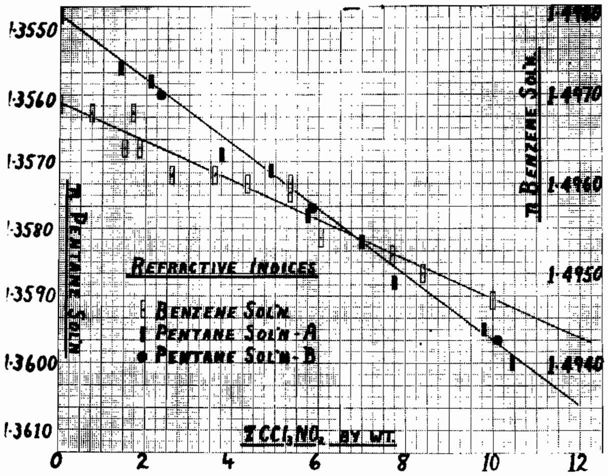
1·3550
1·3560
1·3570
1·3580
1·3590
1·3600
1·3610
n Pentane Sol'n
1·4980
1·4970
1·4960
1·4950
1·4940
n Benzene Sol'n
Refractive Indices
Benzene Sol'n
Pentane Sol'n - A
Pentane Sol'n - B
% CCl3NO2 by wt.
0
2
4
6
8
10
12

Figure 27.

was obtained by fractionating Ether Petroleum Pure 30° - 70°C. (Mallinckrodt) and removing the 30° - 40°C. portion. Figure 27 shows that if a correction was applied to the refractive index of pentane B (i.e. -0.0012) the latter followed the same slope as the pentane A.

TABLE XXIII

Kerosene - Chloropicrin

Wt. CCl_3NO_2	Wt. Kerosene	%CCl_3NO_2	n
0.000 gm.	4.000 gm.	0.00 %	1.4474
0.072	3.952	1.82	1.4476
0.144	3.972	3.65	1.4477
0.221	3.989	5.50	1.4479

It was seen immediately that the kerosene-chloropicrin refractive indices did not give any appreciable slope for considerable changes in the percent composition by weight of chloropicrin, since for pure kerosene n = 1.4474 and for pure chloropicrin n = 1.4596 and these are too close to show appreciable changes in n for small changes in the chloropicrin concentration.

Results with Benzene and Kerosene: 76.0 gm. benzene were used as the solvent in the reflux apparatus and the benzene refluxed for 6 hours.

Weight of charcoal	24.635 gm.
Weight of sorbed chloropicrin	6.360 gm.
Weight of benzene	76.0 gm.
Time of reflux	6 hrs.

% chloropicrin recovered	7.7	%
Wt. chloropicrin recovered	3.48	gm.
% efficiency	54	%

When it was attempted to separate the chloropicrin from the solution by gently boiling off the benzene (b.pt. 88°C.), the chloropicrin (b.pt. 112°C.) decomposed as the benzene boiled to give reddish fumes of NOCl(33, 34).

Since kerosene has a higher boiling point than chloropicrin, it was thought that it would displace the chloropicrin on the charcoal (29), but if the chloropicrin could not be recovered from the kerosene solution, the method would be of no avail. For this reason a 10% solution of chloropicrin in kerosene was distilled slowly to see if a separation could be effected, but the chloropicrin decomposed at the boiling point. Hence the use of both benzene and kerosene as solvents proved unsatisfactory as any chloropicrin, which they removed from the charcoal, could not be recovered from the solution by distillation.

Results with pentane

Reflux Method Several preliminary reflux experiments were run with pentane until the most suitable apparatus was finally developed and as these first results were not consistent due to evaporation losses, they were discarded. At the end of a run, before taking the refractive index, the solution was treated with some $CaCl_2$ to remove the moisture displaced from the surface of the charcoal. Results obtained with varying amounts of solvent are given in Table XXIV.

TABLE XXIV

	1.	2.	3.	4.
Wt. Charcoal	24.450 gm.	24.910 gm.	25.255 gm.	25.075 gm.
Wt. CCl_3NO_2	6.390 gm.	6.380 gm.	6.195 gm.	6.335 gm.
Wt. Pentane	30.0 gm.	74.0 gm.	155.5 gm.	223.5 gm.
Time refluxing	6 hr.	6 hr.	6 hr.	6 hr.
% CCl_3NO_2 in soln.	14.3 %	9.1 %	3.7 %	2.5 %
Wt. CCl_3NO_2 in soln.	4.33 gm.	4.40 gm.	5.00 gm.	5.50 gm.
% Efficiency	67 %	70 %	81.5 %	87 %

The efficiency of removal has been plotted against the weight of pentane in Figure 28.

A 280 gm. solution containing 6.6% by weight of chloropicrin was fractionated in a Whitmore column, the distillation flask being heated on a water bath, using a reflux ratio of 1:1. The temperature and refractive index were noted every 10 cc. in order to follow the course of the distillation. After 8 hours, 26.0 gm. of liquid with a refractive index of 1.4050 (n pure CCl_3NO_2 = 1.4596) were left in the flask. Although pure chloropicrin was not obtained, due to the pentane hold-up in the column at the end of the distillation, nevertheless it was evident from the results that chloropicrin could be separated from a pentane solution, without decomposition, by fractional distillation.

Standing Method: To determine the amounts of chloropicrin which could be recovered at room temperature using pentane, varying amounts of pentane were poured over samples of

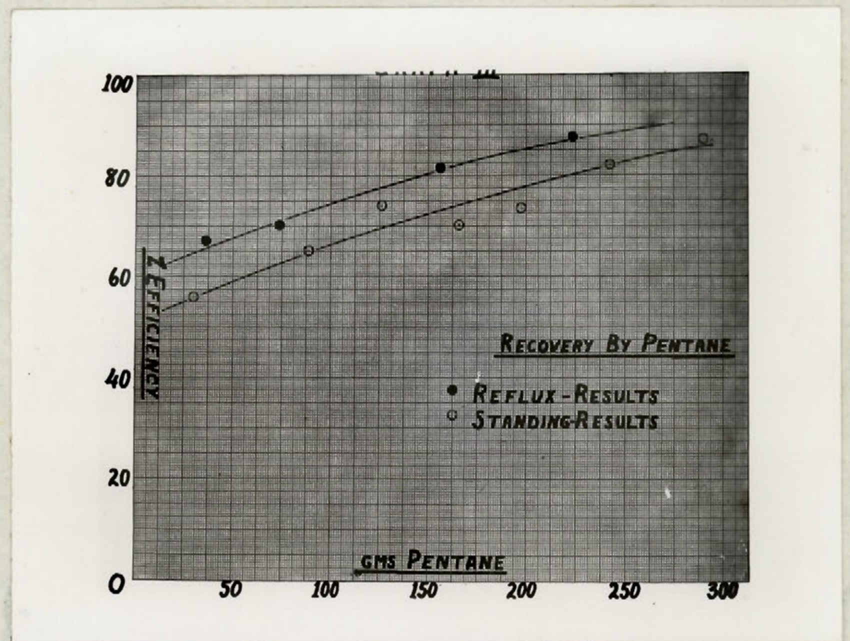
100
80
60
40
20
0
% Efficiency
50
100
150
200
250
300
GMS Pentane
Recovery By Pentane
● Reflux-Results
○ Standing-Results

Figure 28.

the charcoal and allowed to stand for several days. The flasks were kept tightly corked and with large volumes of pentane, the stoppers were sealed by painting with a solution of Gelva in benzene. In all cases tin foil was used to cover the corks. Results for the varying amounts of pentane are given in Table XXV.

TABLE XXV

Run No.	Weight of Charcoal	Weight of CCl_3NO_2	Weight of pentane	Time of standing	% CCl_3NO_2 recovered	Wt. CCl_3NO_2 recovered	% Efficiency
1	25.540gm.	6.120gm.	27.5gm.	2 days	12.5%	3.44gm.	56%
2	25.280	6.170	89.5	2	4.5	4.04	65
3	24.730	6.310	126.0	2	3.1	4.65	74
4	25.540	6.215	165.3	7	2.64	4.35	70
5	24.560	6.145	198.4	5	2.25	4.47	73
6	25.400	6.165	247.7	3	2.05	5.05	82
7	25.400	6.165	285.9	5	1.85	5.29	86

(a) Here the weight of pentane signifies the final weight of the solution after the samples for refractive index readings had been removed.

(b) In Run 3, the liquid which yielded the 74% efficiency was decanted, and 35 gm. of fresh pentane added. It was found that after 2 more days an additional 0.7 gm. of chloropicrin was removed.

(c) Run 7 was made up by adding an additional 38.2 gm. of pentane to Run 6, and the increased efficiency noted.

(d) A blank run with pure pentane was made to see if the sorption of pentane by charcoal would alter the refractive index of the solvent. Result showed that no correction was required.

The efficiency of removal has been plotted against the weight of pentane in Figure 28.

Drainage Method: Pentane was allowed to drain slowly through the charcoal from a separatory funnel so as to have fresh pentane constantly coming into contact with the charcoal. This was to remove the pentane, which had an equilibrium concentration of chloropicrin dissolved in it, and the fresh pentane, which followed, should remove more chloropicrin and hence yield a higher efficiency. However, the apparatus was cumbersome requiring a constant level device to maintain the height of liquid on the charcoal and a small condenser on a side arm to prevent pressures from building up in the apparatus. The results are given in Table XXVI.

TABLE XXVI

Weight of Charcoal	24.890	gm.
Weight of CCl_3NO_2	6.23	gm.
Weight of Pentane	45.5	gm.
% CCl_3NO_2 in solution	7.6	%
Wt. CCl_3NO_2 in solution	3.48	gm.
% Efficiency	55	%

This result was observed to be of the same order as results obtained with the standing method for the same given amount of solvent, but as the latter method is so much simpler it is preferable.

DISCUSSION

The removal of the chloropicrin by the two liquids may be explained by a consideration of the partial pressures of the gas existing in the different phases present. In the first place, it is reasonably safe to assume that at least a large part, if not all, of the chloropicrin is taken up on the charcoal by the mechanism of equilibrium adsorption, as outlined originally by Langmuir. Such a mechanism calls for the following condition:--If the charcoal is saturated with gas at some given partial pressure and then the partial pressure of the gas phase is reduced, some of the sorbed gas will distil off the charcoal and a new equilibrium will be set up in accordance with the Adsorption Isotherm.

With this in mind, consider the condition when some charcoal saturated with chloropicrin is allowed to stand in pentane. At the start, the chloropicrin will distil off the charcoal and will be dissolved in the pentane, gradually building up a partial pressure in the pentane. Finally a point will be reached at which as much chloropicrin is being re-sorbed by the charcoal as is distilling off the surface and an equilibrium condition is set up. If now, more fresh pentane is added, this will lower the chloropicrin partial pressure in the pentane and in consequence more will distil off to give a new equilibrium and the efficiency of the removal will be improved. This argument can be applied to the chloropicrin in the charcoal pores as well as that sorbed on the surface. Although the pentane cannot penetrate to the bottom of the pores, nevertheless the vapour space between the penetrating pentane surface and the bottom of the pore will contain a partial pressure of chloropicrin vapour, which will be dissolved by the pentane until the equilibrium is set up. As the temperature of the pentane removal is increased, the vapour pressure of the chloropicrin on the charcoal increases more rapidly than the partial pressure of the chloropicrin dissolved in the pentane and in consequence the chloropicrin removal is more efficient with increasing temperature.

In the case of the steam distillation, the chloropicrin is only slightly soluble in water and in the experiments carried out, the water was saturated with chloropicrin from the outset. This means that there can be no distillation of the chloropicrin from the charcoal to the liquid, as in the case of pentane. In other words, there is no chloropicrin removed from the pores of the charcoal, because the water above the pores is already saturated and as a result has a chloropicrin partial pressure, which is at least as great as that on the charcoal in the pores. However, the water comes in contact with the chloropicrin, which is loosely held on the surface of the charcoal grains, and a mixture of the two substances distils out due to the combined effects of their partial pressures, as is always the case in a two phase distillation.

It can be easily seen from the above that a much lower efficiency of removal is obtained for steam than for pentane. This is borne out by experiment.

The relative costs, in calories of heat, of the steam distillation and the standing pentane methods are given below. From the tables it can be seen that if the two methods had the same efficiency of removal, the pentane would still be preferable, as it only requires about a quarter as much heat to recover the chloropicrin. Therefore it can be definitely stated that the standing method using pentane is to be preferred both for its high efficiency of removal and low heat requirements for recovery. This work was done as a result of a request from the National Research Council. However, the large amount of solvent and equipment necessary for the pentane method would not permit an economical recovery of the chloropicrin from the comparatively small amount of charcoal being proofed at Ottawa.

<u>Relative cost of methods</u> --- in calories heat.

1. <u>Steam distillation</u>   Time for maximum efficiency: 3 hr.

Latent heat evap. water at 100°..........540 cal./gm.

Water boiled at rate of ....163 ml./hr.

Time required ....3 hours

Volume water boiled ....500 ml.

Total heat required for 6 gm. CCl_3NO_2 ...270,000 cal.

Heat required for 1 gm. CCl_3NO_2 ....45,000 cal.

2. Standing (Pentane) Time for maximum efficiency: 3 days

No heat required except for recovery of CCl_3NO_2 from pentane solution.

Recovery from solution Reflux ratio 3:1 Time: 8 hours

Heat required to vaporize pentane ....22,000 cal.

Total heat required ....88,000 cal.

Heat required for 1 gm. CCl_3NO_2 ....14,700 cal.

APPENDIX II

EXPERIMENTS ON
THE PREPARATION OF DISULFUR DECAFLUORIDE

The work reported here was done as the result of an urgent need for 60 gm. of disulfur decafluoride at the National Research Council in Ottawa. To meet the emergency, a group of six C.W. workers at McGill University (R. Mungen, A.P. Stuart, F.P. Lossing, L. Siminovitch, J. Davis and J.C. Arnell) were formed into three teams of two men each and the manufacture of the fluoride continued 24 hours a day over a period of several weeks.

INTRODUCTION

Disulfur decafluoride (S_2F_{10}) was first reported by Denbigh and Whytlaw-Gray, who isolated a small amount from sulfur hexafluoride (SF_6) by fractionation (35). In the Fall of 1940, during a general investigation of fluorides as toxic agents, R. Mungen and J.T. Hugill, working at McGill University, prepared sulfur hexafluoride by passing a stream of fluorine gas over powdered sulfur in a copper tube and condensing the products formed in a glass trap cooled with liquid air. The sulfur hexafluoride, thus made, had a molecular weight which was slightly higher than the theoretical and also showed toxic properties, whereas pure hexafluoride did not. A series of careful fractionations from a dry ice-acetone cooling mixture into liquid air yielded a small amount of a colourless liquid, boiling at 29°C., with a molecular weight of 254 (M.W. SF_6 = 146), which agreed with the molecular weight of the formula S_2F_{10}. This liquid was very toxic which led to further study of its properties as a possible Chemical Warfare agent. But as it only appeared as less than 1% of the total yield, its production on a large scale was not feasible. The investigation was carried on by the above-mentioned workers and later by W. Schneider at the National Research Council and F.P. Lossing and L. Simonovitch at McGill, and it was found that by mixing the sulfur with certain fluorides, such as sodium fluoride, potassium bifluoride, cryolite, etc. that the yield of disulfur decafluoride was increased in varying amounts. American Chemical Warfare workers found that diluting the fluorine with a nitrogen stream also improved the yield of the decafluoride.

In addition to the two above sulfur fluorides, several other low boiling fluorides (b.pt. about -40°C.) were formed at the same time. These were thought to be probably disulfur difluoride (S_2F_2), sulfur difluoride (SF_2) and sulfur tetrafluoride (SF_4), although only the last of these appeared in any quantity. These three fluorides were very reactive and were removed from the reaction products by bubbling slowly through a sodium hydroxide solution, where the following reactions were assumed to take place (36, 37):

$$2\ S_2F_2 + 6\ NaOH = 2\ NaF + Na_2SO_3 + 3\ S + 3\ H_2O$$

$$SF_4 + 6\ NaOH = 4\ NaF + Na_2SO_3 + 3\ H_2O$$

Once these lower fluorides had been removed, the sulfur hexafluoride and the decafluoride were separated by fractional distillation.

The work reported here describes the establishment of an analytical method for determining the sulfur balance by estimation of the lower fluorides, the sulfur hexafluoride and the disulfur decafluoride and the determination of the most suitable experimental conditions to give a high yield of the decafluoride.

APPARATUS AND TECHNIQUE

The fluorine was made in a Mathers-type electrolytic fluorine generator (58) made of copper, molten potassium acid fluoride being used as the electrolyte. As hydrogen fluoride was continually evolved from the molten electrolyte and consequently appearing as an impurity in the fluorine, a copper trap, packed in ice, and a series of glass traps, cooled with liquid air, were connected to the delivery tube of the generator to remove the hydrogen fluoride. The purified fluorine was then led into a glass mixing chamber where it could be mixed with nitrogen, if so desired. The nitrogen used was supplied in tanks by Canadian Liquid Air and it was dried by passing first through a tower of potassium hydroxide pellets and then bubbling through two scrubbers filled with concentrated sulfuric acid. The nitrogen flow was measured by a Venturi type flowmeter (cf. p. 16). The mixing chamber was connected to the reaction chamber, which consisted of a piece of copper tube about 3 ft. long and 3 cm. inside diameter with removable ends, which screwed on to give gas-tight seals. These ends had been turned out of solid copper and had 6 mm. delivery tubes connected through them. The end nearest the generator also had a thin-walled copper thermocouple tube running through it and extending the length of the reaction tube, so that the temperatures inside the tube could be measured along its length during the reaction. The delivery tube from the reaction tube led through a series of glass traps cooled in liquid air, where the products of the reaction were condensed. The last trap in the series was packed with small pieces of copper gauze to prevent any loss of the products when high flow rates of nitrogen were used.

The products were then purified in a separate apparatus, which has been shown diagrammatically in Figure 29. The products, which had been condensed in liquid air, were allowed to evaporate slowly by controlled warming and the resulting gases were passed slowly through a scrubbing train to remove the lower fluorides and were then recondensed in liquid air. The scrubbing train consisted of five 250 cc. Erlenmeyer flasks. The first two flasks (A and B) were filled with a sodium hydroxide solution, which reacted with the lower fluorides; flask C was filled with water to wash the purified SF_6 and S_2F_{10}; flask D was left empty to prevent the concentrated sulfuric acid in flask E (to dry the gases) from sucking back into the water in flask C and producing an error in the mass sulfur balance. The gas was then condensed in trap F, which was cooled in

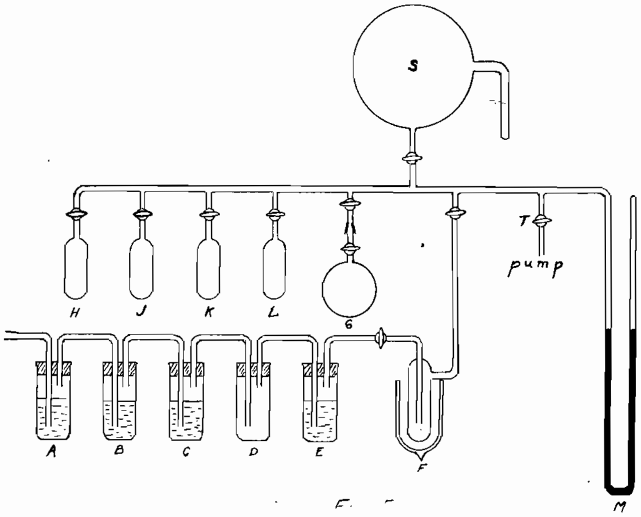

Figure 29.

liquid air, and, during the purification, open to the atmosphere. After all the products had been expanded through the scrubbing train, a slight suction was put on trap F and the trap containing the reaction products, which had been closed by a piece of rubber tubing and a pinch cock for the expansion, opened to the air. This allowed a small flow of air to sweep any gas remaining in the first trap or the scrubbing train into trap F, where it was condensed.

When all the gas had been purified, a stopcock between E and F was closed and the stopcock at T, which led to a Cenco Hyvac pump, opened and the trap F evacuated, as was the whole of the upper part of the apparatus. Liquid air in a Dewar flask was put around one of the four bulbs (H, J, K and L) and the liquid air was removed from F and the purified gas distilled up into the cooled bulb. The stopcock connecting trap F to the upper apparatus was closed when the distillation was complete. Sometimes, after this distillation, a certain amount of non-condensable gas appeared in the apparatus and had to be pumped off. This was generally considered to be some carbon fluoride, formed at the graphite anode of the generator. This must have been occluded in the condensed gas in trap F, as the carbon fluorides are not condensable at liquid air temperatures. The molecular weight of the purified gas was determined in the earlier experiments by expanding the gas first into the large storage bulb (S) and immediately into the density bulb (G). The pressure of the gas was read off the mercury manometer (M) and the volume of the expanded gas was known from a previous calibration. From these values and the weight of gas in the density bulb, the molecular weight was calculated and the relative amounts of the two constituents obtained. It was found, however, that the molecular weight was usually a little high due to the fact that during the expansion the sulfur hexafluoride, which sublimed at -64°C., distilled off first and filled the storage bulb and the decafluoride (b.pt. 29°C.) was left lying in the manifold. This resulted in more decafluoride entering the density bulb, when it was opened, than would have if the two constituents had been completely mixed. To eliminate this error, a side arm was blown on the storage bulb and the gas condensed in this side arm and the stopcock connecting the storage bulb to the remainder of the apparatus closed. The gas was then allowed to expand, and left for several hours in the storage bulb to ensure uniformity in the gas sample before it was allowed to expand into the density bulb for a molecular weight determination.

The small bulbs (H, J, K and L) were used for storing the fluorides and also for fractionating the mixtures of the hexa- and decafluorides. To fractionate the two, a dry ice-acetone mixture was put around the gas mixture and the hexafluoride sublimed out and was collected in a second bulb cooled in liquid air. This was repeated about three times, after which the hexafluoride was pure and was discarded, but the decafluoride still had traces of hexafluoride. These traces were only removed after repeated evaporations and re-condensations.

EXPERIMENTAL

The Mass Sulfur Balance

In order to determine the mass balance on the weight of sulfur that was fluorinated during a run, it was necessary to find an accurate method of analyzing the sodium hydroxide solution and water in the first three flasks (A, B, and C) of the scrubbing train. These three flasks contained sulfites and some sulfates (as the sulfites were partially oxidized by traces of fluorine left in the reaction product traps) which were the decomposition products of the lower fluorides. Under ordinary conditions, this analysis would have been very simple: The sulfites could have been oxidized to sulfates by hydrogen peroxide and the sulfates then precipitated as barium sulfate by the addition of barium chloride. However, when this method was tried on the solutions from the scrubbing train, which contained the sulfites and sulfates in a saturated solution of sodium fluoride, barium fluoride was precipitated along with the barium sulfate, which ruined the analysis.

The next method tried was the precipitation of the sulfates as benzidine hydrogen sulfate using the standard benzidine hydrochloride method (39). This method was also found to be unsatisfactory, giving too low values in the presence of fluoride ions.

Experiment indicated that the removal of the fluoride ions, as active agents, from the solution was necessary before accurate sulfur determinations could be obtained. Borkovskii and Porfir'ev (40) found that the addition of boric acid to a sulfate-fluoride solution resulted in the formation of the fluoborate ion ($BF_4^{=}$) and this coordinated fluorine did not form barium fluoride when barium chloride was added to precipitate the sulfate. This method was tried and found to be satisfactory, giving check results on a series of solutions containing known sulfate and fluoride concentrations. The final procedure, as used throughout this work, has been outlined below.

The sodium hydroxide and water solutions were transferred from the scrubbing train to a litre measuring flask. The resulting solution was diluted with distilled water to 1000 cc. From this solution a 50 cc. aliquot part was removed and the sodium hydroxide neutralized with hydrochloric acid using phenolphthalein as the indicator. One cc. of concentrated hydrochloric acid was then added in excess and followed by five cc. of 30% hydrogen peroxide and the solution diluted to 300 cc. After boiling for half an hour, four grams of boric acid were added and the sulfate precipitated by adding barium chloride (40 mg./litre) in slight excess. The solution was then filtered through a fine sintered glass Gooch crucible and the precipitate washed with 10 cc. of distilled water and then 10 cc. of acetone. The crucible was dried in an oven at 120°C. and weighed. The amount of sulfur was calculated on the basis of barium sulfate. This weight of sulfur multiplied by 100 and divided by the total weight of sulfur fluorinated during a run gave the percentage of sulfur present as lower fluorides. This percentage added to the percentages of sulfur as sulfur hexafluoride and disulfur decafluoride, calculated from the pressure, volume and molecular weight of the purified gas, should equal 100% to give the mass balance. In most of the experiments carried out all the sulfur could be accounted for within 5%, which was considered close enough for the present work.

The Preparation of Disulfur Decafluoride

This work was an investigation of the effect of diluting the fluorine with varying amounts of nitrogen on the percentage of disulfur decafluoride produced. Except for a few runs, the five grams of oven-dried sulfur were mixed with 75 grams of dried sodium fluoride and the mixture put in the reaction tube. The amount of sulfur fluorinated was determined either by weighing the filled reaction tube before and after a run, in the case of the uncooled experiments, or weighing the sodium fluoride-sulfur mixture before and after a run, in the case of the cooled experiments. The first method was to be preferred as it eliminated any chance of loss during transfer of the powder, but with the cooled experiments an ice bath was cemented around the reaction tube with Picene cement and this prevented the use of this method. The temperatures inside the reaction tube were measured at regular intervals during a run at four points along the tube. In this way the progress of the reaction could be followed by the linear displacement of the temperature peak along the tube. The passage of the fluorine was continued until the temperature had returned to its original value. Fluorine could usually be detected escaping through the product trap for at least half an hour before a run was stopped. The results of the experiments have been tabulated in Tables XXVII, XXVIII and XXIX. The results in Table XXVII were only qualitative as the previously mentioned error in the molecular weight determinations had not been eliminated and the lower fluoride analysis had not been satisfactorily worked out. A number of runs have been omitted due to spoiled results and faulty experiment. The runs in Table XXVIII were made with the reaction tube at room temperature and in Table XXIX with the reaction tube cooled by an ice bath.

TABLE XXVII

Run No.	Nitrogen cc./min.	Ratio NaF/S	Sulfur used	Time of run	Max. Temp.	%S as S_2F_{10}	%S as SF_6	%S as SF_4+S_2F_2	%Total Sulfur Analyzed
3	0	0/5	5 gm.	180 min.	--	0	63.8	15.5	79.3
4	0	0/5	5	240	--	0	69.6	14.5	84.1
5	0	0/5	5	165	--	0	73.1	14.2	87.3
7	100	0/5	5	180	68°C.	4.2	56.8	15.5	76.4
11	100	0/5	5	220	70	4.72	30.2	8.32	43.2
16	250	75/5	1.83	60	45	16.6	23.7	20.7	60.0
17	250	75/5	4.5	120	68	24.0	25.4	26.2	75.6
12	300	75/5	3.82	120	64	24.1	22.4	27.6	74.2
21	300	75/5	2.78	80	53	11.9	12.9	49.6	74.4
25	300	50/5	4.72	115	55	21.6	15.5	25.7	62.8
26	300	50/5	2.10	60	--	16.6	17.3	83.8	117.7
27	300	50/5	3.74	120	68	16.1	38.6	42.5	97.2

TABLE XXVIII

Run No.	Nitrogen cc./min.	Ratio NaF/S	Sulfur used	Time of run	Max. Temp.	%S as S_2F_{10}	%S as SF_6	%S as SF_4+S_2F_2	%Total Sulfur Analyzed
41	0	75/5	4.84gm.	190 min.	72°C.	5.0	58.2	29.3	92.5
40	100	75/5	4.94	190	60	12.6	35.8	44.3	92.7
39	200	75/5	4.72	175	81	12.3	28.0	50.7	91.0
38	300	75/5	4.69	140	64	15.2	23.7	61.1	100.0
30	300	75/5	4.51	180	68	21.5	30.0	45.8	97.3
28	300	50/5	4.65	155	62	18.2	34.2	51.6	94.0
29	300	40/5	4.27	---	60	27.7	34.8	55.0	117.5

TABLE XXVIII (Cont'd)

Run No.	Nitrogen cc./min.	Ratio NaF/S	Sulfur used	Time of run	Max. Temp.	%S as S_2F_{10}	%S as SF_6	%S as $SF_4+S_2F_2$	%Total Sulfur Analyzed
31	400	75/5	4.81gm.	170 min.	66	20.0	20.8	59.5	100.3
48	400	75/5	4.68	210	54	15.5	25.5	57.5	98.5
52	500	75/5	4.34	215	69	16.7	25.0	53.3	95.0

TABLE XXIX

Run No.	Nitrogen cc./min.	Ratio NaF/S	Sulfur used	Time of run	Max. Temp.	%S as S_2F_{10}	%S as SF_6	%S as $SF_4+S_2F_2$	%Total Sulfur Analyzed
42	0	75/5	5.0 gm.	120	40	3.5	33.2	25.3	62.0
43	100	75/5	5.0	230	20	15.7	18.3	61.8	95.8
44	200	75/5	4.9	165	16	9.6	13.4	70.0	93.1
54	200	75/5	4.81	160	46	20.3	24.9	50.4	95.6
56	200	75/5	5.0	160	16	19.9	35.1	49.5	104.4
45	300	75/5	4.95	150	20	17.5	11.1	63.1	91.7
50	300	75/5	4.97	210	18	24.1	18.2	55.3	97.6
49	400	75/5	4.83	190	18	17.2	16.0	67.3	100.5
55	400	75/5	4.99	225	12	18.7	18.1	64.7	101.5
51	500	75/5	4.90	160	36	14.5	15.1	67.8	97.4

The average values of Tables XXVIII and XXIX for different flow rates of nitrogen have been given in Tables XXX and XXXI.

TABLE XXX

Nitrogen cc./min.	Ratio NaF/S	% S as S_2F_{10}	% S as SF_6	% S as $SF_4+S_2F_2$	Total S Analyzed
0	75/5	5.0	58.2	29.2	92.5
100	75/5	12.6	35.8	44.3	92.7
200	75/5	12.3	28.0	50.7	91.0
300	75/5	18.4	26.9	53.5	98.8
400	75/5	17.8	23.2	58.5	99.4
500	75/5	16.7	25.0	53.3	95.0

TABLE XXXI

Nitrogen cc./min	Ratio NaF/S	% S as S_2F_{10}	% S as SF_6	% S as $SF_4+S_2F_2$	Total S Analyzed
0	75/5	3.5	33.2	25.3	62.0
100	75/5	15.7	18.3	61.8	95.8
200	75/5	16.6	24.5	56.6	97.7
300	75/5	20.8	14.6	59.2	94.0
400	75/5	18.0	17.0	66.0	101.0
500	75/5	14.5	15.1	67.8	97.4

The values in Tables XXX and XXXI have been plotted in Figure 30.

DISCUSSION

Disulfur decafluoride is a chemically inert substance at room temperature. It is not attacked by strong acids or bases and fluorine appears to have no effect on it even at temperatures approaching its thermal decomposition temperature. Laidler at the National Research

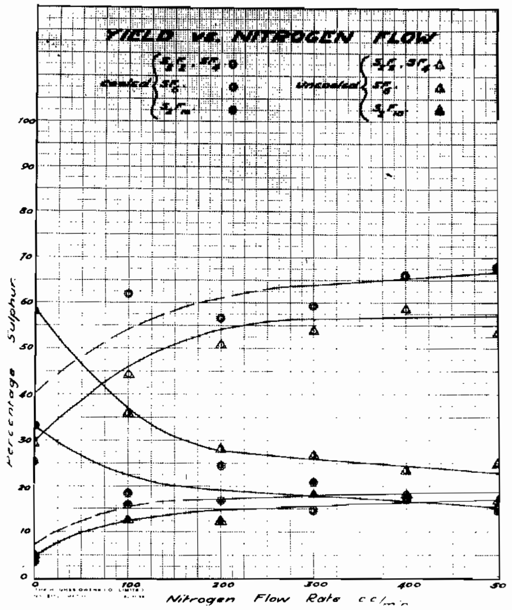
YIELD vs. NITROGEN FLOW
cooled
$S_2F_2 \cdot SF_4$ ⊕
SF_6 ◉
S_2F_{10} ●
uncooled
$S_2F_2 \cdot SF_4$ △
SF_6 ▲
S_2F_{10} ▲
Percentage Sulphur
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
50
Nitrogen Flow Rate cc/min

Figure 30.

Council in Ottawa has found that it decomposes at temperatures as low as 160°C. and Mungen found that it decomposes quite rapidly at 210°C. to give sulfur hexafluoride and free sulfur. This reaction may be:

$$3\ S_2F_{10} = 5\ SF_6 + S \qquad (1)$$

The reaction of fluorine on sulfur is thought to be a series of reactions, the first of which consists of the formation of a lower fluoride and this in turn is fluorinated to a higher fluoride and the fluorination continues until the end product, sulfur hexafluoride, is reached. The possible steps in the reaction are given below:

$$3\ S + 3\ F_2 = 3\ SF_2 \qquad (2)$$

$$3\ SF_2 + 3\ F_2 = 3\ SF_4 \qquad (3)$$

$$2\ SF_4 = S_2F_8 \qquad (4)$$

$$S_2F_8 + F_2 = S_2F_{10} \qquad (5)$$

$$SF_4 + F_2 = SF_6 \qquad (6)$$

and there is also the possibility that S_2F_{10} might be fluorinated to sulfur hexafluoride, giving

$$S_2F_{10} + F_2 = 2\ SF_6 \qquad (7)$$

If these six equations are summed, the apparent complete reaction is:

$$3\ S + 9\ F_2 = 3\ SF_6 \qquad (8)$$

Equation (8) represents the case of the complete reaction and has never been obtained in the McGill Laboratories. The nearest approach to it occured in the experiments

(Runs No. 3, 4, and 5, Table XXVII) where the fluorine was not diluted with nitrogen and no solid diluent was mixed with the sulfur. These experiments showed no trace of the decafluoride and only about 15% of the lower fluorides, the remainder of the yield being sulfur hexafluoride.

There is a second possible mechanism for the formation of the disulfur decafluoride. This is based on the fluorination of disulfur difluoride (S_2F_2). This would also be a stepwise reaction, the equations of which are given below:

$$S_2 + F_2 = S_2F_2 \qquad (9)$$

$$S_2F_2 + F_2 = S_2F_4 = 2\ SF_2 \qquad (10)$$

$$S_2F_4 + F_2 = S_2F_6 \qquad (11)$$

$$S_2F_6 + F_2 = S_2F_8 = 2\ SF_4 \qquad (12)$$

$$S_2F_8 + F_2 = S_2F_{10} \qquad (13)$$

$$S_2F_{10} + F_2 = S_2F_{12} = 2\ SF_6 \qquad (14)$$

The sum of these reactions gives:

$$S_2 + 6\ F_2 = 2\ SF_6 \qquad (15)$$

These two mechanisms are very similar. In the second mechanism, there are a few more steps and the lower fluorides are assumed to be double molecules. In equation (9) the sulfur has been taken as a double molecule. This is allowable because ordinary powdered sulfur at room temperature is made up mainly of S_8 molecules with lesser amounts of S_6, S_4, S_2 and S. There is, however, some doubt as to whether any disulfur difluoride was formed in the above experiments. As mentioned in the

Introduction, when two molecules of disulfur difluoride are destroyed by sodium hydroxide, three molecules of free sulfur are formed. As no evidence of free sulfur was observed in the sodium hydroxide scrubbers during purification, the absence of any difluoride was indicated.

Whichever of the two mechanisms is correct, it is obvious that the fluorination of sulfur takes place in a series of steps. On this basis, dilution of the fluorine by mixing it with a stream of nitrogen should increase the yield of the lower fluorides because with increasing nitrogen flow the lower fluorides will be swept out of the reaction tube more rapidly and condensed in the product traps, where at liquid air temperatures no fluorination appears to take place. At the same time the sulfur hexafluoride yield should be reduced, as a smaller amount of the lower fluoride is being fluorinated to this end compound. Experiment has confirmed this as a comparison with Table XXX shows. The experiments listed in Table XXX, however, seem to point to a maximum effective flow rate, above which the relative amounts of the three fluorides remain constant.

The temperature in the reaction tube should also have a marked effect because a lower temperature would decrease the rate of fluorination of the lower fluorides and at the same time cut down the amount of thermal decomposition of the decafluoride. This would result in a decrease in the amount of sulfur hexafluoride and an increase in the other fluorides at a lower temperature, with other experimental conditions left unchanged. Experiment has also confirmed this, the values given below being taken from Tables XXX and XXXI:

Nitrogen (cc./min.)	200		300	
Reaction tube temp.	25°C.	0°C.	25°C.	0°C.
% S as L.F.	50.7	56.6	53.5	59.2
% S as SF_6	28.0	24.5	26.7	14.6
% S as S_2F_{10}	12.3	16.1	18.4	20.8

Originally it was thought that mixing the sulfur with some powdered fluoride gave higher yields of disulfur decafluoride due to some catalytic effect of the salt, as some salts gave higher yields than others. However, very recently F.P. Lossing and his co-workers have found that mixing the sulfur with powdered copper gives as high yields as powdered sodium fluoride, which was the best of the salts tried. This cannot be due to catalysis as the reaction tube is also copper but points rather to the temperature effect mentioned above. The sulfur diluent conducts the heat of reaction away from the products of the fluorination before the decafluoride undergoes thermal decomposition. The different effects of the various salts can be explained by their different heat conductivities. Increased nitrogen flow rates give higher decafluoride yields due partly to the fact that decafluoride is swept away from the seat of the reaction before it can decompose and also to the fact that the heat of reaction is absorbed by the gas and conducted away. This is borne out by the increased disulfur decafluoride yields with increasing flow rates of nitrogen as given in Table XXVIII.

If, instead of collecting all the products together in liquid air cooled traps, the products could be collected separately by means of fractional condensation, the action of fluorine on the lower fluorides could be studied. A system of traps cooled with a dry ice-acetone mixture followed by liquid air cooled traps should separate the decafluoride from the other fluorides. The lower fluorides could then be recovered by distilling off the sulfur hexafluoride. Several experiments could then be carried out on the lower fluorides in an attempt to prove the above assumptions and to try and increase the decafluoride yield.

The lower fluorides could be:

(1) Recycled through the reaction tube while an ordinary run was being made. This might improve the decafluoride yield.

(2) Fluorinated and the products analyzed. This would test the validity of the above equations.

(3) Mixed with sulfur hexafluoride and stored under pressure in a bomb at different temperatures. This would show whether the following reaction were possible:

$$SF_4 + SF_6 = S_2F_{10} \qquad (16)$$

A more complete picture of the reactions taking place seems to be essential before the conditions that will give the highest decafluoride yields can be worked out.

SUMMARY

The points of interest that have been brought out by the experiments discussed in this thesis are summed up below.

(1) The service time-bed length plot was linear, when the bed length was greater than the length of the sorption gradient. But for shorter bed lengths, the line curved in towards the origin, showing longer service times than predicted by linear law. This was in complete agreement with the theory of Mecklenberg (2, 7), but disagreed with Hinshelwood (1), who predicted that the linear relation should hold down to a service time of zero, giving at that point the "critical length".

(2) The maximum weight of gas capable of being sorbed by a gram of charcoal from an air stream flowing through a charcoal bed varied with the partial pressure of the gas in the air stream in accordance with the Langmuir Adsorption Isotherm equation. This dynamic Isotherm appeared to have the same two constants as the Isotherm obtained for a static system. This agreed with Mecklenberg, who found that the Freundlich Adsorption Isotherm held for the dynamic sorption of chlorine.

(3) The extrapolated value of the service time-bed length line to a zero service time, the "critical length", varied linearly with the initial concentration of the gas in the air stream. This disagreed with Hinshelwood who predicted that the critical length would vary as the logarithm of the initial concentration.

(4) The "dead length", which is a measure of the residual activity of a charcoal bed at service time and related to the area above the sorption gradient in a differential sorption graph, was proportional to the logarithm of the initial concentration of the gas in the air stream. This was a confirmation of the theory worked out by Mecklenberg.

(5) The weight of gas sorbed by the charcoal at any length, l, from the front face of the bed increased with time in accordance with the formula:

$$x = Ke^{-k/t} \quad . \quad . \quad . \qquad \text{(xxiv)}$$

where x is the weight of gas sorbed at time t, K a constant related to the maximum weight of gas capable of being sorbed by the charcoal at a gas concentration, c_o, and k a second constant, which appeared to be directly proportional to the square root of the length, l.

(6) At the start of a run, the weight of gas sorbed by the charcoal near the front face of the bed appeared to increase with time in accordance with the exponential relation, found by Syrkin and Kondraschow (8) for a charcoal bed which was only partly sorbing the gas from an air stream:

$$x = W_s (1 - e^{-bt}) \quad . \quad . \qquad \text{(xxiii)}$$

where x is the weight of gas sorbed at time t, W_s the equilibrium weight and b a constant.

(7) The chloropicrin sorbed on activated charcoal could be recovered with increasing efficiency

by: (a) steam distillation - 50%; (b) treatment with commercial pentane at room temperature - 85%; and (c) refluxing with pentane at its boiling point, ca. 35°C. - 90%. Chloropicrin was decomposed and brown fumes evolved, when mixtures with benzene and kerosene were boiled.

(8) In the fluorination of sulfur, sulfur hexafluoride, disulfur decafluoride and several lower sulfur fluorides were formed. The lower fluorides were destroyed during the purification by bubbling the gas through a sodium hydroxide solution to form sodium sulfite and sodium fluoride. The amount of sulfur present as lower fluorides was determined accurately by oxidizing the sulfite to sulfate and fixing the fluoride ions by the addition of boric acid to form fluoborate ions and precipitating the sulfur as barium sulfate. This sulfur balance checked within 5% of the theoretical in most of the runs.

Diluting the fluorine with nitrogen increased the decafluoride and lower fluoride yields, while the hexafluoride yield was decreased. The same effect was obtained when the reaction tube was cooled with ice.

CLAIMS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

Two new valves for producing an alternating flow through two charcoal cells were developed. In the first design a glass bulb containing a small piece of iron alternated between two valve seats as a circuit through an electromagnet was made and broken. In the second design a brass stopcock was modified in such a manner that a gas - air mixture could be led in the bottom of the stopcock and alternately out the two side tubes as the barrel of the stopcock was rotated.

A sectionalized charcoal cell was designed. Each section was a centimeter deep and had threads on both ends, so that a cell of depths could be constructed by threading a number of sections together.

A graphical method for obtaining the sorption gradient in a charcoal bed by graphically differentiating the integral sorption curve was developed.

The contributions to the knowledge of charcoal sorption under dynamic conditions include.

(1) The relationship between the equilibrium sorption of sulfur dioxide and carbon tetrachloride and the initial concentration of the gas in the air stream.

(2) The discrepancy in the relation predicted by

Hinshelwood of the "critical length" and the initial concentration.

(3) The effect of the initial concentration of sulfur dioxide on the length of sorption gradient and the residual activity of a charcoal bed.

(4) The equation relating the weight of gas sorbed at any point in a charcoal bed to the time of gas passage.

A contribution to the knowledge of other Chemical Warfare studies includes the efficiency of removal of chloropicrin from charcoal by steam distillation and treatment with commercial pentane.

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