# CC.—*The Heat of Adsorption of Gases by Charcoal.*

By SIDNEY JOHN GREGG.

AN examination of the literature dealing with the theories of the adsorption of gases by charcoal showed that one particular experimental quantity—the heat of adsorption—is especially important in testing them; and since the relevant data are very scanty, the following series of experiments was undertaken in order to measure this quantity, together with the more usual ones, equilibrium pressure and amount adsorbed. Measurements were therefore carried out at 0° with the aid of a Bunsen ice calorimeter, and also at 40° using the same calorimeter filled with phenol instead of ice. The adsorption of eight different gases on a standard charcoal was studied, and also the adsorption of a given gas on several different charcoals.

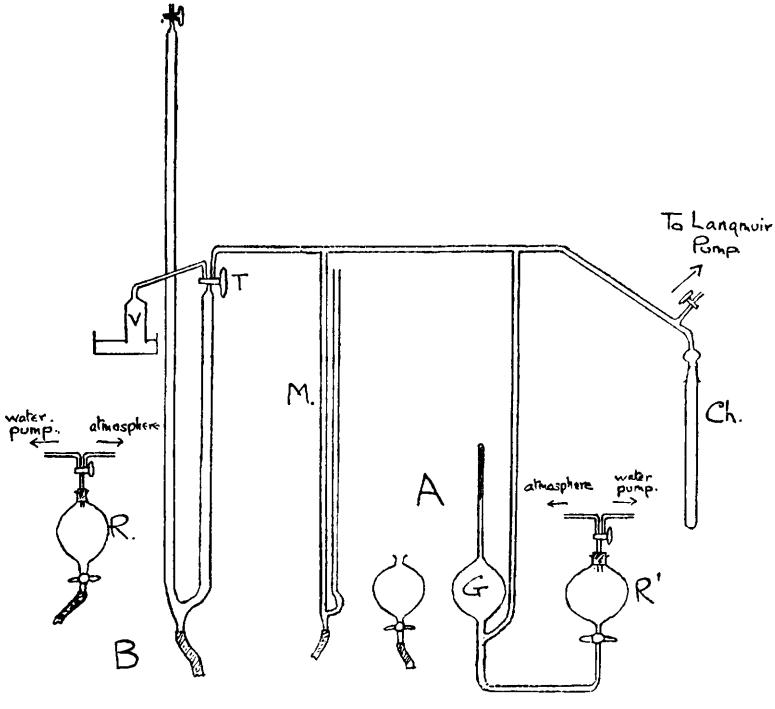
## EXPERIMENTAL.

The apparatus (Fig. 1) consists of two main parts, the gas burette, B, and the adsorption system, A, sealed together and mounted on a board, which can slide vertically, thus allowing the charcoal tube, Ch, to be lowered into the calorimeter.

The gas burette is a modification of that used in the Bone–Wheeler gas-analysis apparatus. The gas to be measured is drawn from the reservoir, V, where it is stored over mercury, into the shorter limb of the burette *via* the three-way tap, T. Since a Torricellian vacuum (produced by previous sweeping out of the air) exists above the mercury in the longer limb, the pressure of the gas in the shorter limb is given directly by the difference of mercury levels in the two limbs. The volume of the gas is known from the calibration figures for the shorter limb, and its temperature is also known, so that the quantity of gas can be calculated. It can then be admitted to the adsorption system by means of the tap T.

The adsorption system consists of an ordinary open tube manometer, M, a McLeod gauge, G, and the charcoal tube, which is joined to the rest of the apparatus by a ground glass joint. The McLeod gauge is joined to its mercury reservoir, R′, by an all-glass connexion, the raising or lowering of the mercury levels in this case, as also with the gas burette, being accomplished by applying atmospheric pressure or a water-pump vacuum, respectively, to the space above the mercury in the reservoir.

FIG. 1.



The ice calorimeter is of the usual type, but is fitted with an outer jacket which can be evacuated by means of a Langmuir pump. A simple Geissler tube connected with this jacket gives a ready means of testing the vacuum from time to time, and whenever this falls much below $X$-ray hardness, the jacket must be re-evacuated. This jacket, in conjunction with a very large and amply lagged bath of ice (diameter, 14 inches; depth, 16 inches) from which the water was frequently siphoned off, made it possible normally to obtain a leak of only 0·02 or 0·03 calorie per hour, though on occasions it rose much higher than this.

The desirability of measuring the heat of adsorption at a temperature other than 0° led to the attempt to use other working substances in the Bunsen calorimeter. Owing to the difficulty of keeping a thermostat sufficiently constant at the m. p. of anethole (19·5°), this substance was not satisfactory (compare Grassi, *Atti R. Accad. Lincei*, 1913, **22**, I, 304), but ultimately phenol was found to be a fairly suitable substitute. For accurate working, the normal heat leaks from the surroundings of the calorimeter should be constant enough to produce a small and steady creep of the mercury meniscus in the capillary in one direction; actually, it was found that a bath showing no variation on a Beckmann thermometer still gave unsteady heat leaks, and even in the best cases the mercury meniscus oscillated in the capillary over a range of some 0·6 cm., so that the readings are always uncertain to at least this extent. This is, unfortunately, an appreciable fraction of the movement due to the heat of adsorption itself, which was usually of the order of 10 cm. at each reading. In order to achieve even this degree of success, it was necessary to have very rapid stirring of the bath, to employ a large thermo-regulator, and to cover the top of the bath to minimise irregular evaporation.

*Calibration of the Calorimeters.*—The standard figure 1 cal. $\equiv$ 0·001132 c.c. was adopted for the ice calorimeter. The phenol calorimeter was calibrated by an electrical method, a known quantity of electrical energy being passed through a heating coil immersed in mercury, contained in the reaction tube of the calorimeter. The coil was of nichrome wire, welded on to copper leads, and was rendered insulating by momentary heating in a Bunsen flame, whereby a coating was formed on it such that on immersion in mercury it suffered no reduction in resistance. A voltmeter was connected across the terminals, and a known current passed for a definite period, the change in volume of the phenol being read on the capillary. A mean of several determinations gave 1 cal. $\equiv$ 0·00169 ± 0·00002 c.c. Finally, the temperature of operation was found to be 40·35° by immersing a standard thermometer in mercury contained in the reaction tube.

*Charcoals.*—A stock of charcoal was prepared by heating small cubes of birch wood in a large silica test tube in an electric furnace for 4 hours at about 400°. Four different samples were then prepared by activating separate charges of the stock at different temperatures in a very slow stream of nitrogen (containing 0·5% of oxygen). Details of these are :

| Charcoal No. | I | II | III | IV |
|---|---|---|---|---|
| Time of activation (hrs.) | 3 | 4 | 4 | 3 |
| Temp. of activation | 600° | 800° | 500° | 450° |

*Manipulation.*—The charcoal was dried in a vacuum desiccator for 5 hours, and 3—5 g. were accurately weighed into the charcoal tube, which was then placed in position on the adsorption apparatus and surrounded by an electric furnace. The charcoal was then evacuated by a mercury condensation pump for 24 hours, its temperature being maintained at 400°, as read by a pyrometer whose junction was in contact with the bottom of the charcoal tube. At the end of this time the pressure was of the order 0·0001 mm., and on cooling, it always became so low as to be unreadable. By means of the sliding board, the charcoal tube was now lowered into the reaction tube of the calorimeter, into which mercury was poured in order to facilitate heat conduction from the charcoal to the calorimeter during the subsequent measurements; to prevent heat losses by convection from the top of the reaction tube, the space between this and the charcoal tube was covered with a piece of plasticine. As soon as the movement in the capillary became constant, the first charge of gas was admitted, and readings of the pressure were taken every few minutes until two consecutive readings were identical, showing that equilibrium had been reached. When the calorimeter was working well, it was possible to use the heat readings as a check on the attainment of equilibrium, for when the creep became the same as before the admission of gas, one could assume that equilibrium had been reached.

The sorption curve was obtained by adding successive small quantities of gas from the burette, as outlined above, whilst, in order to obtain the desorption curve, the burette was opened to the adsorption system, thus enlarging the volume of the dead space. After a minute or so, the burette was shut off, the volume of gas withdrawn was read, and the attainment of equilibrium awaited.

In most cases, fresh samples of charcoal were used for each experiment. In a few instances, however, the supply of fresh charcoal was insufficient, and on these occasions, samples of charcoal that had been used for previous experiments had to be employed; in order to reduce the activating effect in such cases to a minimum, the charcoals were freed from gas at a lower temperature than before, *viz.*, at 150°, and in some cases even at room temperature. Nevertheless, as will be explained later, a small activating effect was still present, the charcoal being slightly altered during each removal of gas.

*Calculations.*—In calculating volumes of gas, correction is made for the deviation from Boyle's law, and the volume which would be occupied ideally by the gas at *N.T.P.* thus obtained. To calculate the amount of gas $v_a$ that has been adsorbed up to a given reading, the amount $v_u$ remaining unadsorbed in the dead space is subtracted from the total amount $v_t$ which has been admitted to the system; in calculating $v_u$, it must be remembered that part of the dead space is at room temperature and part at that of the calorimeter. In order to obtain the heat of adsorption corresponding to a given charge of gas, a correction must be made for the heat communicated to the calorimeter by the gas when changing from room temperature to 0° or 40·35° as the case may be. This correction is $v_c s(t_1 - t_2)$, where $s$ is the specific heat of the gas per c.c. at constant volume, and $v_c$ is the amount of gas that has been changed from the temperature of the atmosphere, $t_1$, to that of the calorimeter, $t_2$.

*Degree of Accuracy.*—No attempt has been made to attain to any great degree of accuracy for two main reasons : (i) Charcoal itself is such an indefinite substance, and is so difficult to obtain in a perfectly homogeneous condition, that excessive accuracy in the measurements would be superfluous; and (ii) the accuracy attainable with the ice calorimeter is not so high as to justify great accuracy in the measurement of the other two quantities. A rough estimate of the probable error of the respective measurements is as follows :

*Pressure :* Never greater than $\pm$ 1%, and for higher pressures (10 cm. or more), of the order $\pm$ 0·2%.

*Amount adsorbed :* Between $\pm$ 0·5% and $\pm$ 1·0%.

*Heat :* Very variable, but of the order $\pm$ 2% for the ice-, and $\pm$ 5% for the phenol-calorimeter.

*Note on the Purity of the Gases.*—In these experiments, the fact that hysteresis (see " Discussion ") was absent, was assumed to prove that the gas was pure, since the presence of air as an impurity immediately produced the phenomenon. The author has since recognised that this is inadequate evidence of purity, however, for the work of Lorenz and Wiedbrauck (*Z. anorg. Chem.*, 1925, **143**, 268) indicates that only when gases differ widely in physical properties do they interfere with each other's adsorption. Hence the absence of hysteresis does not necessarily indicate the absence of impurities similar in physical properties to the gas in question; such impurities, however, would have but a very slight effect on the adsorption measurements.

## *Results.*

The following quantities are given for each reading :

$x$ = total number of g.-mols. of gas adsorbed per g. of charcoal (= $v_a/22414\ w$, where $w$ is the weight of charcoal).

$p$ = equilibrium pressure (cm. of Hg).

$Q$ = integral heat of adsorption per g. of charcoal, $= \Sigma h$, where $h$ is the amount of heat evolved per g. of charcoal at a given reading.

In the curves, desorption points are denoted by a small tail attached to the circle, etc., which surrounds the point, thus ⊙.

Experiment 1 : Nitrous oxide + Charcoal I at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·383 | $\bar{1}$·715 | 0·280 | $\bar{3}$·294 | 1·351 | 1·160 | $\bar{3}$·433 | 1·764 | 1·284 |
| $\bar{4}$·669 | 0·106 | 0·557 | $\bar{3}$·337 | 1·464 | 1·195 | $\bar{3}$·413 | 1·677 | 1·264 |
| $\bar{4}$·861 | 0·405 | 0·754 | $\bar{3}$·373 | 1·582 | 1·227 | $\bar{3}$·383 | 1·596 | 1·238 |
| $\bar{4}$·992 | 0·662 | 0·871 | $\bar{3}$·406 | 1·684 | 1·255 | $\bar{3}$·335 | 1·411 | 1·193 |
| $\bar{3}$·097 | 0·873 | 0·981 | $\bar{3}$·432 | 1·781 | 1·281 | $\bar{3}$·282 | 1·259 | 1·145 |
| $\bar{3}$·173 | 1·073 | 1·057 | $\bar{3}$·456 | 1·862 | 1·305 | $\bar{3}$·242 | 1·151 | 1·106 |
| $\bar{3}$·240 | 1·224 | 1·114 | | | | | | |

*Preparation of gas.* Sodium nitrite solution was slowly dropped into warm hydroxylamine hydrochloride solution, and the nitrous oxide evolved was passed in succession through potassium hydroxide solution, over solid potassium hydroxide, through concentrated sulphuric acid, and finally over phosphorus pentoxide.

Experiment 1*a* : Nitrous oxide + Charcoal I at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·714 | 0·173 | 0·560 | $\bar{3}$·345 | 1·461 | 1·159 | $\bar{3}$·405 | 1·665 | 1·209 |
| $\bar{3}$·085 | 0·834 | 0·905 | $\bar{3}$·416 | 1·706 | 1·222 | $\bar{3}$·349 | 1·473 | 1·155 |
| $\bar{3}$·255 | 1·216 | 1·075 | $\bar{3}$·449 | 1·839 | 1·250 | | | |

*Charcoal.* The charcoal from Expt. 1 was freed from gas at room temperature without intermediate exposure to air.

*Preparation of gas.* As for Expt. 1.

Experiment 2 : Nitrous oxide + Charcoal I at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·434 | $\bar{1}$·734 | 0·161 | $\bar{3}$·247 | 1·152 | 1·060 | $\bar{3}$·460 | 1·840 | 1·259 |
| $\bar{4}$·744 | 0·167 | 0·557 | $\bar{3}$·322 | 1·360 | 1·136 | $\bar{3}$·485 | 1·944 | 1·267 |
| $\bar{4}$·936 | 0·498 | 0·759 | $\bar{3}$·364 | 1·486 | 1·176 | $\bar{3}$·446 | 1·793 | 1·244 |
| $\bar{3}$·055 | 0·736 | 0·884 | $\bar{3}$·395 | 1·590 | 1·207 | $\bar{3}$·393 | 1·579 | 1·175 |
| $\bar{3}$·163 | 0·951 | 0·978 | $\bar{3}$·428 | 1·722 | 1·241 | | | |

*Preparation of gas.* After being prepared as in Expt. 1, it was liquefied by cooling in liquid air, and then distilled in a vacuum.

Experiment 3 : Nitrous oxide + Charcoal I at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|
| $\bar{4}$·803 | 0·281 | 0·657 | $\bar{3}$·360 | 1·493 | 1·216 |
| $\bar{3}$·288 | 1·274 | 1·148 | $\bar{3}$·415 | 1·671 | 1·264 |

*Preparation of gas.* As in Expt. 2.

Experiment 4 : Acetylene + Charcoal I at 0°.

| log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·494 | $\bar{1}$·537 | 0·458 | $\bar{3}$·328 | 1·298 | 1·250 | $\bar{3}$·438 | 1·790 | 1·351 |
| $\bar{4}$·798 | 0·034 | 0·749 | $\bar{3}$·375 | 1·480 | 1·290 | $\bar{3}$·417 | 1·667 | 1·338 |
| $\bar{4}$·995 | 0·412 | 0·922 | $\bar{3}$·412 | 1·644 | 1·323 | $\bar{3}$·370 | 1·454 | 1·295 |
| $\bar{3}$·167 | 0·809 | 1·081 | $\bar{3}$·441 | 1·797 | 1·349 | $\bar{3}$·305 | 1·202 | 1·238 |
| $\bar{3}$·254 | 1·051 | 1·179 | $\bar{3}$·462 | 1·915 | 1·370 | $\bar{3}$·227 | 0·952 | 1·155 |

*Preparation of gas.* Water was dropped on calcium carbide in an evacuated apparatus, and the acetylene was passed through saturated potassium permanganate solution, over solid potassium hydroxide and phosphorus pentoxide, then solidified and redistilled in a high vacuum.

Experiment 5 : Ethane + Charcoal I at 0°.

| log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·524 | $\bar{1}$·282 | 0·505 | $\bar{3}$·197 | 0·467 | 1·150 | $\bar{3}$·416 | 1·425 | 1·361 |
| $\bar{4}$·866 | $\bar{1}$·785 | 0·831 | $\bar{3}$·313 | 0·874 | 1·258 | $\bar{3}$·444 | 1·638 | 1·386 |
| $\bar{4}$·053 | 0·070 | 1·013 | $\bar{3}$·373 | 1·146 | | | | |

*Preparation of gas.* Propionitrile was dropped on sodium wire in an evacuated apparatus (see Stähler *et al.*, " Arbeitsmethoden der Anorganischen Chemie," 1926, IV, p. 93), and the ethane passed in succession through tubes containing the following reagents: potassium hydroxide solution, solid potassium hydroxide, concentrated sulphuric acid, and phosphorus pentoxide. It was then solidified and redistilled in high vacuum. The presence of hysteresis showed that the gas was not pure, although Cardoso and Bell (*J. Chim. physique*, 1912, **10**, 498) endorse the method as giving pure ethane.

*Remark.* The attainment of equilibrium at some readings required several hours, again indicating that the gas was not pure.

Experiment 6 : Carbon monoxide + Charcoal I at 0°.

| log $x$. | log $p$. | log $x$. | log $p$. | log $x$. | log $p$. | log $x$. | log $p$. |
|---|---|---|---|---|---|---|---|
| $\bar{5}$·973 | 0·845 | $\bar{4}$·521 | 1·494 | $\bar{4}$·753 | 1·831 | $\bar{4}$·576 | 1·566 |
| $\bar{4}$·199 | 1·098 | $\bar{4}$·588 | 1·582 | $\bar{4}$·824 | 1·920 | $\bar{4}$·444 | 1·388 |
| $\bar{4}$·403 | 1·339 | $\bar{4}$·686 | 1·723 | $\bar{4}$·709 | 1·754 | $\bar{4}$·176 | 1·065 |

*Preparation of gas.* Concentrated sulphuric acid was dropped on sodium formate, and the gas passed through tubes of potassium hydroxide solution, solid potassium hydroxide, and phosphorus pentoxide. The apparatus was alternately evacuated and filled with carbon monoxide three times before the gas was collected.

Experiment 7 : Sulphur dioxide + Charcoal I at 0°.

| log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. |
|---|---|---|---|---|---|---|---|---|
| $\bar{3}$·210 | $\bar{1}$·330 | 1·287 | $\bar{3}$·606 | 1·517 | 1·655 | $\bar{3}$·589 | 1·263 | 1·639 |
| $\bar{3}$·495 | 0·430 | — | $\bar{3}$·623 | 1·708 | 1·669 | $\bar{3}$·567 | 1·072 | 1·624 |
| $\bar{3}$·567 | 1·013 | 1·621 | $\bar{3}$·606 | 1·467 | 1·653 | $\bar{3}$·531 | 0·722 | 1·597 |
| $\bar{3}$·590 | 1·367 | 1·645 | | | | | | |

*Preparation of gas.* Sulphur dioxide from a cylinder was passed through tubes of concentrated sulphuric acid and phosphorus pentoxide. It was then solidified and redistilled in a high vacuum.

Experiment 8 : Carbon dioxide + Charcoal I at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·315 | $\bar{1}$·844 | 0·212 | $\bar{3}$·162 | 1·183 | 1·016 | $\bar{3}$·432 | 1·910 | 1·272 |
| $\bar{4}$·573 | 0·201 | 0·455 | $\bar{3}$·238 | 1·360 | 1·083 | $\bar{3}$·450 | 1·984 | 1·293 |
| $\bar{4}$·811 | 0·555 | 0·680 | $\bar{3}$·299 | 1·522 | 1·145 | $\bar{3}$·408 | 1·833 | 1·252 |
| $\bar{4}$·948 | 0·779 | 0·810 | $\bar{3}$·354 | 1·654 | 1·194 | $\bar{3}$·360 | 1·657 | 1·199 |
| $\bar{3}$·066 | 0·989 | 0·921 | $\bar{3}$·408 | 1·820 | 1·246 | $\bar{3}$·305 | 1·493 | 1·146 |

*Preparation of gas.* Concentrated sulphuric acid was dropped on solid sodium carbonate in an evacuated apparatus. The gas was dried by concentrated sulphuric acid and phosphorus pentoxide, solidified, and redistilled in a vacuum.

Experiment 9 : Ethylene + Charcoal I at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·280 | $\bar{1}$·071 | 0·187 | $\bar{3}$·298 | 1·345 | 1·130 | $\bar{3}$·347 | 1·589 | 1·170 |
| $\bar{4}$·537 | $\bar{1}$·452 | 0·444 | $\bar{3}$·333 | 1·545 | 1·165 | $\bar{3}$·304 | 1·346 | 1·131 |
| $\bar{4}$·765 | $\bar{1}$·822 | 0·652 | $\bar{3}$·363 | 1·713 | 1·188 | $\bar{3}$·247 | 1·201 | 1·104 |
| $\bar{4}$·945 | 0·195 | 0·811 | $\bar{3}$·383 | 1·846 | 1·206 | $\bar{3}$·183 | 0·945 | 1·049 |
| $\bar{3}$·063 | 0·513 | 0·917 | $\bar{3}$·396 | 1·953 | 1·218 | $\bar{3}$·101 | 0·647 | 0·972 |
| $\bar{3}$·163 | 0·805 | 1·010 | $\bar{3}$·377 | 1·790 | 1·198 | $\bar{4}$·957 | 0·245 | 0·842 |
| $\bar{3}$·237 | 1·074 | 1·074 | | | | | | |

*Preparation of gas.* A mixture of 50 c.c. each of concentrated sulphuric acid and absolute alcohol was placed in a distilling flask, and a little sand (previously washed with concentrated hydrochloric acid and ignited) was added. A mixture of 50 c.c. of concentrated sulphuric acid with 25 c.c. of absolute alcohol was slowly added from a dropping funnel, the flask being warmed. The whole apparatus was previously evacuated. The ethylene was passed successively through tubes containing solid potassium hydroxide, concentrated sulphuric acid, and phosphorus pentoxide; it was then solidified and redistilled in a vacuum.

Experiment 9*a* : Ethylene + Charcoal I at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·818 | 0·000 | 0·665 | $\bar{3}$·301 | 1·396 | 1·114 | $\bar{3}$·341 | 1·599 | 1·148 |
| $\bar{3}$·132 | 0·730 | 0·955 | $\bar{3}$·376 | 1·831 | 1·184 | $\bar{3}$·292 | 1·325 | 1·104 |

*Charcoal.* The charcoal from Expt. 9 was freed from gas at room temperature without intermediate exposure to air.

*Preparation of gas.* As for Expt. 9.

Experiment 10 : Nitrogen + Charcoal I at 0°.

| log *x*. | log *p*. | log *x*. | log *p*. | log *x*. | log *p*. | log *x*. | log *p*. |
|---|---|---|---|---|---|---|---|
| $\bar{5}$·578 | 0·656 | $\bar{4}$·260 | 1·398 | $\bar{4}$·573 | 1·790 | $\bar{4}$·238 | 1·376 |
| $\bar{5}$·971 | 1·073 | $\bar{4}$·391 | 1·554 | $\bar{4}$·646 | 1·884 | $\bar{4}$·095 | 1·188 |
| $\bar{4}$·168 | 1·291 | $\bar{4}$·492 | 1·684 | $\bar{4}$·564 | 1·777 | $\bar{5}$·935 | 1·002 |

*Preparation of gas.* Nitrogen from a cylinder was used; it contained 0·5% of oxygen.

The gases used in the remaining experiments were prepared as described in the corresponding preceding experiments.

Experiment 11 : Nitrous oxide + Charcoal II at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·573 | $\bar{1}$·872 | 0·498 | $\bar{3}$·215 | 1·005 | 1·103 | $\bar{3}$·442 | 1·637 | 1·312 |
| $\bar{4}$·893 | 0·389 | 0·806 | $\bar{3}$·314 | 1·252 | 1·194 | $\bar{3}$·474 | 1·752 | 1·342 |
| $\bar{3}$·103 | 0·757 | 0·997 | $\bar{3}$·390 | 1·473 | 1·265 | $\bar{3}$·503 | 1·864 | 1·370 |

Experiment 12 : Sulphur dioxide + Charcoal II at 0°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·685 | $\bar{2}$·633 | 0·755 | $\bar{3}$·620 | 1·412 | 1·639 | $\bar{3}$·642 | 1·559 | 1·657 |
| $\bar{3}$·084 | $\bar{1}$·124 | 1·133 | $\bar{3}$·638 | 1·660 | 1·652 | $\bar{3}$·626 | 1·344 | 1·643 |
| $\bar{3}$·405 | $\bar{1}$·935 | 1·425 | $\bar{3}$·651 | 1·834 | 1·665 | $\bar{3}$·611 | 1·148 | 1·623 |
| $\bar{3}$·511 | 0·398 | 1·522 | $\bar{3}$·659 | 1·923 | 1·672 | $\bar{3}$·599 | 1·985 | 1·609 |
| $\bar{3}$·584 | 0·969 | 1·601 | $\bar{3}$·650 | 1·683 | 1·662 | $\bar{3}$·585 | 0·848 | 1·598 |

*Charcoal.* This charcoal had been previously used for Expt. 11 and was freed from gas at room temperature.

Experiment 13 : Nitrogen + Charcoal II at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·121 | 1·139 | $\bar{1}$·761 | $\bar{4}$·645 | 1·781 | 0·301 | $\bar{4}$·653 | 1·774 | 0·305 |
| $\bar{4}$·387 | 1·446 | 0·041 | $\bar{4}$·712 | 1·892 | 0·387 | $\bar{4}$·577 | 1·663 | 0·240 |
| $\bar{4}$·539 | 1·641 | 0·196 | $\bar{4}$·780 | 1·969 | 0·433 | | | |

Experiment 14 : Nitrous oxide + Charcoal III at 0°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·610 | 0·137 | 0·318 | $\bar{3}$·277 | 1·406 | 1·003 | $\bar{3}$·380 | 1·752 | 1·101 |
| $\bar{4}$·912 | 0·610 | 0·617 | $\bar{3}$·331 | 1·577 | 1·061 | $\bar{3}$·352 | 1·647 | 1·067 |
| $\bar{3}$·094 | 0·955 | 0·802 | $\bar{3}$·373 | 1·725 | 1·104 | $\bar{3}$·328 | 1·562 | 1·041 |
| $\bar{3}$·204 | 1·209 | 0·921 | $\bar{3}$·405 | 1·856 | 1·133 | $\bar{3}$·308 | 1·477 | 1·015 |

*Charcoal.* This had been previously used for Expt. 15 and was freed from gas at room temperature.

*Remark.* The calorimeter was working very badly during this experiment, and the heat measurements are therefore untrustworthy.

Experiment 15 : Sulphur dioxide + Charcoal III at 0°.

| log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. | log *x*. | log *p*. | log *Q*. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·960 | $\bar{2}$·875 | 1·040 | $\bar{3}$·552 | 1·109 | 1·575 | $\bar{3}$·633 | 1·881 | 1·654 |
| $\bar{3}$·270 | $\bar{1}$·432 | — | $\bar{3}$·582 | 1·396 | 1·606 | $\bar{3}$·612 | 1·680 | 1·641 |
| $\bar{3}$·442 | 0·272 | 1·485 | $\bar{3}$·604 | 1·605 | 1·625 | $\bar{3}$·590 | 1·478 | 1·621 |
| $\bar{3}$·507 | 0·705 | 1·540 | $\bar{3}$·620 | 1·759 | 1·641 | $\bar{3}$·570 | 1·298 | 1·613 |

Experiment 16 : Nitrogen + Charcoal III at 0°.

| log *x*. | log *p*. | log *x*. | log *p*. | log *x*. | log *p*. | log *x*. | log *p*. |
|---|---|---|---|---|---|---|---|
| $\bar{5}$·882 | 1·195 | $\bar{4}$·363 | 1·738 | $\bar{4}$·397 | 1·753 | $\bar{4}$·056 | 1·355 |
| $\bar{4}$·206 | 1·547 | $\bar{4}$·488 | 1·877 | $\bar{4}$·272 | 1·604 | | |

*Charcoal.* This had been used for Expts. 14 and 15 and was freed from gas at room temperature.

Experiment 17 : Sulphur dioxide + Charcoal IV at 0°.

| log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. | log $x$. | log $p$. | log $Q$. |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·606 | $\bar{2}$·484 | 0·740 | $\bar{3}$·477 | 0·968 | 1·510 | $\bar{3}$·588 | 1·621 | 1·597 |
| $\bar{3}$·059 | $\bar{1}$·441 | 1·143 | $\bar{3}$·545 | 1·377 | 1·562 | $\bar{3}$·559 | 1·437 | 1·573 |
| $\bar{3}$·261 | $\bar{1}$·828 | 1·321 | $\bar{3}$·590 | 1·674 | 1·592 | $\bar{3}$·496 | 1·008 | 1·536 |
| $\bar{3}$·382 | 0·389 | 1·426 | $\bar{3}$·622 | 1·856 | 1·614 | | | |

Experiment 18 : Nitrous oxide + Charcoal I at 40·35°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·551 | 0·668 | 0·484 | $\bar{3}$·039 | 1·467 | 0·956 | $\bar{3}$·190 | 1·729 | 1·078 |
| $\bar{4}$·781 | 1·007 | 0·708 | $\bar{3}$·096 | 1·571 | 1·010 | $\bar{3}$·139 | 1·623 | 1·036 |
| $\bar{4}$·882 | 1·184 | 0·805 | $\bar{3}$·178 | 1·733 | 1·090 | $\bar{3}$·093 | 1·525 | 1·996 |
| $\bar{4}$·962 | 1·346 | 0·889 | $\bar{3}$·235 | 1·856 | 1·144 | | | |

Experiment 19 : Sulphur dioxide + Charcoal I at 40·35°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\bar{4}$·589 | $\bar{1}$·459 | 0·837 | $\bar{3}$·451 | 1·285 | 1·561 | $\bar{3}$·430 | 1·035 | 1·531 |
| $\bar{4}$·855 | $\bar{1}$·931 | 1·085 | $\bar{3}$·504 | 1·607 | 1·599 | $\bar{3}$·398 | 0·743 | 1·497 |
| $\bar{3}$·157 | 0·338 | 1·306 | $\bar{3}$·490 | 1·476 | 1·586 | $\bar{3}$·332 | 0·310 | 1·447 |
| $\bar{3}$·288 | 0·650 | 1·422 | $\bar{3}$·451 | 1·184 | 1·550 | $\bar{3}$·206 | 0·272 | 1·338 |
| $\bar{3}$·387 | 0·969 | 1·505 | | | | | | |

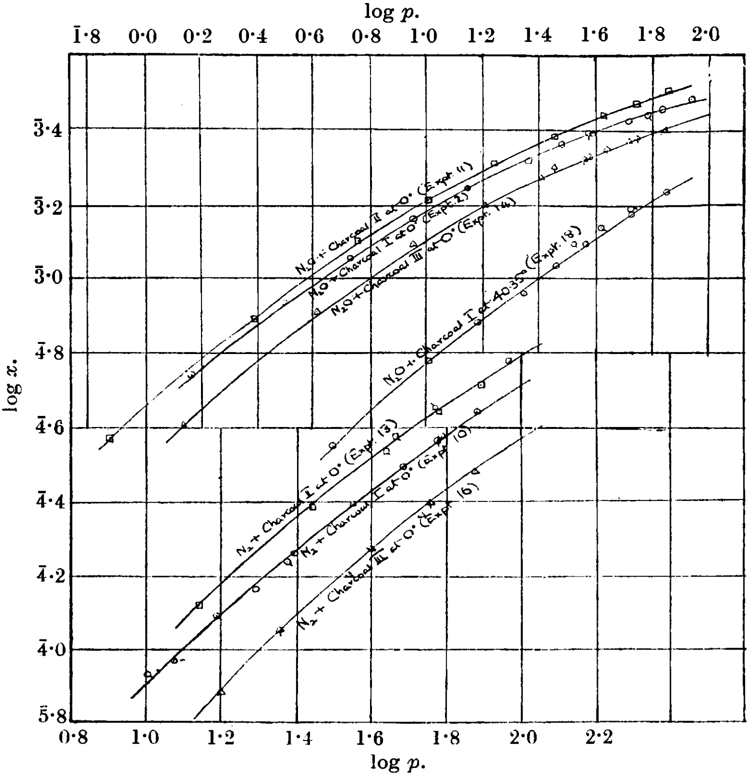
*Charcoal.* This had been previously used for Expt. 6, and was freed from gas at 150°.

### *Discussion.*

During the earlier stages of the work, great trouble was experienced from the occurrence of "hysteresis," which is a well-known phenomenon in adsorption work; the desorption curve, obtained by withdrawing the gas from the charcoal, does not retrace the sorption curve, the charcoal always retaining more gas for a given pressure on the curve of desorption than on that of sorption. Furthermore, the time required to attain equilibrium is much shorter (of the order of one hour) during desorption than during sorption, in which the pressure may continue to fall for several days. In agreement with Patrick (*J. Amer. Chem. Soc.*, 1920, **42**, 946) and others, the trouble was found to be due to traces of non-condensable gas in the system; for when the gas to be adsorbed was liquefied and then distilled in high vacuum, and when the charcoal was thoroughly evacuated, the sorption and desorption curves could be made to agree, and the time for equilibrium in both cases became normal at about one hour. Only with ethyl chloride was this treatment ineffective, for no matter how carefully the gas was prepared, considerable hysteresis was observed; hence adsorption experiments with this gas were abandoned.

As has been shown by many previous workers, neither the $p$–$x$ nor the log $p$–log $x$ curve possesses a simple analytical form; the shape of the latter curve does not even appear to bear any simple relationship to the nature of the adsorbed gas, though it must be remembered that it is difficult to give criteria for selecting comparable parts of the curve for different gases; thus, while the sulphur dioxide curve at atmospheric pressure is approaching the point of saturation, the curve for a permanent gas like nitrogen is still in its early stages. On the other hand, the log $p$-log $x$ curves undergo a regular variation with the change of charcoal, for the order of the curves for the charcoals I, II, and III is the same for the three widely different gases nitrogen, nitrous oxide, and sulphur dioxide—charcoal II always having the greatest adsorption for a given pressure, charcoal I the next, and charcoal III the smallest. This is illustrated for nitrogen and nitrous oxide by the curves in Fig. 2.

FIG. 2.



$Q$ and $x$ are connected by the simple relation $Q = kx^n$, where $k$ and $n$ are constants at constant temperature, a result obtained also by other workers (*e.g.*, Lamb and Coolidge, *J. Amer. Chem. Soc.*, 1920, **42**, 1146). The index $n$ is roughly characteristic of the gas which is adsorbed, for, as will be seen from Table I, it remains approximately constant when one gas is adsorbed on different charcoals, and varies from gas to gas for the same charcoal. The rule is only a rough one, however, for in some cases quite a large difference is obtained for the same gas. This is illustrated by sulphur dioxide with charcoals I and IV (Expts. 7 and 17, respectively).

FIG. 3.

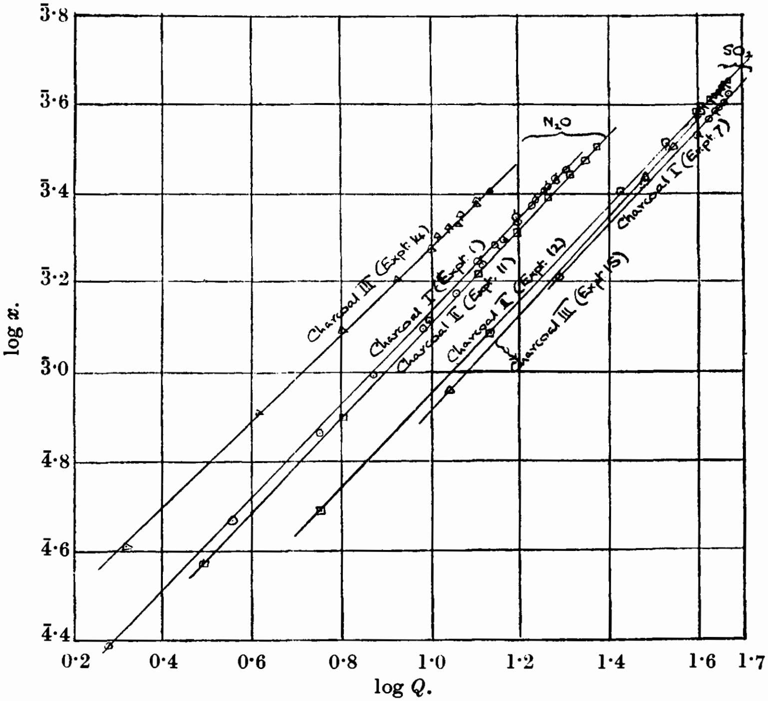


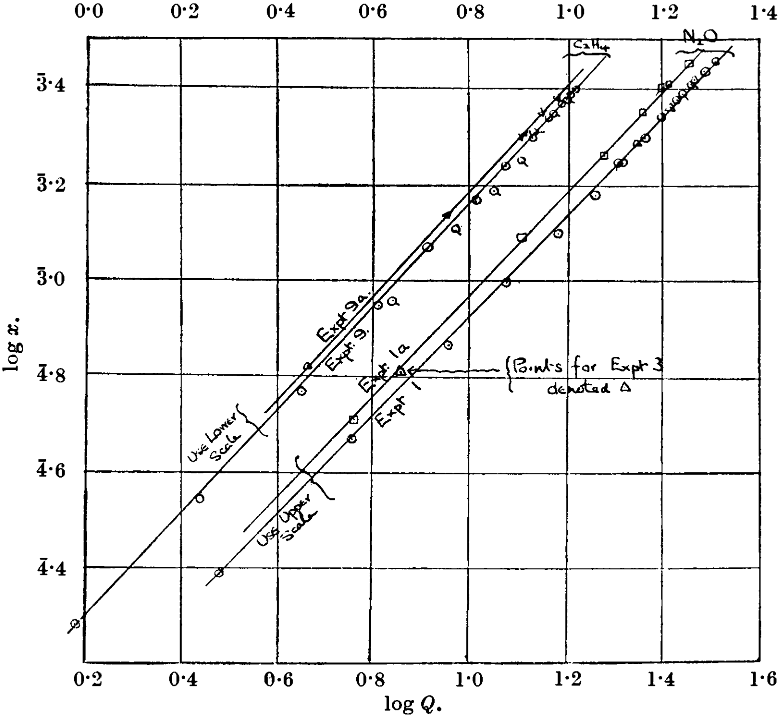
TABLE I.

Values of $k$ and $n$ in the formula $Q = kx^n$.

| Temp. | Expt. No. | Gas. | Charcoal. | $n$. | log $k$. |
|---|---|---|---|---|---|
| 0° | 1 | $N_2O$ | I | 0·940 | $\bar{3}$·703 |
| | 1$a$ | ,, | I | 0·940 | $\bar{3}$·651 |
| | 3 | ,, | I | 0·953 | $\bar{3}$·726 |
| | 11 | ,, | II | 0·933 | $\bar{3}$·706 |
| | 14 | ,, | III | 1·01 (?) | $\bar{3}$·745 (?) |
| 40·35° | 18 | ,, | I | 0·957 | $\bar{3}$·695 |
| 0° | 7 | $SO_2$ | I | 0·915 | $\bar{3}$·843 |
| | 12 | ,, | II | 0·942 | $\bar{3}$·877 |
| | 15 | ,, | III | 0·911 | $\bar{3}$·811 |
| | 17 | ,, | IV | 0·885 | $\bar{3}$·746 |
| 40·35° | 19 | ,, | I | 0·840 | $\bar{3}$·695 |
| 0° | 4 | $C_2H_2$ | I | 0·945 | $\bar{3}$·770 |
| | 5 | $C_2H_6$ | I | 0·966 | $\bar{3}$·963 |
| | 8 | $CO_2$ | I | 0·955 | $\bar{3}$·726 |
| | 9 | $C_2H_4$ | I | 0·924 | $\bar{3}$·627 |
| | 9$a$ | ,, | I | 0·926 | $\bar{3}$·613 |
| | 13 | $N_2$ | II | 1·005 | $\bar{3}$·676 |

The data available are too limited to decide whether any simple rule holds for the variation of $k$; for the nitrous oxide experiments, the log $Q$–log $x$ curves are in the same order as the corresponding isotherms—charcoal II having the largest $k$, charcoal I the next, and charcoal III the smallest (see Fig. 3). It is difficult, however, to pronounce judgment upon the apparently anomalous order of the sulphur dioxide curves, for they lie so close together that a small experimental error would alter their relative order; it is possible that such an error may be present in the experiment with charcoal II, for the abnormally high value of $n$ in this case throws doubt on the accuracy of the curve.

FIG. 4.



It is here appropriate to note the effect of the adsorption of one gas upon the subsequent adsorption of the same or a different gas by a given charcoal. In Fig. 4 are plotted the log $Q$–log $x$ curves for ethylene on charcoal I, Expt. 9 being carried out with fresh charcoal, and Expt. 9*a* after pumping out the gas from the used charcoal at room temperature and without intermediate exposure to the atmosphere. The curves for Expts. 1 and 1*a* represent a similar pair for nitrous oxide, and the curve for Expt. 3 was obtained with charcoal I that had been previously saturated with ammonia and evacuated at room temperature. It will be seen that a small de-activating effect is indicated in the heat curves in each case, the value of $k$ being slightly decreased, though the corresponding $\log p$–$\log x$ curves show no such effect.

The heat of adsorption should now be compared with the latent heat of condensation of the adsorbed gas. For this purpose, one must use the differential heat of adsorption, $dQ/dx = knx^{n-1}$, *i.e.*, the heat evolved per g.-mol. of gas, since this is the quantity comparable with the latent heat; and this must relate to a fixed value of $x$ in each case.

Since $n$ is always less than unity, the differential heat of adsorption decreases as the concentration increases, but its value can be calculated for a given value of $x$ within the range of the experiments, *e.g.*, $x = 1000 \times 10^{-6}$ g.-mol. per g. of charcoal. From Table II it will be seen that this differential heat is in each case 2—3 times as large as the latent heat of condensation of the vapour at 0° (calculated by the Clausius–Clapeyron equation); this agrees with the results of Lamb and Coolidge (*loc. cit.*) for several organic vapours.

TABLE II.

Heats of adsorption and latent heats of condensation.

| Gas. | Molecular latent heat (cal.). | $dQ/dx$ (cal.) for $x = 1000 \times 10^{-6}$. |
|---|---|---|
| Sulphur dioxide | 6,160 | 11,460 |
| Ethylene | 2,050 | 6,620 |
| Acetylene | 2,580 | 8,100 |
| Carbon dioxide | 2,570 | 6,930 |
| Nitrous oxide | 2,510 | 7,180 |
| Nitrogen (Charcoal II) | — | 4,740 |

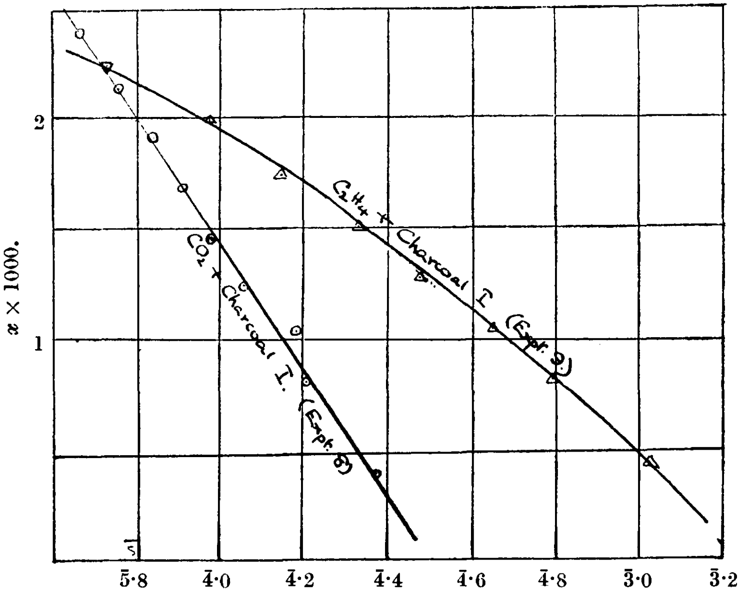
(The charcoal used in the first five cases was No. I.)

It is further of interest to compare the heat of adsorption of nitrous oxide at 0° with that at 40·35°, these temperatures being, respectively, below and above the critical temperature (35—39°). Whilst it must be borne in mind that, owing to the difficulty of working the phenol calorimeter, the measurements at 40·35° give little more than the order of magnitude of the heat of adsorption, yet it will be seen that the values of $k$ and $n$ at the two temperatures are not very different, showing that at a given concentration $x$, the integral heat of adsorption and the differential $dQ/dx$ at the respective temperatures are also not very different.

This approximate constancy, with reference to temperature, of the heat effect of adsorption is confirmed by the fact that the value of the differential heat of adsorption calculated from the van't Hoff isochore, on the assumption that it remains constant between 0° and 40·35°, is close to the experimental value. In the isochore $d \log_e K/dT = - H/RT^2$, where $K$ is the equilibrium constant and $H$ is the heat of reaction, $K$ may be replaced by $p$, and integration then gives $\log_e p_1/p_2 = H(T_2 - T_1)/RT_1T_2$, where $p_1$ and $p_2$ are the equilibrium pressures at temperatures $T_1$ and $T_2$, respectively, for a given value of $x$, so that $H$ becomes the differential heat of adsorption for the same value of $x$.

The values of log $p$ for nitrous oxide on charcoal I at 0° (Expt. 2) and 40·35° (Expt. 18) are, respectively, 0·605 and 1·372 when $x = 1000 \times 10^{-6}$; putting $T_1 = 273$, $T_2 = 313·35$, and $R = 1·98$, $H$ is calculated to be 7442 cals. per g.-mol. per g. of charcoal. This is close to the value 7180 cal. obtained from the formula $dQ/dx = knx^{n-1}$ by using the experimental values of $k$ and $n$ for nitrous oxide at 0° on charcoal I (Expt. 1).

FIG. 5.



Although the $p$–$x$ curve cannot be represented by any simple mathematical equation, the results agree fairly well with an equation of the form $\log x/p = A_0 - A_1x$, which has been deduced thermodynamically by Williams (*Proc. Roy. Soc.*, 1919, **96**, *A*, 287) and from kinetic theory by Henry (*Phil. Mag.*, 1922, **44**, 689). Thus on plotting log $x/p$ against $x$ ( see Fig. 5), a straight line is obtained for carbon dioxide, acetylene, nitrous oxide, carbon monoxide, or nitrogen with charcoal I; but deviations from the rectilinear occur in other cases, *e.g.*, ethylene and nitrogen with charcoals II and III, and also in Homfray's results (*Z. physikal. Chem.*, 1910, **74**, 129) for ethylene and nitrogen, and Richardson's (*J. Amer. Chem. Soc.*, 1917, **39**, 1828) for carbon dioxide. Furthermore, on plotting the results for sulphur dioxide from the present measurements, and also those for ammonia from Richardson's, the curves are not even approximately rectilinear. In general, however, it may be said that the Williams–Henry equation does reproduce moderately well the adsorption measurements at 0° for those gases which are far removed from their condensation point at *N.T.P.*; but, as it is hoped to show elsewhere, this fact is insufficient evidence for the validity of either Williams's or Henry's fundamental assumptions.

TABLE III.

Values of $A_0$ and $A_1$ in the equation $\log x/p = A_0 - A_1 x$.

| Gas. | Charcoal. | $A_1$. | $A_0$. | Gas. | Charcoal. | $A_1$. | $A_0$. |
|---|---|---|---|---|---|---|---|
| $N_2$ | I | 525 | −5·059 | $C_2H_2$ | I | 510 | −2·887 |
| ,, | II | 410 | −4·961 | $N_2O$ | I | 410 | −3·209 |
| ,, | III | 388 | −5·263 | ,, | II | 400 | −3·160 |
| CO | I | 432 | −4·832 | ,, | III | 375 | −3·360 |
| $CO_2$ | I | 355 | −4·490 | ,, (40°) | I | 370 | −3·992 |

The values of the constants $A_0$ and $A_1$ for those cases where the equation holds are given in Table III. The equation put forward by Iljin (*Physikal. Z.*, 1925, **26**, 497) extends to the adsorption of gases by charcoal the results obtained by Szyszkowski (*Z. physikal. Chem.*, 1908, **64**, 385) for the surface tensions of aqueous solutions of certain fatty acids. Szyszkowski found that if $\sigma_0$ is the surface tension of pure water, and $\sigma$ that of a solution of the fatty acid of concentration $c$, then

$$\sigma_0 - \sigma = \beta \log (c/\alpha + 1),$$

where $\alpha$ is a constant decreasing as the length of the carbon chain in the acid increases, and $\beta$ is a constant characteristic of the solvent. Applying this to charcoal adsorption, Iljin puts $\sigma_0 - \sigma = Q/S$, where $S$ is the area of the adsorbing surface of the charcoal, the heat of adsorption thus being taken as a measure of the free energy of adsorption; $c$ must be replaced by $p$, so that $Q = \beta S \log (p/\alpha + 1)$, which is more convenient for plotting if written as $Q = B \log (p + \alpha) - B \log \alpha$, where $B = \beta S$. Then, if Iljin's equation holds, the graph of $\log (p + \alpha)$ against $Q$ should give a straight line intercepting the $\log (p + \alpha)$ axis at $\log \alpha$. The correct value of $\alpha$ is obtained by plotting with successive values of $\alpha$, differing by small increments, until two consecutive values are reached such that one gives a curve convex to one axis, and the next a curve convex to the other axis; the required value of $\alpha$ is then taken as the mean of these two values. Plotting the present results in this way, it was found that the best straight line was one that did not in general intercept the log $(p + \alpha)$ axis at log $\alpha$ (see, *e.g.*, Fig. 6), so that the results only fit a modified Iljin equation of the form $Q = B \log (p/\alpha + 1) + A$, where $A$ is usually a positive quantity, but is occasionally negative. The results for sulphur dioxide do not agree with the equation at all, for even with $\alpha = 0$ (its minimal value, since it is essentially positive), a curved line is still obtained; this is true also of Titoff's results for ammonia (*Z. physikal. Chem.*, 1910, **74**, 641) which Iljin quotes as fitting his equation.

TABLE IV.

Values of $\alpha$ and $B$ from Iljin's equation.

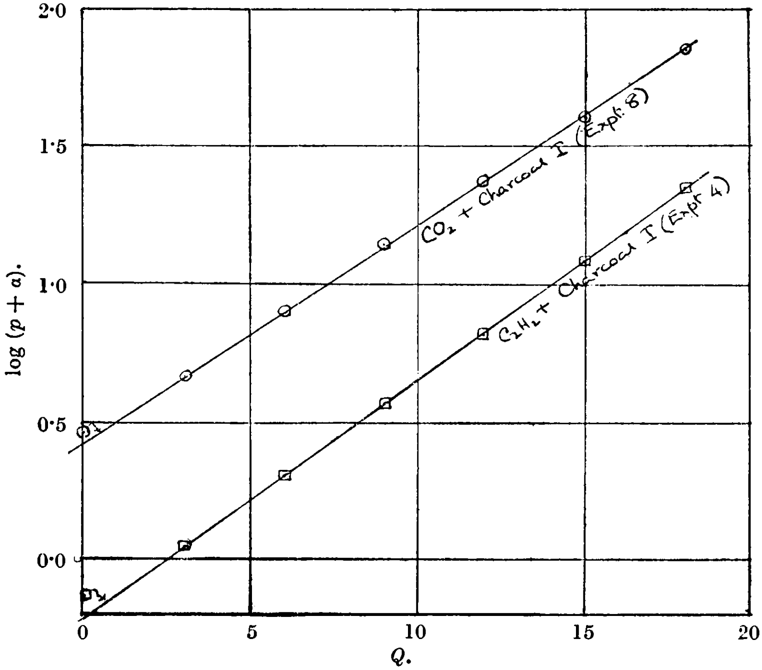
At 0°.

| Gas. | Observer.* | $\alpha_Q$. | $\alpha_x$. | $a \times 10^5$. | $b \times 10^6$. | $B_Q$ |
|---|---|---|---|---|---|---|
| | | (cm. of Hg) | | | | (calc.). |
| A | H. | — | 60 | 259 | 1361 | — |
| $N_2$ | T., Expt. IX | 55 | — | 270 | 1748 | 6·5 |
| | T., Expt. X | 55 | — | ,, | ,, | 7·35 |
| | G., Char. I | — | 50 | ,, | ,, | — |
| | G., Char. II | 50 | 55 | ,, | ,, | 5·98 |
| | G., Char. III | — | 50 | ,, | ,, | — |
| | H. | — | 50 | ,, | ,, | — |
| CO | H. | — | 50 | 285 | 1727 | — |
| | G. | — | 55 | ,, | ,, | — |
| $CH_4$ | H. | — | 15 | 366 | 1591 | — |
| $CO_2$ | T. | 2·80 | 2·80 | 701 | 1862 | 13·2 |
| | R. | — | 0·80 | ,, | ,, | — |
| | G. | 2·95 | 2·95 | ,, | ,, | 12·4 |
| $C_2H_2$ | G. | 0·75 | 0·75 | 875 | 2293 | 11·3 |
| $C_2H_4$ | G., Expt. 9 | 0·20 | — | 889 | 2534 | 6·63 |
| | G., Expt. 9*a* | 0·20 | 0·20 | ,, | ,, | 6·28 |
| $C_2H_6$ | G. | 0·16 | 0·16 | 1060 | 2800 | 11·6 |
| $N_2O$ | G., Char. I | 1·65 | 1·70 | 728 | 1899 | 10·7 |
| | G., Char. II | 1·50 | 1·70 | ,, | ,, | 13·2 |
| | G., Char. III | — | 1·70 | ,, | ,, | — |
| At 40·35°. | | | | | | |
| $N_2O$ | G., Char. I | 10·0 | 12·0 | 728 | 1899 | 14·4 |
| Adsorption by silica gel at 0°. | | | | | | |
| $N_2O$ | P. | — | 35 | 728 | 1899 | — |

* H = Homfray; T = Titoff; G = Gregg; R = Richardson; P = Patrick (*J. Physical Chem.*, 1925, **29**, 421).

The value of $\alpha$ at a given temperature is roughly characteristic of a gas, varying considerably from one to another. This makes it possible to deduce the approximate value of $\alpha$ even when no heat measurements are available. For since $Q = kx^n$, we may put $kx^n = B \log (p + \alpha) - B \log \alpha$; and since $n$ is never far from unity, the graph of log $(p + \alpha)$ against $x$ also gives a nearly straight line; or, alternatively, the values of $\alpha$ necessary to give a straight line with the measurements of $Q$ and $x$, respectively, are quite close to one another, as shown by the figures for $\alpha$ derived by the two methods (Table IV). In this table, the gases are arranged in order of decreasing $\alpha$, and it will be seen that they then stand in order of increasing $a$ and $b$ (the van der Waals constants), so that a complete parallelism exists between $\alpha$, on the one hand, and $a$ and $b$, on the other. (In the table, the suffix indicates whether the value is derived from the $Q$- or $x$-curve.) Moreover, the fact that the value of $\alpha$ decreases as the value of $b$ (which is a measure of the size of the molecule) increases, is analogous to Szyszkowski's result for the surface tension of solutions, in which he found that $\alpha$ decreases with increasing length of the hydrocarbon chain. This indicates that there is a close analogy between adsorption at a charcoal–gas interface and that at a water–gas interface, but it is difficult to pursue the analogy further.

FIG. 6.



Unfortunately, it is impossible to calculate $B$ except by using heat measurements, for the equation $kx^n = B \log (p/\alpha + 1) + A$ shows that a knowledge of $k$ is necessary for obtaining $B$. It will be seen that, in contrast to Szyszkowski's results, $B$ does not remain constant for a given charcoal, though its variation is much less than that of $\alpha$. The non-constancy is possibly due to the fact that $Q$ is not a true measure of the free-energy change; furthermore, the true analogue to Szyszkowski's $\beta$ is not $B$, but $B/S$, and the adsorbing surface $S$ of the charcoal may vary in an unknown way from gas to gas.

It is hoped to discuss more fully elsewhere some of the current theories of adsorption in the light of both the present results and those of other workers.

## *Summary.*

1. Measurements are described of the heat of adsorption, the equilibrium pressure, and the amount adsorbed, for eight gases on a standard charcoal at 0°, with the aid of Bunsen's ice calorimeter. A few experiments were also carried out at 40·35° using a phenol calorimeter, and in some cases the charcoal was replaced by other standard samples.

2. The phenomenon of hysteresis has been traced to the presence of some non-condensable gas in the adsorption system, as other workers have found.

3. For the integral heat of adsorption $Q$, the relationship $Q = kx^n$ has been found to hold, where $x$ is the amount adsorbed and $k$ and $n$ are constants; $n$ is roughly characteristic of the gas and lies between approximately 0·9 and 1·0; $k$ is slightly decreased by previous adsorption and subsequent elimination of the same or another gas.

4. The Williams–Henry equation, $\log x/p = A_0 - A_1x$, where $p$ is the equilibrium pressure and $A_0$ and $A_1$ are constants at constant temperature, is fairly satisfactory for all except the readily condensable gases.

5. With similar limitations, the relationship between $p$ and $Q$ is expressed fairly well by a modified Iljin equation of the form $Q = B \log (p/\alpha + 1) + A$. A close parallelism exists between the value of $\alpha$ and the corresponding values of the constants $a$ and $b$ in van der Waals's equation, a fact which recalls the results of Szyszkowski for the surface tension of aqueous solutions.

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UNIVERSITY OF LONDON,
KING'S COLLEGE, W.C. 2.

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