

STUDIES ON ACTIVE CARBON.

PART I.—EVALUATION OF ACTIVATED CHARCOAL

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I. INTRODUCTION

Activated charcoal serves two important purposes, namely (1) adsorption of gases and vapours and (2) decolorisation of solutions. As an efficient gas-adsorbent, it has found extensive applications in the recovery of gasoline from natural gas and also for the recovery of traces of solvent vapours, apart from its well known military application. As a decolorising agent it has been employed in the decolorisation of sugar solutions and of oils. The technical applications of activated charcoal are, therefore, very wide and extensive, and increasing quantities of this material are being produced. In recent years, improved methods of activation are practised, with the result that several highly active carbons have appeared on the market to meet the demands of industries requiring very efficient adsorbents. Successful methods of "revivifying" spent carbons have also been developed.

Since activated charcoal finds application as an adsorbent its value is judged mainly by its adsorptive power, or its so called "activity". It is well known that the adsorptive power of a sorbent depends not merely on the sorbent but also on other features of the system, such as the substance sought to be sorbed, the solvent medium, other materials co-existing in the system and various experimental conditions. In any industry, the "activity" of a sorbent is best judged by its sorptive efficiency in that particular application. Thus, when active charcoal is employed for solvent recovery, its activity is judged by its sorptive power for vapours; and when it is employed as a decoloriser its activity is estimated by the degree of decolorisation it effects in coloured solutions, such as those of molasses or of certain dyes. Further, when active carbon is employed in gas-masks, or for the abatement of stench, the value of the sorbent

is determined not only by its general sorptive capacity, but also by its "retentivity" and "service time".

Although several methods for measuring sorptive capacity are available, each concern using activated charcoal prefers to evaluate it under the very conditions in which it is to be used. As a result the value of an adsorbent charcoal is found to vary with the mode of application. Recent developments in the technique of carbon-activation have led to the production of carbons which are efficient both as gas-adsorbents and as decolorisers, but even such a general service carbon is likely to give varying results depending on the purpose which it has to serve. If therefore we could find some fundamental property of activated carbon, which could be correlated generally with its sorptive capacities towards various substances, then it would be possible to develop a standard method for the determination of "activity", which would be independent of the manner of application. Such a method of evaluation would be useful both to the consumer and to the producer of activated charcoal. Unfortunately, however, researches on the evaluation of adsorbent charcoals have not kept pace with the rapid developments in the production and application of activated charcoal, and the consequence is that the methods employed in industry for the measurement of activity of adsorbent carbons are not only empirical but also yield conflicting results.

Several methods are available for the evaluation of activated charcoals for industrial purposes. The testing of gas-adsorbent carbons may be done by the determination of (1) the "sorption isotherms" for a chosen gas or vapour, (2) the "saturation value", *i.e.*, the maximum amount of gas or vapour adsorbed at a given temperature and pressure, or (3) the so-called "service-time", by which is meant the time which elapses before a detectable trace of vapour appears in the effluent air, when an air-vapour mixture is passed over the adsorbent under a particular set of conditions (Chaney, Ray and St. John, *Ind. Eng. Chem.*, 1923, **15**, 1244). The evaluation of activated charcoal for decolorising purposes is based on the determination of the extent of decolorisation effected in standard caramellised sugar solutions or of solutions of various

dyes, such as Ponceau Red and Methylene Blue. The amount of iodine adsorbed from solution has also been regarded as a reliable estimate of the activity of adsorbent charcoal, and so the iodine-adsorption values have often been taken to represent its activity for gas-adsorption or for decolorising purposes. Further, more recently, the determination of the heat of wetting of the adsorbent in suitable liquids (such as benzene) has also been suggested as a convenient method for estimating the sorptive power of adsorbents.

Apart from the sorptive capacities of activated charcoal, it is necessary to know certain other characteristics in order to predict the usefulness of the charcoal for a given purpose. The most important of these, perhaps, is the "retentivity" value. Chaney and others (*loc. cit.*) and Allmand and his co-workers (Allmand and Manning, *J. Soc. Chem. Ind.*, 1928, **47**, 368 T; Allmand and Burrage, *ibid.*, 1928, **47**, 372 T; Burrage, *J. Phys. Chem.*, 1930, **34**, 2202) found independently that when pure air was passed over carbon, which had been previously saturated with a given vapour, the rate of removal of adsorbed vapour was at first very high and then decreased gradually to a negligibly low rate. They found that a definite amount of the vapour was retained firmly by the adsorbent. This amount represents the "retentivity" of the carbon. The retentivity values determined for a series of typical carbons bear no fixed relation to their corresponding saturation values. The values obtained by the above mentioned workers showed, however, some correspondence to certain other properties of the carbons such as, (1) their relative activities for removal of different kinds of toxic gases, (2) their relative efficiencies for recovery of vapours at low concentrations, and (3) their ability to adsorb substances from true solution. Chaney *et al* (*loc. cit.*) found that the retentivity values had a linear relationship with the corresponding iodine-adsorption values, and so they concluded that the iodine-adsorption values indicated truly the retentivity values of the corresponding specimens. A high retentivity value is not necessary for all adsorbent chars. Berl (*Trans. Farad. Soc.*, 1938, **34**, 1045) points out that although a high retentivity is necessary for gas-mask carbon, it is not required in carbons which are used for solvent

recovery. In the rayon, smokeless powder and artificial leather industries a low retentivity value is desirable in order to permit the recovery of the greatest amount of the sorbed material.

Another factor of great importance in gas-adsorbent charcoals is the "porosity" or "relative pore volume." Porosity is defined as the ratio of the total pore volume to the external volume of the adsorbent. If V_1 is the volume of the adsorbent and V_2 that of its pores, then the relative pore-volume is equal to V_2/V_1 . One can, therefore, derive the porosity of a specimen of charcoal by the determination of its relative densities with reference to two liquids one of which (*e.g.*, water, benzene, ether) can fill the pores of the carbon and the other (*e.g.*, mercury) cannot. According to Chaney (*loc. cit.*) the maximum efficiency of a specimen of carbon is exhibited at a definite critical density or porosity. The price of gas-adsorbent charcoal is based on the quantity of gas adsorbed per unit *volume* of the specimen.

Other criteria of carbon-activity have been proposed, notably by Lemon (*Physical Review*, 1919, (2), 14, 281) who measured the relative vacua produced in a closed system by the adsorption of air or nitrogen at liquid air temperatures. The pressure curves so obtained were related to the retentivity, or as Briggs (*Proc. Roy. Soc. Edin.*, 1922, 42, 26) defined it, to the "*prehensibility*" of the carbon. The technical difficulties of the method and the difficulty of expressing the results in simple terms have, however, restricted its adoption.

The values furnished by any of the several methods outlined above indicate the activity of the adsorbent. These methods can, therefore, be used to determine the progress of activation during the production of activated charcoal. It must be pointed out at this stage that when several specimens of carbon prepared by different methods are examined, the relative activities of the carbons vary greatly depending on the method of evaluation selected for the purpose.

The object of the present work is to investigate some of the convenient methods available for evaluation of activated charcoal with a view to ascertain if any single method would give a reliable

indication of the activity of the carbon under nearly all circumstances, *viz.*, (1) adsorption of vapours from air-vapour mixtures and (2) adsorption from solutions, *e.g.*, iodine and methylene blue from aqueous solutions. With this object in view, the following studies were carried out on six specimens of adsorbent charcoal: (a) the densities and porosities of the specimens; (b) the sorption of iodine from aqueous solution; (c) the sorption of methylene blue from aqueous solution (d) the sorption of benzene vapour from an air-vapour mixture (e) the heats of wetting of the specimens in benzene.

II. DENSITIES AND POROSITIES OF ACTIVATED CHARCOALS

Many investigators have attached considerable importance to the porosity of carbon for the explanation of its sorptive properties. The idea of a possible connection between porosity and sorption arose from the concept of capillary condensation of vapours in porous sorbents.

McGavack and Patrick (*J. Amer. Chem. Soc.*, 1920, **42**, 946) consider that in the adsorption of gases and vapours by porous adsorbents like charcoal and silica-gel, capillary condensation in the pores plays a predominant role and that adsorbents differ from one another only in their capacity to condense the vapours into liquids. According to them, the role of the adsorbent is simply that of a porous body, its chemical nature being a matter of indifference.

Polanyi (*Trans. Farad. Soc.*, 1932, **28**, 316) points out how in the narrow crevices or fissures of a porous adsorbent, there is an enhancement of the potential energy of the surface. When the pressure of the vapour in equilibrium with the surface approaches the value of the saturation pressure at that temperature capillary condensation takes place, below the critical temperature.

Lamb, Wilson and Chaney (*J. Ind. Eng. Chem.*, 1919, **11**, 420) studied the changes that follow in the apparent density and the porosity of a carbon during progressive gas-activation. They state: "Since the functioning of the charcoal depends primarily upon its surface-adsorptive power, the greater the ratio of its surface to its mass, that is the more highly developed and fine-grained its porosity,

the greater its value. Increase in porosity is naturally accompanied by a fall in apparent density, and starting with any given inactive charcoal, the increase in adsorptive capacity is approximately parallel to this decrease."

Chaney, Ray and St. John (*loc. cit.*) find that up to a definite critical density of the carbon there exists a relation between the activity of the charcoal and its porosity, as expressed by the equation.

$$\frac{\text{Real density}}{\text{Apparent density}} \times \frac{\text{Porosity}}{\text{Activity}} = \text{Constant}$$

Philip, Dunnill and Workman (*J. Chem. Soc.*, 1920, 117, 362) investigated the concomitant changes in adsorptive power and bulk density which occur in the progressive activation of wood-charcoal by heat-treatment alone. They found that the order of the activities of the charcoals thus prepared was very nearly the order of the bulk densities, and they therefore suggest that an intimate correlation exists between the two properties. The mechanism of activation as given by them is that "the heating of the charcoal results in the widening, by progressive oxidation, of the capillary channels with which the granules are riddled. In this way although the external volume of a granule is practically unaltered its bulk density is diminished, and the effective surface enormously increased".

Page (*J. Chem. Soc.*, 1927, 1476) similarly noted the simultaneous changes in the bulk density and the iodine-adsorption brought about by air-activation of charcoal at various temperatures. He obtained data to support the correlation between the bulk density and activity suggested by Philip, Dunnill and Workman (*loc. cit.*). He also agreed with the view of the above mentioned workers that with decrease of bulk density there is an increase in available surface with consequent increase in activity.

In the light of more recent investigations (King and Lawson, *Kolloid Z.*, 1934, 69, 21) our ideas of the mechanism of carbon-activation have undergone very considerable modifications, and the views generally accepted now, point more to changes in the chemical nature of the carbon-surface rather than to changes which are entirely physical. Nevertheless, porosity and bulk density are still considered

to determine the sorptive value of activated charcoal. Since it has been established experimentally that the increase in activity and porosity run parallel to each other in observations made on a series of charcoals prepared from the same raw material and by the same process, it follows that the bulk density can be taken as an index of activity for gauging the progress of activation. But, whether the correlation between activity and porosity can be carried further, is still an open question. It was, therefore, considered worthwhile to ascertain if there was any correlation between the porosities of commercial specimens obtained from widely different sources and their respective adsorptive capacities.

The Four "Densities" of Charcoal.—Besides the *true density* of the close-packed solid material of which carbon is composed, there are three other densities which apply to porous sorbents like charcoal (McBain, "*The Sorption of Gases and Vapours by Solids*", London, 1932, pp. 79-92; Krczil, "*Untersuchung und Bewertung technischer Adsorptionsstoffe*", Akademische Verlagsgesellschaft, Leipzig, 1931, pp. 71-111). These are the *bulk-density*, the *apparent density* and the *real density*. The bulk-density gives the weight per unit volume of the charcoal in bulk, including the spaces between the particles. Although the bulk-density alone is not of much importance in a general consideration of sorptive efficiencies, it is of practical significance where the size of the container is limited, as in gas-masks. The apparent density represents the weight per unit integral volume of the separate grains or particles of the substance. This is usually determined by displacement with mercury which penetrates all the interstices between the grains and the bigger pores but not the sub-microscopic pores or crevices of charcoal. The real density, or specific gravity, as it is otherwise known is determined by the displacement of a wetting liquid, such as water, benzene etc., which fill all the interstices as well as pores, except the very minutest. The difference between the apparent density and the real density is, therefore, due to the difference in the penetrating powers of the liquids employed for their determination. While in the case of the apparent density the unit of volume includes pores and interstices

impermeable to mercury, in the case of the specific gravity, on the other hand, it includes only pores of ultra-microscopic, molecular or atomic dimensions, such as are inaccessible to the liquids used for the determination of the specific gravity. The true density of carbon is that of a close-packed space-lattice, such as graphite or diamond. This was established by Howard and Hulett (*J. Phys. Chem.*, 1924, **28**, 1082) who actually determined the true densities of several specimens of charcoal using gaseous helium at room-temperature as the displaced fluid.

Ordinarily, only pores of microscopic size which are inaccessible to mercury but are accessible to wetting liquids are of any significance in the technical use of activated charcoal. Pores of finer magnitude, which are covered by the term "ultraporosity", are of very limited technical value.

Porosity, or relative pore-volume, is defined as the ratio of the total pore-volume, to the total external volume of the particles. If s is the apparent density of the carbon and d the real density, its porosity P is given by the equation

$$P = \frac{\frac{1}{s} - \frac{1}{d}}{\frac{1}{s}} = \frac{d-s}{d}$$

The above equation is employed for obtaining the porosity of an adsorbent by substituting the values for the apparent and real densities of the specimen under consideration.

The specimens selected for investigation were all in the fine powder form, passing through 150 mesh. Their nature and ash-contents are given in Table I.

Experimental

1. *Bulk-density*.—5 to 10 g. of the specimen, previously dried in an air-oven at 110°C was introduced into a graduated cylinder of known weight. The cylinder was provided with a rubber-stopper carrying a tap. It was slowly evacuated by hand-operation of a Cenco-Hyvac pump in the early stages to prevent loss of fine particles.

TABLE I

Specimen	Nature	Ash %
Blood charcoal	Merck's medicinal product ...	1.86
Carboraffin ...	Vegetable carbon produced by activation with zinc chloride ...	2.89
Norit ...	Vegetable carbon, probably gas-activated.	3.99
Darco ...	Product of carbonisation of lignite and activation with calcium phosphate ...	37.50
Animal charcoal	Bone charcoal (activated) ...	82.10

The pressure was slowly reduced and finally maintained at 0.5 mm. of mercury for nearly two hours, after which the tap was closed and the cylinder was disconnected from the pump. The cylinder was then gently tapped until no further diminution of the bulk-volume of the substance could be observed. The volume of the charcoal was then read off and the cylinder and its contents weighed again to find the weight of the carbon in it. The bulk density of the specimen was then calculated in the usual way. The values thus obtained for the various specimens examined are given in Table II.

2. *Apparent density (s).*—For the determination of the apparent and real densities of the charcoals, the method given by Herbst (*Chem. Zeitg.*, 1926, **50**, 49) was employed with but slight modifications. The method has the advantage of permitting both the determinations to be made with the same apparatus.

The density-apparatus, shown in Fig. 1, consisted of a round-bottomed flask, F, of about 15 cc. capacity, with two necks, one carrying a mercury-reservoir, M, and the other provided with a ground joint, G, and tap, T₂, communicating with a vacuum system. The weight of the apparatus, that is, the flask, F, etc., up to the

rubber connection, R, was about fifty grams. The determination of the apparent density is described below :

Tap- T_1 is kept closed and enough mercury poured into the reservoir M. Keeping the tap- T_2 open, the vessel is now evacuated for a few minutes by means of a Cenco-Hyvac pump, after which the tap- T_2 is closed and T_1 opened to admit mercury from the reservoir

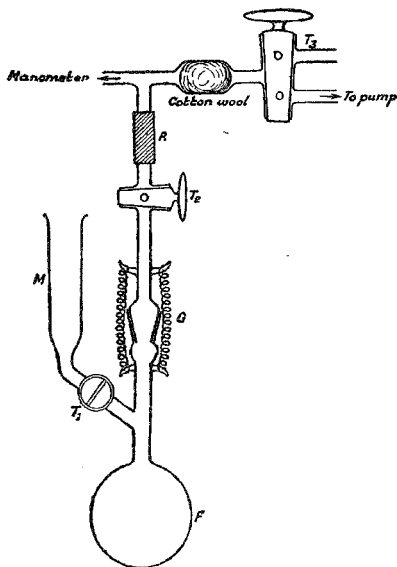


FIG. 1

M up to the tap- T_2 . Tap- T_2 is now momentarily opened and immediately closed with a view to fill the bore of the tap with mercury. The apparatus is then placed in a water-thermostat for some time, after which tap- T_1 is closed. The excess of mercury contained in the reservoir M, is removed completely and the apparatus is again weighed. Let this weight be called g_1 .

The flask is then emptied and about 0.5 g. of the dried

specimen of carbon weighed into it and the apparatus fitted up as before. With taps T_1 closed and T_2 open, the flask is slowly evacuated by means of a Cenco-Hyvac pump operated by the hand in the early stages. The final pressure is maintained at about 0.001 mm. of mercury for two hours, after which the tap- T_2 is closed and mercury run into the flask F. Caution is necessary at this stage to prevent the carbon from floating on the mercury-surface, when the latter rises into the two necks of the flask. A small amount of air collects just below the tap- T_2 which is kept closed during admission of mercury. These air bubbles can be expelled by cautious operation of tap- T_2 so that the mercury just fills the bore of the tap. The apparatus is then disconnected from the pump and kept in the thermostat as before after which the tap- T_1 is closed and the mercury in the reservoir M is removed. The apparatus with its contents is now weighed. Let this weight be g_2 . This includes the weight of the apparatus with the carbon and mercury filling the space not occupied by the charcoal. The larger pores of the carbon (which are not useful from the point of view of adsorption) are also filled with mercury. If a denotes the weight of the carbon, then $g_1 - (g_2 - a)$ would give the weight of mercury corresponding to the external volume of the carbon-particles. If ρ denotes the density of mercury at the temperature of the thermostat (20.5°C in our experiments), this volume is equal to

$$\frac{g_1 - (g_2 - a)}{\rho}$$

Hence, the apparent density, s , of the charcoal is given by the relation

$$s = \frac{a \rho}{g_1 - (g_2 - a)} \text{ grams per c.c.}$$

The values of apparent density of the six specimens investigated are given in Table II.

3. *Real Density, or Specific Gravity (\bar{d}) in benzene.*—The determination of the specific gravity of the charcoals in benzene was done in the same apparatus (Fig. 1) and following the same procedure as described above for the measurement of the apparent density in mercury. When benzene was added to charcoal there was a slight

rise of temperature, and care was taken to ensure that the temperature of benzene attained that of the thermostat before weighings were made. The results obtained are given in Table II.

4. *Porosity or Relative Pore-volume (P)*.—From the apparent density, s , and the real density, d , the relative pore-volume or porosity, P , is derived by means of the formula

$$P = \frac{d-s}{d}$$

The porosity-values of the various specimens are also given in Table II.

TABLE II

Specimen	Bulk density g./c.c.	Apparent density g./c.c.	Real density g./c.c.	Porosity
Blood charcoal ...	0.415	0.387	1.915	0.798
Carboraffin ...	0.347	0.327	1.631	0.800
Norit ...	0.315	0.364	1.801	0.798
Darco ...	0.503	0.503	1.768	0.716
Philburgin ...	0.070	0.286	0.927	0.692
Animal charcoal ...	0.913	0.920	2.425	0.607

III. ADSORPTION OF IODINE

For the determination of the activities of solid adsorbents iodine seems to have been more commonly employed than any other substance. Chaney, Ray and St. John (*loc. cit.*) considered that the amount of iodine adsorbed is truly representative of the "activity" of charcoal. King and his co-workers (King and Lawson, *Trans. Farad. Soc.*, 1934, **30**, 1094; King, *J. Chem. Soc.*, **1936**, 1688; *ibid.*, **1937**, 1489; Chambers and King, *ibid.*, **1938**, 688;

Bennister and King, *ibid.*, 1938, 991) concluded from their investigations on "chemisorption" by charcoal that the amount of iodine adsorbed from aqueous solution was a reliable index of the "specific surface". Page (*loc. cit.*) made a detailed study of the isotherms for the sorption of iodine by charcoals during various stages of air-activation. He found that the constants of the Freundlich-equation for these isotherms changed with progressive oxidation of the carbon.

Iodine-adsorption values for carbons are usually determined in aqueous solution, although a few experiments have been conducted on the sorption of iodine from non-aqueous solvents, such as benzene and chloroform (Firth, *Trans. Farad. Soc.*, 1920, 16, 434).

The amounts of iodine adsorbed by six commercial specimens of activated charcoal, *viz.*, Merck's blood charcoal, Carboraffin, Norit, Darco, Philburgin and animal charcoal, have been determined by us as described below. The ash-contents, densities and porosities of the samples are as shown in Table I and II.

Experimental

About 0.1g. of the specimen, dried in an air-oven at 100°C was accurately weighed into a glass-stoppered bottle of 30 c.c. capacity. 25 c.c. of decinormal iodine solution (aqueous iodine and potassium iodide) were introduced into the bottle which was then securely stoppered and shaken on a horizontal shaking machine for two hours to attain equilibrium. The solution in the bottle was then transferred to a tube and centrifuged at 500 r.p.m. for five minutes. Two c.c. of the clear solution were withdrawn by means of a graduated pipette and titrated against standard thiosulphate solution. The amount of carbon taken was so adjusted as to leave the equilibrium concentration of iodine at about 60% of the initial concentration. From the fall in strength of the iodine solution the amount of iodine adsorbed per gram of charcoal was calculated. The mean results of several experiments with each carbon are given in Table III, in milligrams of iodine adsorbed by one gram of the specimen under consideration.

TABLE III

Specimen of charcoal.	Milligrams of iodine adsorbed per g. of specimen.
Blood charcoal ...	1560
Carboraffin ...	889
Norit ...	716
Darco	401
Philburgin	93
Animal charcoal ...	78

IV. ADSORPTION OF METHYLENE BLUE BY ACTIVATED CHARCOAL

Adsorption of zinc-free methylene blue chloride from aqueous solution has often been employed to estimate the activity of decolorising charcoals, the reason for this being that it is one of the most strongly adsorbed colours.

Paneth and Radu (*Ber*, 1924, **57**, 1221) studied the adsorption of methylene blue and some other dyes on diamond and concluded that the thickness of the adsorbed layer was monomolecular. They extended this hypothesis to all forms of carbons and employed the saturation value of the sorption of methylene blue to calculate the effective surface area of the adsorbent. They also suggested that the sorption of one milligram of methylene blue corresponded to a surface area of one square metre.

In a critical discussion of various methods of evaluating activated carbon, Berl and Herbert (*Z. angew. Chem.*, 1930, **43**, 904) have suggested a method for measuring the sorption of methylene blue. Sixty c.c. of 0.15% aqueous methylene blue solution are shaken with 0.1 g. of the charcoal-specimen for two hours. Thereafter the solution is filtered through a fritted-glass filter, the first few c.c. of the filtrate discarded and the concentration of the remaining solution determined colorimetrically. To avoid errors due to variation of end-concentration, they suggested that the sorption value should be

determined at a standard end-concentration of 1 g. per litre. Since it was very tedious to maintain this condition directly in practice, Berl and Herbert fixed experimentally for a large number of activated charcoals the corrections to be applied in order to derive from the sorption values at the experimental end-concentrations the corresponding values at an end-concentration of 1 g. per litre. These corrections differ from carbon to carbon owing to differences in the shape of their respective sorption isothermals, and the number of carbons examined in this way by Berl and Herbert, large as it was, was by no means exhaustive.

Experimental

The method given by Berl and Herbert (*loc. cit.*) was re-examined by us with a view to simplify the procedure. It was soon noticed that at end-concentrations of 1 g. per litre and above, the adsorption-values corresponded to the saturation-values for the respective specimens. This fact was indicated by the shape of the isothermal, which was almost parallel to the concentration-axis at those concentrations. As the end-concentration was always maintained higher than 1 g. per litre, the corrections employed by Berl and Herbert (*loc. cit.*) were avoided in this work. After a few preliminary trials it was possible to take such a weight of charcoal as would leave after adsorption an end-concentration of 1 g. per litre. The details of the experimental procedure employed in the present work are as follows:—

The purest Kahlbaum's methylene blue chloride was repeatedly recrystallised from alcohol, and dried. An aqueous solution containing 1.5 g. per litre was prepared with this purified material.

Since soft glass was found to adsorb appreciable amounts of methylene blue, the solution was handled only in glass vessels of either Jena or Pyrex variety.

The specimen of charcoal to be examined was dried in an air-oven at 110°C and 0.05 to 0.15 g. of the dried material was accurately weighed into a stoppered-bottle of 100 c.c. capacity and 50 to 75 c.c. of 0.15% methylene blue solution were added

The weight of carbon taken in proportion to the volume of methylene blue solution was such as to leave an end-concentration of approximately 0.1%, that is, not less than 60% of the initial concentration of the solution. The mixture was then shaken mechanically for three hours and then centrifuged for five minutes at 2000 r.p.m. Two c.c. of the supernatant centrifugate were pipetted out and diluted to 100 c.c. Two c.c. of the original 0.15% solution also were similarly diluted to 100 c.c. The two solutions, thus obtained, were compared in a Kober-colorimeter, provided with a Klett top-reader. The fall in concentration of the dye in the centrifugate and hence the amount of methylene blue adsorbed by 1 g. of the charcoal was calculated from the readings of the instrument. The results obtained are given below in Table IV.

TABLE IV

Specimen	Milligrams Methylene blue adsorbed per g. carbon
Blood-charcoal ...	586
Carboraffin	334
Norit ...	167
Darco ...	103
Philburgin ...	34
Animal charcoal ...	32

V. ADSORPTION OF BENZENE VAPOUR BY ACTIVATED CHARCOAL

One of the well-known methods for the evaluation of gas-adsorbent carbon is by the determination of the sorption of some selected gas or vapour under a given set of conditions. Thus the activity of a carbon employed for the recovery of gasolene and of some solvents is judged by the amount of vapour, such as benzene, ether,

carbon tetrachloride etc., adsorbed by the particular specimen. This method of estimation is helpful only when the experiments are carried out under strictly controlled conditions as, for example, the maintenance of the partial pressure of the vapour to be sorbed at a constant value. This condition is important because the sorptive capacities of charcoals for vapours have been found to depend upon the partial pressure of the vapour.

The variations in the sorption of vapours by charcoals at high and at low vapour-pressures have been brought out clearly by Chaney and his co-workers, (*J. Ind. Eng. Chem.*, 1919, **11**, 420; *Ind. Eng. Chem.*, 1923, **15**, 1244), by Briggs, (*Proc. Roy. Soc. Edin.*, 1922, **42**, 26) and by Allmand and Manning (*J. Soc. Chem. Ind.*, 1928, **47**, 368T). They have shown that for a complete and satisfactory evaluation of the relative vapour-sorbing properties of a set of charcoals a full knowledge of the respective sorption isotherms is necessary. The value of a solid adsorbent, such as charcoal, for removing small amounts of a given vapour from a stream of air containing the vapour is primarily determined by the nature of its sorption isotherm. Berl, (*Trans. Farad. Soc.*, 1938, **34**, 1050) therefore, considers that the best valuation of gas-adsorbing carbons is made by the determination of the adsorption isotherms for a given temperature.

Both static and dynamic techniques are available for the determination of sorption isotherms. The former method has found use only in purely academic studies; for technical purposes, however, dynamic methods are employed (Lamb, Wilson and Chaney, *loc. cit.*; Allmand and Manning, *loc. cit.*; Fieldner, Oberfell, Teague and Lawrence, *J. Ind. Eng. Chem.*, 1919, **11**, 519; Berl and Andress, *Z. angew. Chem.*, 1921, **34**, 377). In the dynamic methods for the study of the sorption of vapours, the vapour to be sorbed is drawn in a current of indifferent gas (or air) over the charcoal until equilibrium is established. The amount of vapour sorbed is usually ascertained by direct weighing. To make sure that true equilibrium conditions are obtained the vapour-mixture is passed over the adsorbent either until the amount of vapour adsorbed has

reached a constant value or until the issuing gas has the same composition as that which is led into the adsorption vessel. Allmand, Manning and Burrage (*Allmand and Manning, loc. cit.*; Allmand and Burrage, *J. Soc. Chem. Ind.*, 1928, **47**, 372T; Burrage, *J. Phys. Chem.*, 1930, **34**, 2202) have introduced a novel reversal of the usual dynamic technique of determining sorption isothermals. Briefly, their method consists in saturating a known weight of the charcoal with the vapour concerned at a definite temperature and pressure, and re-weighing to determine the extent of adsorption. Dry air is then passed through the charcoal at a known rate, and the process is interrupted at intervals in order to find the weight of the charcoal container. The weights of "retained" vapour so found (q) are plotted against the total volume of air passed (v). Tangents to this *retentivity curve* are drawn for different q -values. The value of any such tangent, $-\left(\frac{\delta q}{\delta v}\right)$ represents the rate of loss of sorbed vapour at the corresponding q -value and is proportional to the equilibrium pressure of the vapour. If the values of the tangents $-\left(\frac{\delta q}{\delta v}\right)$ be plotted against their corresponding q -values, a curve closely resembling the usual sorption isothermal is obtained. If the initial slope of the retentivity curve be compared with the original vapour-pressure at which the charcoal was saturated with vapour, the actual isothermal relation between equilibrium pressure and the quantity sorbed is obtained. This method, although useful as a rapid and reliable comparative test for charcoal at relatively low pressures, often gave misleading results at intermediate pressures (Burrage, *loc. cit.*). Consequently, it is difficult to obtain accurate sorption isotherms over a wide pressure range by this indirect technique.

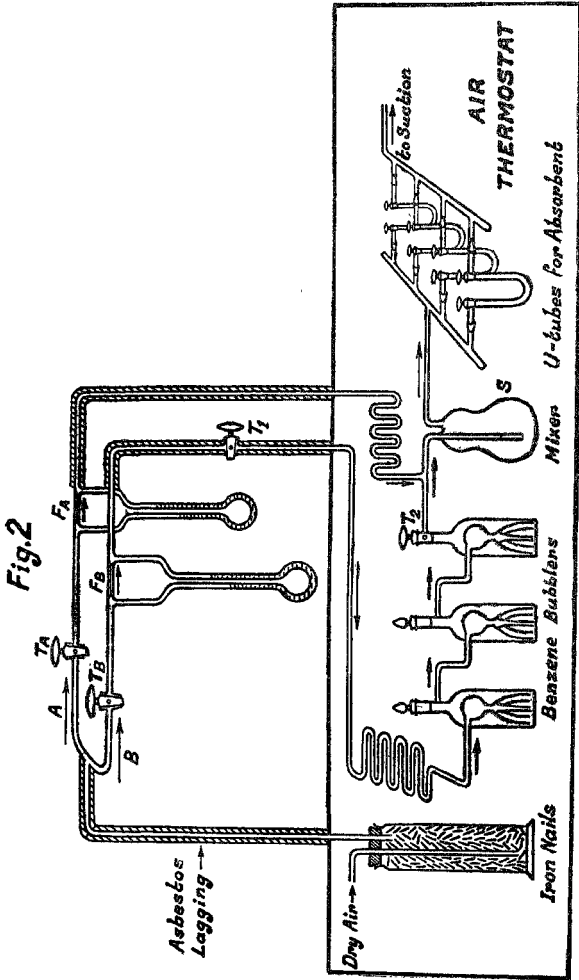
We, therefore, preferred to employ a *direct* dynamic technique for the determination of sorption isothermals for the six specimens of activated charcoal selected for investigation. The method practised by the Carbo-Norit Union (Kausch, "*Die Aktive Kohle*" Wilhelm Knapp, Halle, 1932, p.15) proved to be suitable for studying the

adsorption of benzene vapour at partial pressures ranging from $\frac{1}{10}$ to full saturation value.

Experimental

The adsorption of benzene vapour by active carbon was measured by a simple dynamic technique in which air containing known amounts of benzene vapour was drawn over the adsorbent and the amounts of benzene vapour adsorbed were ascertained by the direct weighing. The temperature was kept constant during the experiment. A diagrammatic sketch of the apparatus employed is shown in Fig. 2. The entire apparatus, with the exception of the flow-meters which had to be kept outside for convenience, was placed in an electrically operated air-thermostat maintained at $29.60^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$. A current of air, dried by anhydrous calcium chloride and then by pumice stones soaked in strong sulphuric acid was drawn through a tower packed with iron nails in order to ensure that it attained the temperature of the thermostat. The air-current was then led along two paths, A and B, at rates of flow which could be adjusted by the taps, T_a and T_b , as indicated by the flow-meters, F_a and F_b , respectively. The air by path B was then bubbled through purified and dried benzene, contained in three efficient bubblers. The air by path A entered directly the mixing bulb, S, where it mixed with air saturated with benzene vapour coming along the path B. It is easily seen that the concentration of the benzene vapour in the final gas-mixture leaving the bulb S will depend upon the rates at which air is fed along the two paths. The composition of the mixture could, therefore, be varied by manipulating the taps T_a and T_b and could be calculated from the readings of the flow-meters. The air-vapour mixture next passed over the specimens of charcoal kept in stoppered U-tubes, which were held in position by means of ground-glass joints. Suction was effected by an ordinary aspirator arrangement. Apiezon-B oil was employed as the manometric fluid, and the tap- T_1 was shut off when the apparatus was not in use, in order to prevent absorption of benzene vapour by the oil. The experimental procedure was briefly as follows:—

Suitable amounts of carbon (previously dried in the oven at



110°C.) were accurately weighed in the U-tubes, the amounts taken being just sufficient to permit the gas to pass freely. The U-tubes were then attached to the ground joints in the apparatus, and the adsorbent was subjected to further drying by passing over it a slow stream of dry air at the temperature of the thermostat, the taps T_b , T_1 and T_2 being kept closed. Tap- T_2 , when shut off, ensured that the air in the bulb S was free from benzene vapour likely to come from benzene in the bubblers. When the weights of the U-tubes became constant, taps T_b , T_1 and T_2 were opened and a mixture of dry air and benzene vapour was passed over the adsorbent at the rate of 12 to 15 litres per hour until all the tubes had attained constant weight, that is, until equilibrium was established. This took between four and six hours. As mentioned earlier, the relative pressure of benzene vapour in the air-vapour mixture could be adjusted to any desired value and could be ascertained from the readings of the flow-meters F_A and F_B .

Starting with a relative pressure of $\frac{1}{5}$, the sorption experiments were continued further with the same lots of the carbons at progressively higher relative pressures of benzene vapour, namely $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$ and finally at full saturation vapour-pressure at the temperature of the thermostat. The method presented no difficulty in manipulation and was found to be capable of giving values which could be reproduced to within 0.5 per cent.

Trouton and Pool (*Proc. Roy. Soc., A*, 1906, **77**, 292) have shown that, in the study of the sorption-isothermals of vapours, it is preferable to express the concentration of the vapour in terms of the relative partial pressure $\frac{p}{p_s}$, where p is the actual partial pressure of the vapour and p_s the saturation vapour pressure at the temperature concerned. This suggestion has been adopted by us and the percentages by weight (x) of benzene vapour, adsorbed by the charcoals investigated at various relative pressures and at a temperature of $29.60^\circ\text{C} \pm 0.05^\circ$, are given in Table V, and also shown graphically in Fig. 3.

TABLE V

p P _s	Grams of benzene vapour adsorbed by 100 g. of carbon					
	Blood charcoal	Carboraffin	Norit	Darco	Philburgin	Animal charcoal
1/10	40.8	29.3	11.6	7.5	—	—
1/4	51.0	44.4	18.7	11.1	6.54	2.25
1/3	53.9	49.8	21.9	12.5	7.62	2.96
1/2	56.8	57.8	26.5	15.4	9.55	3.50
2/3	58.9	68.6	31.7	19.9	16.7	4.74
3/4	59.3	73.0	33.2	23.5	23.5	5.57
1	90	101	68	62	90	12

It should be pointed out here that at saturation pressure ($p/p_s = 1$) the values tended to increase and a few droplets of liquid collected in the adsorption tubes.

Isothermals for the sorption of benzene vapour by outgassed activated sugar charcoal have been studied by static methods by Coolidge (*J. Amer. Chem. Soc.*, 1924, **46**, 610) and McBain, Jackman, Bakr and Smith (*J. Phys. Chem.*, 1930, **34**, 1444). The former employed a volumetric method for the measurement of sorption and obtained adsorption isotherms which exhibited the following typical features: (1) applicability of the Freundlich equation ($x = kp^{1/n}$) at low pressures, (2) asymptotic rise in sorption in the neighbourhood of the saturation vapour pressure, and (3) tendency to attain a state of saturation at intermediate pressures, the amount adsorbed being lower than what corresponds to the Freundlich formula.

McBain and his co-workers measured the sorption with the well-known sorption-balance. Their isotherms for acetone, toluene,

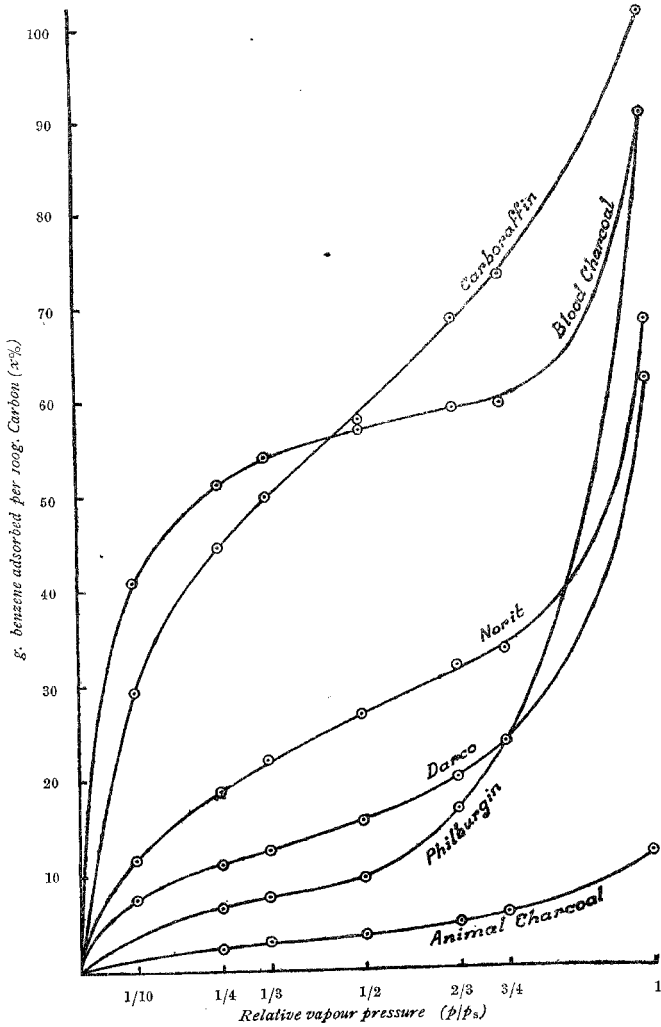


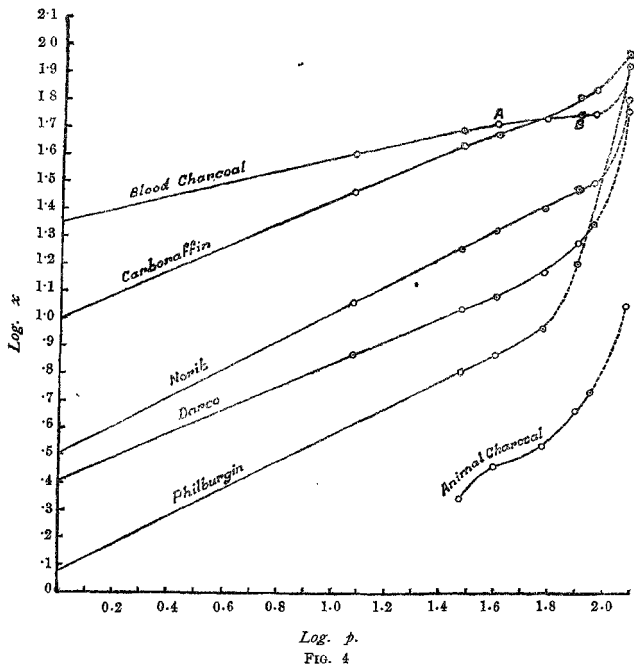
FIG. 3

octane, benzene etc., differed from those obtained by Coolidge. They found that adsorption was almost complete at infinitesimal relative pressures, the amount adsorbed, thereafter, increasing only to a minor extent with increase of pressure. This "rectangular" type of isotherms, obtained for many gases and vapours by McBain and his collaborators, does not fit in with the Freundlich equation. Even at relative pressures as low as one-tenth, the amount adsorbed reaches a saturation value, becoming independent of the pressure. The results obtained by these workers do not show a tendency to give an undue rise in sorption at the saturation pressure as found by Coolidge and other workers. McBain considers his isotherms as representing correctly the sorption of *pure* gases and vapours and he explains this as being due to a complete elimination of foreign gases in the system prior to sorption-measurements.

The isotherms obtained by us are shown in Fig. 3. It is seen that they conform to the type described by Coolidge. The applicability of the Freundlich equation at lower pressures is shown in Fig. 4, where $\log p$ has been plotted against $\log x$. The values of the partial pressures (p mm.) of benzene in the vapour-phase were calculated from the saturation vapour-pressure of benzene at the temperature of the experiment, *viz.*, 118.0 mm. at 29.6°C (Landolt-Bornstein, *Physikalisch-Chemische Tabellen*, II, 1370). A noteworthy feature of all the isotherms is that the curve rises very steeply at pressures approaching the saturation pressure of benzene at the temperature of the experiment. It is, therefore, clear that measurements in this region are subject to serious errors. It is interesting to note that the "double-log isotherm" for blood charcoal (Fig. 4) exhibits an inflexion at the point A. In the region of pressures between the points A and B the values found for adsorption are lower than those calculated from the Freundlich-equation.

The amounts of benzene vapour adsorbed by the various specimens were compared with those adsorbed by Darco under the same conditions, and the values so obtained are shown in Table VI. It is seen from the table that the relative adsorptive capacities of the

specimens change with the partial pressure at which the determinations are made. For example, blood charcoal is more active than Carboraffin at relative pressures less than $1/2$, while at higher pressures the reverse is true. This point is also seen from the isothermals in Fig. 3, where the curves for blood charcoal and Carboraffin intersect each other at p/p_s value of roughly $1/2$.



In a critical discussion of various sorption hypotheses Coolidge (*J. Amer. Chem. Soc.*, 1926, **48**, 1795) has given an interpretation of the observed form of isotherms for the sorption of vapours on charcoal. The "capillary condensation" theory was examined and was found inadequate to account for the observed facts, except with the aid of

TABLE VI

P/P _s	Relative adsorptive capacities (Darco=1)				
	Blood charcoal	Carboraffin	Norit	Philburgin	Animal charcoal
1/10	5.44	3.90	1.54
1/4	4.60	4.00	1.69	0.59	0.21
1/3	4.33	3.98	1.75	0.61	0.24
1/2	3.70	3.77	1.76	0.62	0.23
2/3	2.96	3.45	1.59	0.84	0.24
3/4	2.53	3.11	1.41	1.00	0.24

ad hoc assumptions. Coolidge formulated his views on the general mechanism of the adsorption of vapour on the basis of the theory of adsorption potentials, which was developed by Polanyi (*Verh. deut. Physik. Ges.*, 1916, **18**, 55). All the adsorbed molecules come directly under the "attractive force" of the adsorbent. The adsorption space is considered as the seat of a field of force exerted by the adsorbent and the "potential" at any point is the work done in moving a sorbate molecule from 'infinity' to the point. This potential is influenced neither by the temperature nor by the proximity of other adsorbed molecules. The force exerted upon each molecule in the adsorption space is specific as to the chemical nature of the molecule, but otherwise it depends only upon its position relative to the adsorbent. The van der Waals' forces, or forces of cohesion, are unaffected by the sorption so that the ordinary equation of state will apply even within the sorbed layer. At very low pressures, the sorbate molecule comes solely under the influence of the "potential forces" of the adsorbent and the relation of concentration to adsorption is linear. As the pressure is increased, the cohesive

forces become more and more predominant until at some stage the vapour passes to the liquid state. Consequently, after the linear portion of the isotherm in the highly dilute range, there follows a sudden transition to the ordinary curved form tending to saturation.

In porous bodies there is, in effect, an enhancement of the potential energy due to the fissures in the surface. Coolidge considers that the vapour sorbed in porous sorbents, such as charcoal, is always present in the liquid state, except at very low pressures. Working on these principles, Coolidge has been able to account for the validity of the Freundlich equation over a wide range of pressures. Taking into account the complete heterogeneity of the surface, pores and cavities of all sizes and shapes being present, he could also explain why, near the saturation pressure, the isotherm becomes discontinuous and takes a slope which is smaller and usually more finite than that given by the Freundlich formula. These discontinuities refer to the inflexion marked A in the double-log isotherm for blood-charcoal in Fig. 4. At still higher pressures, *i.e.*, beyond the point B on the same isotherm, capillary condensation sets in, due to Thomson-effect, and the isothermal curve asymptotically approaches the vapour-pressure line of the liquid.

In the range of concentrations employed in the present study of the adsorption of benzene vapour by charcoal, cohesive forces must play by far the most predominant part. The observed adsorption isotherm being, as it were, an average of the isotherms for the individual pores and cavities in the sorbent body, the sizes, the shapes and the relative distribution of the pores and fissures are perhaps the most important factors in determining the courses of the various isotherms. At low pressures of the order of a millimetre, the effect of cohesive forces is small, the purely adsorptive forces of the solid being predominant. Even in this range the operation of the capillary forces cannot entirely be ignored. The relative importance of the potential and cohesive forces acting on the vapour depends not only on the relative pressure but also on the "fine structure" of the adsorbent. Both the potential and the cohesive forces are important in the sorption of vapours on charcoal, and so for a proper evaluation

of the vapour-sorbing capacity of a specimen of active carbon it is essential to determine its sorption isotherm at some suitable temperature.

VII. THE HEAT OF WETTING OF ACTIVATED CHARCOAL IN BENZENE

The heat of wetting of a solid by a liquid is generally defined as the number of calories evolved when the liquid comes in contact with one gram of the solid. The heat thus liberated represents the decrease of total surface energy when the liquid covers the solid surface.

Berl and Andress (*Z. angew. Chem.* 1922, **35**, 722) reported that the ether-isotherms for the various charcoals were almost quantitatively related to their respective heats of wetting in benzene, and they therefore considered the heat of wetting to be a function of both the "saturation capacity" and the "intensity factor" of an adsorbent. Herbst (*Kolloid Z.*, 1926, **22**, 320) found that the heats of wetting of some specimens of charcoal in benzene and in water were proportional to the adsorbing capacities of the specimens. Honig (*Kolloidchem. Beih.*, 1926, **22**, 345) also noticed a close relationship between the heat of wetting and the adsorbing power of charcoal, and observed that with progressive steam-activation, the specimen showed a steady increase in the heat of wetting. Burstin and Winkler (*Brennstoff Chem.*, 1929, **10**, 121) concluded from their investigations that the heat of wetting in benzene was directly proportional to the maximum adsorption of benzene vapour at saturation vapour-pressure. Berl and Burkhardt (*Z. angew. Chem.*, 1930, **43**, 330) found that the heat of wetting of a charcoal was proportional to its capacity to adsorb methylene blue from aqueous solution. Bartell and Fu (*Colloid Symposium Annual*, 1930, **7**, 135) found that the heat of wetting was directly proportional to the surface area of an adsorbent. Macy (*J. Phys. Chem.*, 1931, **35**, 1397) stated that the heat of wetting is at once the most rapid and one of the best criteria for estimating the quality of a charcoal for gas-adsorption. Further, he found that the heat was proportional not so much to the total

adsorptive capacity as it was to the retentivity. Bell and Philip (*J. Chem. Soc.*, 1934, 1164) found that charcoals activated for different periods showed a steady rise in their heats of wetting with progress of activation. They also confirmed Macy's view that the heat of wetting was more a measure of the retentivity than of the saturation capacity for vapour. It was, therefore, considered desirable to determine the heats of wetting of the carbons which had been studied in other respects also with a view to establish any possible correlation of the heat of wetting with the sorptive capacities of the carbons.

Experimental

The method employed in the present work followed closely that described by Bartell and Fu (*loc. cit.*) The wetting liquid chosen was benzene, and this was purified from "A. R." grade by repeated fractional crystallisation.

The determination consists in breaking a sealed bulb containing the specimen of charcoal under pure benzene in a Dewar vessel and reading the temperature-rise on a Beckmann thermometer. The water-equivalent of the calorimeter was previously ascertained by an electrical method. The heat liberated from one gram of the specimen was then calculated and what may be called the "*absolute value*" of the heat of wetting of that specimen was thus determined.

Taking the mean absolute value for one of the specimens as standard, a "*relative value*" for the heat of wetting of another specimen was obtained by successive determinations of the rise in temperature of the two specimens when they were brought into contact with the same lot of benzene. The terms, "absolute" and "relative", are used here only to distinguish between the two methods of deriving the values. It was possible to determine both the "absolute" and "relative" values in one and the same experiment.

Preparation of Specimens.—About 1 g. of the powdered specimen previously dried in an air-oven at 110° for 24 hours, was accurately weighed in a thin walled glass bulb provided with a re-entrant bottom, as shown in Fig. 5, to facilitate easy breaking. The capacity of the

bulb was 3 to 5 cc. and the length of the stem was initially about three inches. A suitable length (6 to 8 inches) of glass tubing, with a fine constriction about one inch from one end of the tube, was fused on to the stem of the bulb, with the constriction near to the bulb. A plug of cotton was inserted at the open end of the tube. The bulb was immersed in a bath of boiling water, and slowly evacuated by means of a mercury diffusion pump (Leybold) to 10^{-4} mm. for four hours, a U-tube containing phosphoric anhydride being interposed between the specimen tube and the pump. Thereafter, the bulb was sealed in vacuo by melting down the glass at the constriction. The tube was taken out of the hot water bath, wiped, and allowed to attain room-temperature. The tubes, thus prepared, were inserted in batches of three through three holes in the cork-lid of the calorimeter and suspended at a suitable height. A slotted piece of thick-walled rubber tubing about a centimetre in length, was used as a clip to hold the tube in position.

The Calorimeter.—The calorimeter (Fig. 5) consisted of a cylindrical, silvered Dewar-vessel D, with an internal diameter of 70 mm. and a depth of 180 mm. The vessel was closed by means of a cork-lid through which passed (1) a stirrer S, (2) a Beckmann thermometer T, graduated in hundredths of a degree, (3) a heating element H of platinum spiral with a resistance of 1 ohm, and (4) a set of tubes B containing the dried and evacuated specimens. The calorimeter was lagged with felt and placed in a larger Dewar-vessel which was also insulated with felt. The temperature of the benzene in the calorimeter did not change by even 0.005° in 15 minutes, when the difference in temperature between it and the atmosphere was 1° . Since in our experiments the temperature-rise due to wetting reached the maximum value within two minutes, errors due to radiation were negligible.

The stirrer was of a robust anchor type with pointed ends (as shown in the figure) which served to break the bulbs containing the specimens, when required. The stirrer was driven by a motor and a rate of about 200 r.p.m. was always maintained.

The heating-element consisted of a spiral of fine platinum wire (about 40 S. W. G.), the two ends of which were fused into two glass-

tubes and connected to external leads through about a centimeter depth of mercury in each of these tubes. The current required for heating was drawn from a six-volt accumulator. A milliammeter, a rheostat and a knife-switch were connected in series with the heater, and a millivoltmeter was connected across the terminals of the heater.

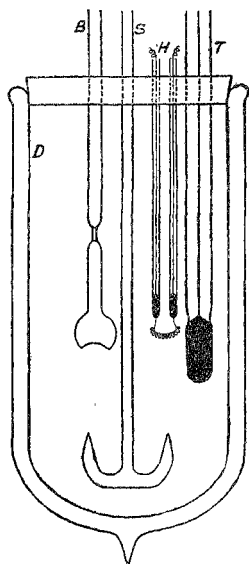


FIG. 5

The experimental details involved in the determination of the "absolute" values may be divided into two parts, *viz.*, (1) determination of the heat-capacity or the water-equivalent of the calorimeter and its contents, and (2) measurement of the temperature-rise due to the wetting of the specimen with benzene.

(1) *Heat-capacity of the Calorimeter and contents.*—About 400 g. of purified benzene were placed in the Dewar-vessel and the apparatus was assembled as described above with the three

specimen-tubes containing weighed amounts of the same specimen of carbon. When required the benzene could be heated by the spiral to attain atmospheric temperature, and then allowed to stand for some time to ensure that the temperature remained constant to within 0.005° C. When this condition was satisfied, the heater current was switched on. The stirrer-speed was regulated to about 200 r.p.m. It was noticed that at lower speeds of stirring there were serious temperature-lags due to ineffective stirring, while at too high a speed the frictional heat became considerable. The heating current was adjusted to a uniform temperature-rise of about 0.04° C per minute.

The rise in temperature during the first two or three minutes was neglected. Thereafter, readings of the temperature, current and voltage were noted down at intervals of exactly sixty seconds for about five or six minutes. The temperature-rise between successive sixty-second intervals in the steady period were concordant to within 0.002° . The heat capacity of the entire calorimeter-system was derived by means of the following equation :—

$$\text{Heat Capacity (W)} = \frac{E \cdot C \cdot t}{4.2 \times T} \text{ Calories,}$$

where E=the potential in volts across the ends of the heating-element,

C=the current in amperes,

t =the number of seconds,

and T=the temperature-rise in degrees Centigrade.

(2) *Heat of Wetting*.—The rise in temperature due to wetting was next determined as follows :

After making sure that the temperature of the benzene in the calorimeter remained constant to within 0.005° C for a period of ten minutes, the reading of the thermometer was noted. The stirrer was stopped and so aligned that one of its pointed ends was directly below one of the three bulbs containing the carbon. The bulb was then broken by knocking its re-entrant bottom gently on the stirrer-end. At once, benzene rushed into the evacuated tube and flushed out the carbon. The tube was then lifted up to its original position and clipp-

ed as before with the slotted rubber tube. The stirrer was started again within about fifteen seconds after breaking the bulb. Temperature readings were taken at intervals of thirty seconds. In all cases, the maximum temperature was reached within two minutes. Thereafter, the temperature of the calorimeter was constant for five minutes and then commenced to fall very slowly. The thermometer-reading during the steady period was noted as the maximum and the rise in temperature due to wetting was obtained.

The second and the third bulbs were then broken in turn on the stirrer and the temperature-rise in each case was determined in precisely the same way as with the first one. Before breaking each bulb the important precaution was taken that the temperature of the calorimeter remained constant to within 0.005°C for at least ten minutes.

From the experimental data the heat of wetting "absolute" was calculated according to the formula :

$$H = \frac{W \times \Delta t}{w} \text{ calories,}$$

where W = the heat-capacity of the calorimeter,

Δt = the rise in temperature produced by wetting,

and w = the weight in grams of the charcoal in the bulb.

The absolute values of the heats of wetting of four specimens of active charcoal *viz.*, Merck's blood charcoal, Carboraffin, Norit and Darco, were determined by this method. At least six determinations were made on each carbon and the mean values obtained are given in Table VI. Philburgin and animal charcoal were not included in these determinations, since they did not give any significant rise in temperature when wetted with benzene under the experimental conditions stated above.

"Relative" Heats of Wetting.—The mean "absolute" heat of wetting obtained from the above mentioned experiments with blood charcoal, *viz.*, 43 calories per gram, was adopted as the arbitrary standard for the determination of the relative values of the other three carbons. In these experiments the determination of the heat capacity of the calorimeter was not necessary. One of the specimen bulbs

contained a known weight of blood charcoal, while the other two bulbs contained weighed amounts of another specimen whose relative heat of wetting was to be determined. After making sure that the temperature remained constant for ten minutes, the bulbs were broken one after another and the temperature-rise in each case was measured in exactly the same way as in the determination of the absolute values.

If H denotes the heat of wetting of Merck's blood charcoal taken as the arbitrary standard, Δt the temperature-rise produced when w grams of blood-charcoal were wetted with benzene, and Δt_1 , the temperature-rise given by w_1 grams of the test specimen in the same experiment, then H_1 the "relative" heat of wetting of the latter is given by

$$H_1 = \frac{H.w. \Delta t_1}{w_1. \Delta t} \text{ calories per gram.}$$

By including in the above experiment the direct determination of heat-capacity of the calorimeter, both the "absolute" and the "relative" values could be obtained in the same set up. At least six such experiments were made on each carbon and the mean values obtained are given in Table VII.

TABLE VII

Specimen	Heat of Wetting Calories/gram		
	"absolute"	"relative"	Mean
Merck's blood-charcoal ...	43.0	43.0	43.0
Carboraffin ...	30.1	29.6	29.9
Norit ...	23.4	23.9	23.7
Darco ...	18.0	17.9	18.0

VIII DISCUSSION

The results of our investigations of commercial specimens of adsorbent charcoal are grouped together for convenience in Table

VIII. For a qualitative comparison with the sorption of substances in solution and with the heats of wetting and porosities, the values for the sorption of benzene vapour, given in this table, are those corresponding to a low pressure of the vapour, *viz.*, $p/p_s = 1/4$. The reason for this choice is that at higher partial pressures errors due to capillary condensation of the vapour lead to anomalous variations in the sorptive capacities of the specimens, such as the reversal of the order of the activities of blood charcoal and Carboraffin at $p/p_s = 1/2$.

TABLE VIII

Specimen	Porosity	Sorptive capacities			Heat of wetting cal./g.
		Iodine mg./g.	Methy- lene blue mg./g.	Benzene ($p/p_s = \frac{1}{4}$) mg./g.	
Blood charcoal ...	0.798	1560	586	510	43.0
Carboraffin ...	0.800	889	334	444	29.9
Norit ...	0.798	716	167	187	23.7
Darco ...	0.716	401	103	111	18.0
Philburgin ...	0.692	93	34	65	—
Animal charcoal ...	0.607	78	32	23	—

It is seen from the above table that although the porosities of the various specimens are nearly the same, their adsorptive capacities and heats of wetting vary widely. For instance, blood charcoal, Carboraffin and Norit have almost identical porosity-values, but they differ very much in activity. Porosity is, therefore, of little help in evaluating sorptive power.

The function of activated charcoal is not merely that of a porous body. Different specimens of charcoal vary not only in their porous structure and total area of the surface, but also in "*specific*

activity" per unit area. Recent studies on the activation of carbon by various methods show that the chemical nature of the surface and hence its specific activity or affinity undergoes marked changes in the process of activation. At the same time, the carbon develops a highly porous structure also, with consequent increase of surface area, due to the continuous oxidation and "volatilisation" (as oxides of carbon) of the surface layers. The two changes, one in the chemical nature and the other in the physical structure and area of the carbon-surface, take place simultaneously but independently of each other during the process of activation. So, it would not be correct to speak of a correlation between the two when it is only a matter of concomitance. Nevertheless, the determination of porosity, or of bulk-density, has been found in practice to be useful in judging the progress of activation in manufacturing processes. Further, a knowledge of the bulk-densities of gas-mask carbons is necessary, because their activities are expressed per unit volume. It is, therefore, essential in the case of gas-adsorbent charcoals to have the maximum bulk-density compatible with activity.

The data given in table VIII show also that there is qualitative agreement among the relative orders of the sorptive capacities of the various specimens for iodine and methylene blue in aqueous solution, the sorption of benzene-vapour at low partial pressures and the heats of wetting in benzene.

For a quantitative comparison of the various methods of evaluating adsorbent charcoal, the amounts of iodine and methylene blue adsorbed from aqueous solution, the adsorption of benzene-vapour at various partial pressures and heats of wetting of the various specimens have been plotted against one another. In the curves so obtained (Figs. 6 to 10) the points marked B, C, N, D, P and A represent, respectively, the values for blood charcoal, Carboraffin, Norit, Darco, Philburgin and animal charcoal. In Figs. 7 to 9, where the amounts of benzene vapour adsorbed are compared with other values, the firm lines represent experimental results for benzene-adsorption, while the dotted lines are drawn from values at low partial pressures given by the $\log p - \log x$ isotherms. Correlation between two functions would be recognised by a smooth continuous curve when

the two are connected graphically, and in the limiting case proportionality between them would give a straight line. On the other hand, a discontinuous curve with sharp breaks or inflexions would represent lack of correlation between the properties compared. Thus it is seen from the nature of the curve in Fig. 6, the methylene blue-adsorption cannot be quantitatively correlated with iodine-adsorption. In Figs. 7 and 8, in which these two values are compared with the

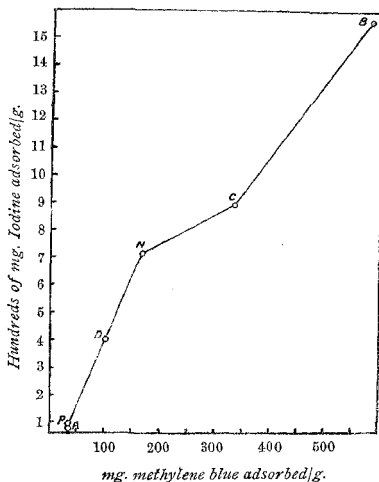


FIG. 6

adsorption of benzene at various partial pressures, it is noticed that the deflexions in the curves become less prominent at low partial pressures, while at higher concentrations, of benzene vapour these become more and more pronounced. At a relative pressure of one-half the order of benzene-adsorption values is even reversed, Carboraffin sorbing more than blood charcoal.

The correlation between adsorption of substances from dilute solution and that of vapours is better the lower the partial pressure, or concentration, of the latter. At high partial pressures, a good

proportion of the total amount of the vapour sorbed is due to capillary condensation. At low pressures, very little condensation is possible with the pore radii ordinarily present in activated charcoal and so the effect of capillarity becomes negligible. Therefore, sorption of the vapour at low pressures must be due almost entirely to the purely "adsorptive" or "potential" forces of the solid-surface. The adsorption of methylene blue, iodine and, in general, many substances in solution depends largely on these forces, and so agreement could be

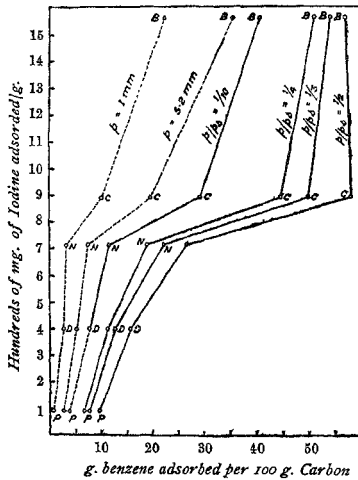


FIG. 7

expected between such adsorption and the sorption of vapours only at low partial pressures of the vapour.

Another interesting observation made from the shape of the curves in Figs. 7 and 8 is that the adsorption of methylene blue stands in better relationship with the sorption of benzene vapour at low pressures than does iodine-adsorption. This is clearly shown by the curves comparing the amounts of iodine and methylene blue adsorbed with the values of benzene-adsorption at relative pressures of one-tenth and less. The inflexions at the points C and N which

are very prominent in the iodine-benzene curves even at such low pressures are much smaller in the methylene blue-benzene curves at corresponding pressures. Indeed, the relation between the sorption of methylene blue and that of benzene-vapour at low partial pressures can be said to be roughly linear.

In Fig. 9, the heats of wetting of the various specimens in benzene are plotted against the amounts of benzene adsorbed at different partial pressures. Though the comparison between the two values improves with decreasing partial pressure of the vapour the

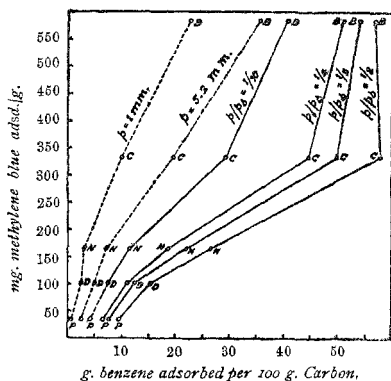


FIG. 8

curve shows sharp breaks even at relative pressures as low as one-tenth. However, at very low pressures, say 1 mm., an almost linear relationship is obtained. It, therefore, appears that the heat of wetting is almost proportional to the adsorption of vapours at very low partial pressures, *viz.*, at pressures of the order of 1 mm. Since the adsorption of vapours at such low pressures is almost entirely due to "potential" forces acting on the surface of the solid, it follows that the heat of wetting is a measure of these forces. This indirectly confirms the results of Macy (*J. Phys. Chem.*, 1931, **35**, 1397) who found that the heat of wetting is roughly proportional to the retentivity of the adsorbent for a given vapour. The relation between

the heat of wetting and the sorption of methylene blue on the one hand and the sorption of iodine on the other is shown in Fig. 10. In both cases, the correlation is more or less linear, that with the sorption of iodine being slightly closer than the other. The heat of wetting is, therefore, found to be almost proportional to the sorption of iodine and methylene blue. This is interesting in view of the want of correlation between the amounts of iodine and methylene blue adsorbed by the specimens (Fig. 6).

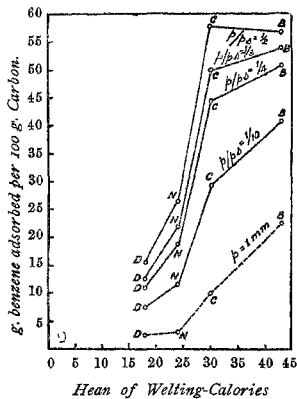


FIG. 9

It follows, therefore, that the heat of wetting of activated charcoal gives a measure of its sorptive capacities not only towards vapour at low pressures but also towards substances in solution as, for example, iodine and methylene blue in water. The heat of wetting, therefore, represents the "specific activity" or "specific adsorptive power" of the adsorbent. This is so, because whatever the mechanism of adsorption and whatever the nature of the adsorbent-surface, adsorption is accompanied by a decrease of surface energy and the heat liberated measures this energy-decrease.

For a rapid evaluation of active carbon it would suffice if one compared the temperature effects produced with fixed weights of

the specimens and the wetting liquid. For testing decolorising chars Berl (*Trans. Farad. Soc.*, 1938, **34**, 1045) suggests the determination of the temperature-rise produced when 1.5 g. of the carbon is wetted with 10 c.c. of benzene in an insulated vessel. A rise in temperature of 1°C. under those conditions is said to correspond roughly with the adsorption of 60 mg. of methylene blue per gram of carbon. When, however, a specimen is examined for use with gases and vapours, it must be borne in mind that the calorimetric method

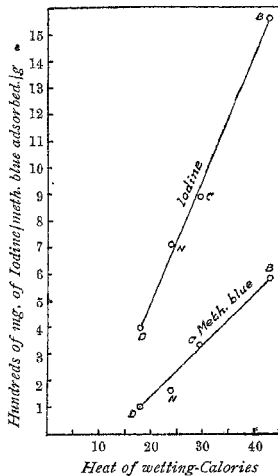


FIG. 10

can only give an estimate of the adsorbent's capacity for *firmly held* gas or vapour, that is to say, its retentivity, but will furnish no idea of sorption due to forces other than those of pure adsorption, such as cohesive or capillary forces. Where a fuller knowledge of the behaviour of a sorbent towards gases or vapours is desired, as for instance in the case of charcoals employed for the recovery of gasoline, solvent vapours etc., it will be necessary to determine their vapour adsorption isotherms in addition to their heats of wetting.

IX. SUMMARY

1. The common methods for determining the activity of adsorbent charcoal are discussed in detail. Six commercial specimens of active charcoal, obtained from widely different sources are employed in the present investigation for examining the various methods of evaluation.

2. Methods are given for the determination of the "bulk" "real" and "apparent" densities of activated charcoals and their porosities have been derived from the real and apparent densities. The results obtained show that the porosity factor bears little relation to the activity of the specimen.

3. The amounts of iodine adsorbed from aqueous solution by active charcoal were determined.

4. A standard procedure is given for the determination of the amount of methylene blue adsorbed by charcoal from a dilute aqueous solution of the dye.

5. A dynamic technique is described for the determination of the isothermals for the sorption of benzene vapour by activated charcoal. The nature of the isotherms and the significance of potential and cohesive forces of adsorption are discussed.

6. A comparison has been made of the adsorptive capacities of the various specimens of charcoal for iodine and methylene blue and benzene-vapour at various partial pressures. The results show a lack of correlation between the amounts of iodine and methylene blue adsorbed from solution. An approximately linear relation is obtained when these two values are compared with the adsorption of benzene-vapour at low partial pressures.

7. An accurate method for the determination of the heat of wetting of active charcoal is described. The significance of the heat of wetting in relation to the activity of charcoal is discussed, and a method has been suggested for the evaluation of active carbon.

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