Acknowledgment is made of a studentship and a fellowship granted to one of us by the Research Council of Canada.

Summary

The preparation and purification of hydrogen disulfide have been described and the conditions investigated for obtaining large yields. It was shown that the higher persulfides are not formed by the solution of sulfur in hydrogen disulfide. The solubility of sulfur in the hydrogen disulfide was measured. The melting point, vapor pressures, density of the liquid, surface tension, refractive index, specific heat and latent heat of fusion of hydrogen disulfide were determined, and related constants were calculated. A comparison of the physical properties of hydrogen sulfide, hydrogen disulfide, water and hydrogen peroxide brings out the relations existing between these compounds.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THE NATURE OF THE SORPTION BY CHARCOAL OF GASES AND VAPORS UNDER GREAT PRESSURE

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The McBain–Bakr sorption balance[1] has enabled regions of sorption previously inaccessible to be explored with comparative ease. Nearly all studies of sorption have been broken off below atmospheric pressure,[2]

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[1] The microbalance described by McBain and Tanner [*Proc. Roy. Soc.* (London), **A125,** 579 (1929)] has many points of superiority over the McBain–Bakr balance. It is of the beam type, of extreme sensitivity, robust and compact enough to be placed within a glass tube and subjected to great extremes of temperature and pressure while in use.

[2] The chief investigations in which higher pressures have been used are: J. Hunter [*J. Chem. Soc.*, **24,** 76 (1871)], charcoal with ammonia and cyanogen to 3.5 atmospheres and carbon monoxide to 5.3 atmospheres in a Fontana experiment; E. W. R. Pfeiffer ["Dissertation," Erlangen, **1882,** *cf. Beiblätter,* **8,** 630 (1884)], glass wool or charcoal with glass wool in Cailletet's compression apparatus with carbon dioxide or ammonia between 2 and 8 atmospheres, showing no saturation value; Sir James Dewar [*Proc. Roy. Inst.*, **18,** 437 (1906)], 1 g. of charcoal at −185° sorbed 9.3 cc. of hydrogen at 1 atmosphere pressure; this was raised to 13.81, 156.7, 149.3, 145.5 and 138.1 cc. at 5, 10, 15, 20 and 25 atmospheres, respectively; Dewar regarded this as constancy. J. I. Graham [*The Colliery Guardian,* **122,** 809 (1921)], carbon dioxide, methane and nitrogen by dry and moist coal up to about 30 atmospheres. The moist sorbed about one-third as much as the dry coal dust, 1 g. of which, together with a small amount of glass wool, at 30 atmospheres, sorbed about 10 cc. of nitrogen, the amount still apparently rising with increase in pressure. H. Briggs and W. Cooper [*Proc. Roy. Soc. Edinburgh,* **41,** 119 (1921)] tested the capacity of steel cylinders partly filled with moist or dry charcoal or silica, using nitrogen, oxygen and hydrogen in some cases up to 100 atmospheres. They found agreement between their results and the Williams–Henry formula, but in some cases the term $k_2 \times x/m$ of that formula was negligible. F. A. Henglein and M. Grzen-

chiefly because of the rapidly growing inaccuracy and uncertainty of measurements where sorption is increasing only slowly with pressure, and the amount of gas or vapor in the poorly defined "dead space" within the apparatus is rapidly becoming the dominant quantity observed.

The present communication describes measurements of the sorption of nitrogen, nitrous oxide and ethylene at pressures up to 60 atmospheres, which were completed at Bristol University, England, early in 1927. The results are of especial interest in that, being carried out with a permanent gas and with vapors above and below critical temperatures and pressures, they enable a decision to be reached between rival views as to the nature of sorption by charcoal.

Experimental

Apart from minor modifications introduced to suit each gas studied, the apparatus consists essentially of the main experimental glass tube A which contains the vapor or gas to be studied and in the upper half of which there is a spiral spring S of fused silica[3] supported from a bent wire C, which is held by friction in the tube, and carrying at its lower end a platinum bucket B filled with charcoal. The temperature of the charcoal is kept constant by means of a thermostat surrounding the upper half of the glass tube. The sorption isotherm is obtained by measuring at a series of pressures the weight of gas sorbed by the charcoal as determined by the increase in length of the silica spring.

Kahlbaum's pure sugar charcoal was used in all experiments after activation either in steam or in air. The former (referred to in another communication[4] as "Wright's Steam D" charcoal) was prepared by heating at 700° in a silica flask for thirty minutes, a current of steam blown against the powdered charcoal, with frequent shaking, at the same temperature for forty-five minutes and the heating continued for ten minutes.

Another portion of the same sugar charcoal was activated by heating in a porcelain tube in an electric furnace at 1140° for twelve hours. During this time a slow stream of air was passed over the charcoal at intervals, so that about 20% of the original charcoal was oxidized. This is elsewhere[5,4] referred to as "Smith's Air C" charcoal.

In all cases the charcoal was evacuated after the apparatus had been set up, keeping the charcoal at 450° by an improvised heating coil[6] of nichrome wire embedded in a hollow tube of asbestos. The vacuum must be applied very slowly to avoid the charcoal blowing out of the bucket. Evacuation was continued until the charcoal had been exposed to a vacuum of less than 10^{-4} mm. for four or five hours. After the charcoal had stood in contact with the nitrous oxide, ethylene or nitrogen at one atmosphere pressure or more for many hours, the evacuation of the charcoal was repeated with the

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kowski [*Z. angew. Chem.*, **38,** 1186 (1925)], ammonia, sulfur dioxide and chlorine by carbon up to several atmospheres.

[3] For details see J. W. McBain and A. M. Bakr, THIS JOURNAL, **48,** 690 (1926). Silica fibers about 0.1 mm. thick and one meter long are supplied by the Silica Syndicate.

[4] J. W. McBain, H. P. Lucas and P. F. Chapman, communicated to THIS JOURNAL.

[5] J. W. McBain, D. N. Jackman, A. M. Bakr and H. G. Smith, *J. Phys. Chem.*, **34** (1930).

[6] A strip of asbestos paper about $^1/_{16}$ inch thick soaked in water was wrapped once around a glass tube and the edges kneaded together. Nichrome wire (15 feet, 15 ohms) was wound upon this and covered with further layers of soaked asbestos with the edges well kneaded together. The wet cylinder was slid off the tube by firm pressure and dried by an electric current of about two amperes.

same care as before. This is effective in displacing some of the residual impurities in the charcoal.

Sorption of Nitrous Oxide

The nitrous oxide used was obtained from a small cylinder as supplied for dental purposes.

The sorption tube A, Fig. 1, was 12 mm. in internal diameter, 18 mm. in external diameter and approximately 40 cm. in length and was carefully sealed at the bottom before use, the balance being introduced from the top. Sufficient space was left below the bucket of charcoal so that liquefied gas could be present in excess and yet be far enough from the bucket to allow the temperature of the liquid to be controlled over the range −96.5 to +20.9° without disturbing the temperature of the charcoal. The top of the tube was carefully drawn out, while the tube was in the clamp, until the internal diameter was 1 to 2 mm., the walls being nowhere thinner than 5 mm. on the tapering portion of the tube. The completed sorption tube was sealed onto an apparatus constructed of glass tubing and designed to allow evacuation via tap T_1 and also to allow the admission of nitrous oxide via tap T_2 at pressures up to 80 cm. of mercury. Taps T_1 and T_2 were mercury sealed, and O was a mercury trap which acted as a safety valve.

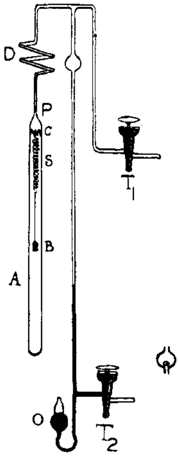

Fig. 1.—The sorption balance connections as used for nitrous oxide.

The general principle of the apparatus described above was due to Mr. H. H. M. Wright, who began the experimental work. His values for the sorption of nitrous oxide at 15° by steam activated charcoal ("Steam D"), which had been previously evacuated to less than 0.0001 mm. at 470°, were $x/m = 0.099$ and 0.106 at one atmosphere. For the same charcoal evacuated only to 0.007 mm. at 470° the value of x/m was 0.204 at 19 atmospheres and 15°.

The silica spring was calibrated both before and after the experiment, but the latter calibration has invariably been used for calculating the results presented. Experience has shown that any considerable elevation in temperature produces a change in the length of such a spring, which decreases in magnitude with time and may be due to the reattainment of an equilibrium of state in the silica disturbed by the heating during bending.[7] The effect is most noticeable in the period of evacuation when the charcoal is heated to 450–500°. In later experiments on nitrogen and ethylene the spring was not heated during evacuation, the bucket being hung on a fiber 10 cm. long from the end of the spring. It is now our custom to anneal springs for thirty to forty hours at 200° before use, as this is found to remove the effect.

The buckets B were made of the thinnest platinum foil, free from pinholes and supplied by Johnston Matthey and Co., London. They were welded upon a carbon

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[7] I. Sawai and O. Morisawa [*Z. anorg. allgem. Chem.*, **173**, 361 (1928)] found similarly that threads of lead borate glass when first heated to temperatures between 180 and 395° shrink on account of release of the longitudinal strains produced when they are being drawn. This effect did not occur if the thread were sufficiently loaded. A careful, extensive study of the increase in the elastic constants of fused quartz upon heating has recently been published by H. D. H. Drane, *Proc. Roy. Soc.* (London), **122A**, 274 (1929). See also the data of the Bureau of Standards quoted in *Ind. Eng. Chem., News Edition*, **8**, 14 (1930).

rod as a form and were about 15 mm. deep and 5 or 6 mm. in diameter, weighing from 0.09 to 0.12 g. and holding about 0.12 g. of charcoal.

A Kaye–Backhurst steel mercury pump, backed by a Cenco "hyvac" pump, was used, the combination readily producing 10^{-5} mm. The pumps were joined to a wide tube branching into mercury sealed taps, one of which was T_1, Fig. 1; another led to a McLeod gage reading to 10^{-5} mm. and a Pirani gage, while a third tap led to a tube of calcium chloride and phosphorus pentoxide by which air could be admitted when desired without admitting moisture.

After the second evacuation, the charcoal and tube were allowed to cool, while tap T_1 was left open, the length of the spring S read carefully with a Wilson traveling microscope,[8] three or four concordant values being obtained, and from this value the weight of gas free charcoal was calculated.

In order to introduce the nitrous oxide into the apparatus, the lower tip of the sorption tube A, Fig. 1, was cooled in liquid air, and the gas was supplied at about 80 cm. of mercury pressure through tap T_2. The mercury trap O acted as a safety valve, preventing a rise of pressure when the level of the liquid air fell, or the rate of condensation decreased for any other reason. The liquid air level was gradually raised until a column of solid nitrous oxide about 4 inches deep was obtained. Tap T_2 was then closed and T_1 opened. Tube A was pumped out to about 2 mm. and refilled with nitrous oxide several times to remove traces of nitrogen likely to come from the nitrous oxide cylinder. The sorption tube was then sealed off at P under vacuum and set up in the screen, Fig. 2. After sealing off the capillary tube, it was found advisable not to allow the internal pressure to rise above atmospheric for twelve hours. In nearly every case impatience led to blowing off the tip at some stage of the experiment.

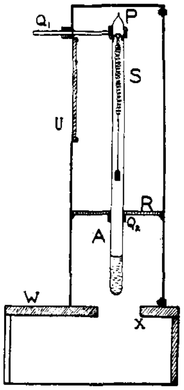

Fig. 2.—Protecting screen.

The screen, Fig. 2, consisted of a sheet-iron box 6 inches square and 18 inches long, having one side removable by undoing nuts and opening only at one end. A slit U, 0.5 inch wide, was cut in the face opposite the removable one, and a sheet of plate glass 0.25 inch thick fitted behind the slit. The box stood on the open end with slit to the front. Above the slit and also in one side about 6 inches from the bottom, two brass cylinders of 1-inch diameter were mounted. They were drilled so that the brass rods Q_1 and Q_2, 0.25 inch in diameter, could slide in them. Two ends of a steel helix were secured to the end of each rod like a spring fountain pen clip so that the tube could be slid into them and be firmly held without straining the glass. Since these rods were at right angles, it was possible to adjust the tube A very easily and allow the spring S to swing freely. An asbestos partition R was mounted below the level of the bucket and nichrome coils were introduced above the partition so that the bucket and charcoal could be warmed to any desired temperature. The screen stood upon a bench W about 7 inches high, 15 inches wide and 18 inches long, having a hole X cut in the top. In operation a Dewar vessel was raised through X to surround the liquid nitrous oxide, and the door of W replaced.

A Dewar vessel containing carbon dioxide snow and ether was used as a bath for maintaining the liquid nitrous oxide at any desired temperature below 0°. Stirring and frequent small additions of solid carbon dioxide sufficed to keep the temperature constant within 0.5° of the desired value. The temperatures were observed by a pentane thermometer which was calibrated at the time of performing the experiment by ob-

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[8] W. Wilson, Gourley Works, Seven Sisters Road, South Tottenham, London, E. C., England. This microscope could be read to ±0.001 cm.

serving the freezing points of pure liquids. The vapor tension corresponding to the observed temperature of the liquefied nitrous oxide was obtained from the vapor tension–temperature graph determined in a previous paper,[9] and the length of the spring S was read by the traveling microscope after an interval of not less than two hours since the last change in temperature of the bath. It was found that no change in length of the spring occurred over longer periods, and values of sorption approached from either side of the equilibrium lay on the same curve. Since the same traveling microscope was used for calibrating the springs as for taking sorption measurements, no calibration of the scale was necessary, as any errors were automatically eliminated. Care was taken that all final movements of screws for fine adjustment of height or focus were carried out in the same direction. For higher pressures, necessitating baths with temperatures above 0°, mixtures of tap water and ice water were used and were maintained constant by occasional addition of small quantities of ice water.

The data for nitrous oxide are tabulated in Tables I–III, in which T is the temperature of the liquid nitrous oxide in degrees centigrade, and p is the corresponding vapor tension in atmospheres. To save space, only the first part of Table I is given in full. The apparent weight of gas sorbed, given as x uncorrected in Table I, equaled the difference in length of the spring at pressure p and the zero reading ($L_p - L_0$) divided by the sensitivity of the spring. The sensitivity of the spring is ten times the extension produced by 0.1 g. increase in load. A correction for buoyancy must be made.

TABLE I

SORPTION OF NITROUS OXIDE BY "STEAM D" CHARCOAL. TUBE III

Mass of charcoal, m = 0.1023 g. Sensitivity of spring, S = 15.25 cm./g. Total volume of charcoal and platinum bucket, 0.06087 cc.

T, °C.	p, atm.	ρ G./cc.	$L_p - L_0$, cm.	x (uncorr.), g.	Buoyancy, g.	x (corr.), g.	x/m
Temperature of charcoal, 20°. Zero reading of spring, S = 8.647 cm.							
-96.5^a	0.6	0.000923	0.237	0.01554	0.00006	0.0156	0.153
-87.0	1.1	.00204	.233	.01528	.00012	.0154	.151
-72.5^a	2.4	.00449	.274	.01797	.00027	.0182	.178
-62.0	4.0	.00758	.288	.01889	.00046	.0194	.189
-50.5^a	6.3	.0123	.282	.01849	.00075	.0192	.188
-41.5	8.8	.0178	.280	.01836	.00109	.0195	.190
-39.0^a	9.7	.0199	.289	.01895	.00121	.0202	.197
-30.5	13.0	.0280	.287	.01882	.00170	.0205	.201
-18.0^a	19.3	.0450	.278	.01823	.00274	.0210	.205
-18.0^a	19.3	.0450	.278	.01823	.00274	.0210	.205
-18.0^a	19.3	.0450	.285	.01869	.00274	.0214	.210
-17.0^a	19.8	.0464	.279	.01830	.00283	.0211	.207
$+0.5^a$	31.1	.0814	.255	.01672	.00496	.0217	.212
$+0.5$	31.1	.0814	.251	.01646	.00496	.0214	.209
$+3.8$	33.4	.0895	.246	.01613	.00545	.0216	.211
$+7.4$	36.3	.100	.233	.01528	.00611	.0214	.209
$+9.4$	38.0	.107	.225	.01475	.00650	.0213	.208
$+12.9$	41.6	.122	.215	.01410	.00741	.0215	.210
$+13.9$	42.8	.127	.205	.01344	.00772	.0212	.207

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[9] G. T. Britton, *Trans. Faraday Soc.*, **25,** 520 (1929).

TABLE I (*Concluded*)

T, °C.	*p*, atm.	Buoyancy, g.	*x*/*m*	*T*, °C.	*p*, atm.	Buoyancy, g.	*x*/*m*
Temperature of charcoal, 45°							
−84.0^a	1.3	0.00013	0.126	+ 0.2^a	30.8	0.00388	0.186
−84.0	1.3	.00013	.115	+13.2	42.0	.00582	.192
−42.5^a	8.5	.00090	.167	+14.3^a	43.5	.00608	.189
−40.5^a	9.1	.00096	.170	+14.5	43.8	.00614	.193
−22.5^a	16.9	.00187	.175	+17.5	48.6	.00692	.191
+ 0.2	30.8	.00388	.186	+19.5	49.7	.00707	.185
Temperature of charcoal, 67°							
−88.0^a	1.1	0.000106	0.0869	+ 0.2^a	30.8	0.00360	0.174
−49.5	6.6	.00065	.151	+12.9	41.6	.00506	.175
−45.3^a	7.7	.00076	.141	+20.9	51.3	.00618	.172
−37.0^a	10.3	.00103	.154				

[a] Desorption experiment.

TABLE II

SORPTION OF NITROUS OXIDE BY "STEAM D" CHARCOAL. TUBE IV

Mass of charcoal, m = 0.1463 g. Sensitivity of spring, S = 22.50 cm./g. Total volume of charcoal and platinum bucket, 0.08618 cc.

T, °C.	*p*, atm.	Buoyancy, g.	*x*/*m*	*T*, °C.	*p*, atm.	Buoyancy, g.	*x*/*m*
Temperature of charcoal, 20°							
−88.0^a	1.1	0.00018	0.148	−23.0	16.6	0.00323	0.200
−78.5^a	1.8	.00029	.150	−13.0	21.9	.00452	.200
−77.0^a	2.0	.00032	.160	+ 0.2^a	30.8	.00693	.210
−69.5	2.8	.00045	.181	+ 0.2^a	30.8	.00693	.210
−65.0	3.5	.00057	.183	+ 1.8	32.0	.00728	.205
−53.0	5.8	.00097	.191	+ 8.4	37.1	.00890	.202
−47.0^a	7.3	.00125	.189	+12.9^a	41.6	.01049	.206
−41.5^a	8.8	.00154	.193	+13.9^a	42.8	.01093	.203
−33.0	11.9	.00218	.199	+14.6	43.8	.01131	.207

[a] Desorption experiment.

TABLE III

SORPTION OF NITROUS OXIDE BY "STEAM D" CHARCOAL. TUBE V

Mass of charcoal, m = 0.0943. Sensitivity of spring, S = 12.02 cm./g. Total volume of charcoal and platinum bucket, 0.05644 cc.

T, °C.	*p*, atm.	Buoyancy, g.	*x*/*m*	*T*, ° C.	*p*, atm.	Buoyancy, g.	*x*/*m*
Temperature of charcoal, 20°							
−77.0^a	2.0	0.00021	0.162	−18.0^a	19.3	0.00254	0.214
−75.5^a	2.1	.00022	.161	+ 0.1^a	30.7	.00452	.218
−74.0	2.3	.00024	.171	+ 1.6	31.9	.00475	.218
−64.5	3.5	.00037	.195	+ 9.6^a	38.1	.00605	.208
−55.5^a	5.2	.00056	.198	+10.9	39.4	.00636	.211
−55.5	5.2	.00056	.191	+15.5	45.1	.00773	.208
−43.5	8.2	.00093	.202	+17.7	49.0	.00870	.214
−29.0^a	13.7	.00168	.209				

TABLE III (*Concluded*)

T, °C.	p, atm.	Buoyancy, g.	x/m	T, °C.	p, atm.	Buoyancy, g.	x/m
Temperature of charcoal, 45°							
−74.5[a]	2.2	0.00021	0.127	−17.5	19.5	0.00204	0.187
−57.5[a]	4.8	.00046	.163	−16.6	20.0	.00210	.184
−53.0	5.8	.00056	.150	+ 0.2[a]	30.8	.00360	.193
−45.0[a]	7.8	.00076	.169	+ 8.4	37.1	.00459	.192
−40.5[a]	9.1	.00089	.167	+16.6	46.7	.00614	.185
−27.0	14.6	.00147	.179	+17.0	47.7	.00629	.187
Temperature of charcoal, 67°							
−77.0[a]	2.0	0.000179	0.0910	+ 0.8	31.3	0.00340	0.179
−71.5	2.5	.00022	.110	+11.6	40.1	.00452	.179
−57.0	4.9	.00044	.129	+16.6	46.7	.00526	.177
+ 0.2[a]	30.8	.00334	.170	+17.1[a]	47.8	.00538	.174
+ 0.8[a]	31.3	.00340	.179	+18.3	48.5	.00545	.175

[a] Desorption experiment.

Data for the density of the vapor of nitrous oxide are given in a previous communication.[9] From the plot of pv against p the values of density in g./cc. appropriate to the pressures used in obtaining points on the sorption isotherm were calculated. These are given as ρ in Table I. The total volume displaced in cubic centimeters (the volume of the platinum composing the bucket plus the volume of the charcoal it contained) multiplied by the density gave the buoyancy correction in grams. This was added to the apparent sorption (x uncorrected), and the sum (x corrected) was divided by the mass of charcoal m to give values of sorption designated as x/m in the tables. The volume of the charcoal was calculated from its mass in vacuo by assuming 1.8 g./cc. as its density.

Sorption of Ethylene

The apparatus for measuring the sorption of ethylene was essentially the same as that used for nitrous oxide. Ethylene condenses very much more slowly than nitrous oxide, and hence it was condensed at 2 to 3 atmospheres pressure. Between the sorption tube A and the glass spiral D, Fig. 1, a glass T-piece of capillary tubing was introduced. The third leg of this was bent downward and again branched (see Fig. 3). At the ends of the branches two swellings were made in order that pressure tubing could be wired on safely. The swellings were drawn down into thin tips G and G_1 which were sealed and a slight scratch made on them with a file. Tip G was connected by pressure tubing Y to a closed-end mercury manometer and a cylinder of ethylene, the connecting tubing having first been swept free of air by a current of ethylene.

After the preliminary evacuation ethylene was admitted by turning open the valve of the gas cylinder and breaking the tip G. As G was so fine, no sudden rush of gas took place. The rubber connection was then transferred to the other leg and the fine tip G sealed by a small flame.

Following the second evacuation, the sorption tube was drawn off at Z, and ethylene was introduced via G_1 as before. A Dewar flask of liquid air was placed so that the lower end of the sorption tube just dipped in it, and the ethylene pressure raised to 2 or 3 atmospheres. From time to time the Dewar vessel was raised a little until a suitable depth of ethylene was obtained. Impurities in the gas were swept out by allowing the solid ethylene to melt and boil off, G having been opened. The sorption tube was then sealed off under a slight vacuum obtained by slipping over G a rubber connection to the pumps.

In order to obtain the sorption isotherm of ethylene at 0°, a piece of glass tubing, 2.5 inches in diameter, was drawn down to a neck which would just slide over the sorption tube. A length of 5 inches was left on the neck, and the resulting jacket, which gave a water-tight joint, was secured by a short piece of rubber tubing to the sorption tube at the point where the bucket of charcoal was suspended. This jacket was kept packed with ice. The spring S was thus at room temperature, the charcoal at 0°, and the end of the sorption tube containing the liquid ethylene could still be kept at any desired temperature with carbon dioxide and ether mixtures.

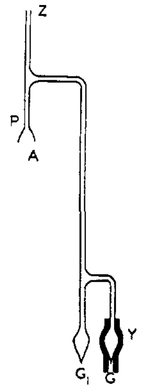

Fig. 3.—Capillary tubing introduced in apparatus for sorption of ethylene.

TABLE IV

SORPTION OF ETHYLENE BY "AIR C" CHARCOAL. TUBE II

Mass of charcoal, m = 0.0789 g. Sensitivity of spring, S = 14.06 cm./g. Total volume of charcoal and platinum bucket, 0.04825 cc.

T, °C.	p, atm.	Buoyancy, g.	x/m	T, °C.	p, atm.	Buoyancy, g.	x/m
Temperature of charcoal, 0°							
−73.0	4.8	0.00031	0.188	−12.5	29.5	0.00274	0.224
−55.7	9.3	.00063	.209	−10.7	30.8	.00293	.222
−30.5	19.5	.00154	.225	− 5.5	34.9	.00358	.222
−28.5	20.5	.00164	.226				
Temperature of charcoal, 20°							
−77.0	4.1	0.00024	0.176	−32.5	18.6	0.00127	0.214
−73.0	4.8	.00028	.186	−25.0	22.2	.00158	.210
−61.0	7.6	.00046	.186	−16.0	27.3	.00207	.214
−57.5	8.7	.00054	.194	− 9.5	31.7	.00254	.208
−49.5	11.5	.00073	.202	0	39.9	.00358	.209
−37.5	16.3	.00109	.203				
Temperature of charcoal, 45°							
−79.0	3.8	0.00020	0.161	−24.5	22.5	0.00143	0.198
−61.0	7.6	.00042	.175	−10.5	30.9	.00213	.200
−49.5	11.5	.00066	.182	− 8.0	32.9	.00232	.201
−42.5	14.2	.00084	.186	0	39.9	.00298	.201
−34.5	17.7	.00108	.198				

Table V

Sorption of Ethylene by "Air C" Charcoal. Tube III

Mass of charcoal, m = 0.1051 g. Sensitivity of spring, S = 19.94 cm./g. Total volume of charcoal and platinum bucket, 0.06288 cc.

T, °C.	p, atm.	Buoyancy, g.	x/m	T, °C.	p, atm.	Buoyancy, g.	x/m
Temperature of charcoal, 0°							
−78.0	4.0	0.00033	0.163	−31.7	19.0	0.00194	0.206
−54.5	9.7	.00087	.189	−25.0	22.2	.00237	.209
−44.5	13.4	.00126	.198	−16.3	27.1	.00314	.206
−42.5	14.2	.00135	.201	−12.0	29.9	.00364	.202
Temperature of charcoal, 20°							
−88.0	2.5	0.00019	0.148	−29.7	19.9	0.00180	0.182
−63.7	6.9	.00054	.166	−22.5	23.5	.00222	.193
−52.0	10.7	.00088	.170	−10.7	30.8	.00318	.191
−49.4	11.6	.00096	.174	0	39.9	.00466	.191
−37.0	16.5	.00144	.185	+ 3.0	42.9	.00524	.191
Temperature of charcoal, 45°							
−82.0	3.3	0.00023	0.132	−11.7	30.2	0.00270	0.169
−48.0	12.1	.00091	.148	− 9.5	31.7	.00287	.166
−28.0	20.8	.00170	.158	0	39.9	.00389	.169

The experimental data found for ethylene are given in Tables IV and V. Tube I burst, which prevented the calibration of the spring from being checked. All calculations were made exactly as for nitrous oxide, and the pressure p and the density were obtained from vapor tension–temperature and p–pv graphs, respectively, which had been determined in the previous communication already mentioned in the case of nitrous oxide.

Sorption of Nitrogen

Mr. H. H. M. Wright placed the balance in a steam boiler water-level gage secured to a heavy iron stand. A passage in the upper casting communicated from the packing gland to a copper tube leading from a cylinder of compressed nitrogen via a constant pressure gas regulator. Another passage led to a gas valve by which the apparatus could be connected to the vacuum pumps by pressure tubing or isolated from them as desired. A passage in the lower casting led to a large brass cylinder bolted by a flanged joint to the casting. The silica spring was placed in the glass tube and the platinum bucket containing charcoal was suspended inside the brass cylinder by a fine fiber from the spring. A small electric heater, made by winding nichrome wire on a silica glass tube, fitted inside the cylinder and heated the charcoal to the desired temperature. This heater was calibrated before use. The leads for the heating current were led through the gaskets between the flanges, which were water-cooled to prevent decomposition of the rubber in the packing gland. Wright's data for nitrogen are graphed in Fig. 4.

A better type of apparatus was then devised. It was necessary to seek a better method of uniting glass and metal with a vacuum and pressure tight joint. Many possible joints[10,11] are described in the literature, but none were successful. A much simpler joint, Fig. 5, which is highly efficient and very easily made, was developed. A cylinder of brass 7 cm. long was drilled out to slide over the given capillary tube N (approximately 7 mm. in diameter), and a length of about 5 cm. was drilled out to 1.5 cm. diameter and tapped to take a small packing nut I, which just slipped over the capillary tube. The copper tube F was soldered into H, and the whole inverted. The capillary N was placed in position, and the brass warmed to the softening point of a good sealing wax. Sealing wax was then melted in until the space was filled, and the hot nut I screwed in about four turns, squeezing soft wax between the brass and the glass, where they were a close fit. The joint was allowed to cool without disturbance and was then ready for use. Such joints have held vacuum to 0.0005 mm. and internal pressures up to 65 atmospheres without any sign of failure or flowing of the wax. They will stand much vibration and rough treatment without failure. Waterston's "Bee Brand" Prize Medal sealing wax proved highly satisfactory.

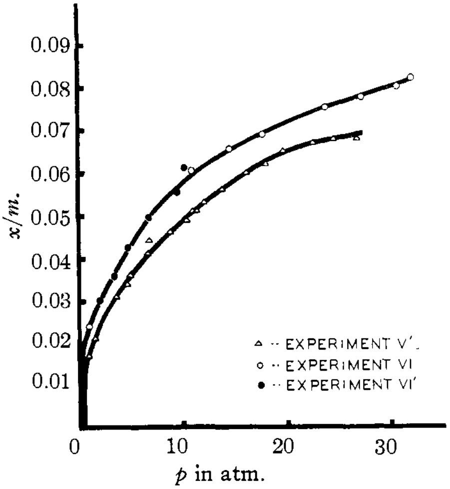

Fig. 4.—Wright's data for sorption of nitrogen by "Steam D" charcoal at 15°. Temperature of evacuation of charcoal is 500°. In Experiment V′, vacuum obtained is 0.5 mm. and time of evacuation is nineteen hours. In Experiments VI and VI′, vacuum attained is 0.02 mm. and time of evacuation is twenty-four hours.

The sorption tube used in these experiments for measuring the sorption of nitrogen was of the same dimensions as that used for nitrous oxide but was carefully drawn out to a thick capillary at the lower end L, Fig. 6. After the introduction of the balance through the top, the upper end of the sorption tube was drawn to a thick capillary and fused onto a glass capillary N which was joined to a copper tube F by means of the special joint J (compare Fig. 5).

A small gas cylinder D, Fig. 7, was surmounted by a brass manifold carrying two good gas regulating valves V_1, V_2 and a pressure gage K reading

[10] M. L. Dundon, This Journal, **45,** 716 (1923).

[11] E. C. McKelvy and C. S. Taylor, *ibid.*, **42,** 1364 (1920).

to 150 atmospheres. V_2 was connected to a large gas cylinder E, and V_1 was joined to the copper tube F. The valves were carefully packed with leather washers and vacuum grease and proved capable of holding a vacuum of 0.0005 mm. The cylinders, valves, gages, unions and copper leads were supplied by the British Oxygen Company and proved satisfactory in use. The nitrogen, which had a purity of 99.5%, was obtained from the same company in cylinders charged to 120 atmospheres. This method of gas control was adopted because the automatic gas regulator previously used by Mr. Wright was very troublesome, allowing the pressure to rise slowly. Leaks, which were rare and slight, were readily compensated by hand operation before the pressure had changed more than a fraction of one atmosphere.

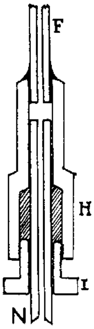

Fig. 5.—A vacuum- and pressure-tight joint for uniting glass and metal by means of sealing wax.

The glass portion of the apparatus was enclosed entirely in a sheet-iron screen with a slit covered by plate glass. A sheet of iron $^1/_{16}$ inch thick was bent into a box of square section 4″ × 4″ with the opening at the back. The opening was sprung out wider to pass the tube and clamp when placing the screen in position and was closed by means of wire tied around the screen.

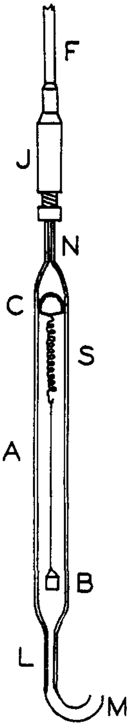

Fig. 6.—The sorption balance as used for nitrogen.

For the evacuation or outgassing of the charcoal the capillary tube L, Fig. 6, was fused to a tube M leading to the vacuum pumps. The charcoal was heated to 450° by an electric heater, and the pumps started up as described for the experiments with nitrous oxide. The valve V_1, Fig. 7, was shut during this operation. The time of evacuation was considerably longer than for nitrous oxide as, owing to small leaks, the pumps were much longer in reaching a low enough vacuum. In view of the number of mechanical joints, any pressure below 10^{-3} mm. was regarded as satisfactory, and outgassing was carried out for four to five hours at the lowest pressure obtainable. After the first outgassing, nitrogen was passed in via V_2 and V_1 from E until the pressure was one atmosphere. After fifteen hours the evacuation was repeated, the charcoal cooled, and the zero reading taken as for nitrous oxide. The tube L, Fig. 6, was carefully warmed up by the blowpipe and sealed off under vacuum, the pumps still running to carry off any gases or vapor given off by the glass.

While measuring the sorption of nitrogen, the valve V_1, Fig. 7, was always left open. The main valve of E was opened, and gas admitted by V_2

into D and A up to any desired pressure as read on K. The cylinder D served to prevent violent inrushes of gas, as its size demanded a considerable quantity of gas to produce small pressure changes. Moreover, any small leakage at valves or unions would be minimized and readily made up by small additions of gas by V_2. The length of the spring S was read after an interval of not less than one hour. A shorter period can be permitted in this experiment than in the nitrous oxide experiment, because there is no liquid–vapor equilibrium to establish in addition to the gas or vapor–solid equilibrium, the pressure being put at its final value in a minute or so. When equilibrium had been approached from both sides, the pressure was lowered by undoing a union or the packing gland of V_2 and allowing gas to leak out. This was more satisfactory than introducing another valve.

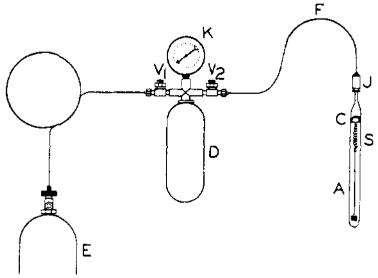

Fig. 7.—Method of gas pressure control used in sorption of nitrogen.

The results were calculated exactly as for nitrous oxide. The density of the nitrogen at 20° was calculated from the data on the compressibility of the gas as measured by Amagat[12] at 16°, taking 1.1650 as the density at 20° and one atmosphere pressure. By plotting the density–pressure graph up to 60 atmospheres, the density of the nitrogen at any pressure could be readily obtained.

The densities for nitrogen at −77° were calculated from the compressibility data of van Urk.[13] The equation of state of nitrogen is given as

$$PV_{\mathrm{A}} = A_{\mathrm{A}} + \frac{B_{\mathrm{A}}}{V_{\mathrm{A}}} + \frac{C_{\mathrm{A}}}{V_{\mathrm{A}}^2} + \frac{D_{\mathrm{A}}}{V_{\mathrm{A}}^4} + \ldots\ldots$$

in which $A_{\mathrm{A}} = 1.00043\ (1 + 0.0036618\ t)$, t being the temperature in degrees centigrade. P is in international atmospheres and V is in normal volume units at 0°. A table of values of B, C, D, etc., is given for various temperatures. The values of the constants B, C, D appropriate to the temperature of −77° were obtained by graphical interpolation. The final equation is thus

$$P = \frac{0.7206}{V} - \frac{1.115 \times 10^{-3}}{V^2} + \frac{2.682 \times 10^{-6}}{V^3}$$

the fourth term having proved negligible. By commencing with unit volume at 0°, 1 atmosphere pressure and density ρ_0 and by substituting fractions x such as 0.25, 0.025, 0.015, 0.01, etc., for V, the corresponding value of P is obtained. Obviously the density ρ of the gas at −77° under

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[12] E. H. Amagat, "International Critical Tables," Vol. III, **1928,** p. 17.

[13] Th. van Urk, Communications from the Physical Laboratory of the University of Leiden, No. 169e, p. 50 (1924).

the pressure P is ρ_0/x,x being the fraction of the volume corresponding to P. The density of nitrogen under standard conditions has the value of 1.25057 grams per liter.

The experimental data obtained from the measurements of the sorption of nitrogen by charcoal are tabulated in Tables VII–X, while Table VI contains a comparison of the conditions of outgassing the charcoal.

TABLE VI

CONDITIONS OF OUTGASSING THE CHARCOAL BEFORE MEASURING THE SORPTION OF NITROGEN

Expt.	Charcoal	Time for const. vacuum, hours	Press., mm.	Time at press., hours	Final press., mm.	Temp. of evacn., °C.	Contact cold N_2, hours
			First Evacuation				
I	Steam D	4	0.0025	2	0.0025	450	16
II	Steam D	8	.0003	12	.0025	490	16
III	Air C	18	.0002	6	.0002	490	16
IV	Air C	3	.0002	8	.0002	490	60
			Second Evacuation				
I	Steam D	3	0.001	4	0.001	450	..
II	Steam D	8	.0005	4	.0005	490	..
III	Air C	4	.0003	6	.0002	490	..
IV	Air C	3	.0001	4	.0001	490	..

In the case of Experiment IV the charcoal was outgassed for ten hours at 460° and 0.001 mm. vacuum, which could not be improved upon owing to a crack in a glass seal. To put this right, air was admitted, and the charcoal was cooled and re-evacuated as above ten hours later.

TABLE VII

SORPTION OF NITROGEN BY "STEAM D" CHARCOAL. TUBE I

Mass of charcoal, m = 0.0960 g. Sensitivity of spring, S = 22.55 cm./g. Total volume of charcoal and platinum bucket, 0.05859 cc.

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g.	x (corr.), g.	x/m
			Temperature of charcoal, 20°				
1.0^{a}	0.002084	0.00215	0.0224	23.0^{a}	0.005188	0.00676	0.0705
1.5	.002749	.00285	.0297	25.0	.005055	.00677	.0705
2.0^{a}	.003237	.00337	.0351	30.0^{a}	.005011	.00707	.0737
5.0	.004169	.00451	.0470	32.0	.005055	.00725	.0755
5.0^{a}	.003991	.00433	.0451	37.0^{a}	.004967	.00751	.0782
7.0	.003991	.00447	.0466	38.0	.004967	.00758	.0790
9.0^{a}	.004213	.00483	.0503	42.7^{a}	.004745	.00769	.0801
10.0^{a}	.004834	.00552	.0575	46.0	.004435	.00761	.0793
11.0	.004789	.00555	.0578	49.0^{a}	.004435	.00782	.0814
12.5^{a}	.004967	.00582	.0607	52.0	.004257	.00785	.0818
13.5	.005144	.00607	.0632	56.0^{a}	.003947	.00781	.0813
16.5^{a}	.005188	.00632	.0658	61.0	.003636	.00784	.0816
20.0	.005100	.00647	.0674				

[a] Desorption experiment.

TABLE VIII

SORPTION OF NITROGEN BY "STEAM D" CHARCOAL. TUBE II

Mass of charcoal, m = 0.0905 g. Sensitivity of spring, S = 19.76 cm./g. Total volume of charcoal and platinum bucket, 0.05556 cc.

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g.	x (corr.), g.	x/m
Temperature of charcoal, 20°							
1.0	0.001063	0.00113	0.0125	16.0	0.004504	0.00554	0.0613
1.1[a]	.001670	.00174	.0193	17.0	.004656	.00576	.0637
3.0	.002075	.00227	.0251	22.5[a]	.005061	.00652	.0721
5.0[a]	.002429	.00275	.0304	26.5	.005010	.00673	.0744
6.0	.003492	.00388	.0429	31.5	.004960	.00701	.0775
6.5	.003036	.00346	.0382	35.2[a]	.005263	.00756	.0835
9.0[a]	.003694	.00428	.0473	37.0	.005314	.00773	.0854
11.0	.004049	.00477	.0527	43.5	.005213	.00806	.0890
13.5[a]	.004302	.00518	.0572	53.0	.004656	.00812	.0898

[a] Desorption experiment.

TABLE IX

SORPTION OF NITROGEN BY "AIR C" CHARCOAL. TUBE III

Mass of charcoal, m = 0.0946 g. Sensitivity of spring S = 15.08 cm./g. Total volume of charcoal and platinum bucket, 0.06248 cc.

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g.	x (corr.), g.	x/m
Temperature of charcoal, 20°							
1.0	0.002255	0.00233	0.0246	20.8	0.007228	0.00875	0.0925
4.1[a]	.003448	.00375	.0396	31.0	.007692	.00996	.105
6.0	.004509	.00495	.0523	33.2[a]	.007958	.0104	.110
10.8	.005504	.00629	.0665	40.9	.007825	.0108	.115
11.0	.005968	.00677	.0716	46.7	.007958	.0114	.120
18.5[a]	.007095	.00845	.0893	50.6	.007692	.0114	.121
20.6[a]	.007493	.00900	.0951				
Temperature of charcoal, −77°							
3.5	0.01154	0.0119	0.126	33.5[a]	0.01558	0.0195	0.206
10.0	.01499	.0161	.170	39.2	.01499	.0196	.207
16.7	.01625	.0181	.192	48.6	.01412	.0199	.211
25.7[a]	.01625	.0192	.203				

[a] Desorption experiment.

TABLE X

SORPTION OF NITROGEN BY "AIR C" CHARCOAL. TUBE IV

Mass of charcoal, m = 0.0851 g. Sensitivity of spring, S = 19.40 cm./g. Total volume of charcoal and platinum bucket = 0.05178 cc.

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g.	x (corr.), g.	x/m
Temperature of charcoal, 20°							
1.0	0.004897	0.00496	0.0583	19.1	0.008608	0.00976	0.115
1.0[a]	.004433	.00450	.0528	31.0	.008866	.0108	.126
6.0[a]	.005979	.00634	.0745	40.0[a]	.009072	.0115	.135
11.1	.007629	.00830	.0976	50.2[a]	.008866	.0119	.140
15.5	.007526	.00846	.0995	58.5	.008918	.0125	.147

TABLE X (*Concluded*)

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g.	x)corr.), g	x/m
Temperature of charcoal, −77°							
1.0	0.009124	0.00921	0.108	25.0	0.01758	0.0195	0.229
8.0[a]	.01479	.0155	.182	29.3[a]	.01861	.0214	.252
10.0	.01546	.0164	.192	35.0[a]	.01840	.0218	.256
13.3[a]	.01716	.0184	.216	35.0	.01814	.0215	.253
17.0	.01778	.0194	.228	44.0	.01747	.0218	.256
17.0[a]	.01716	.0187	.220	48.1[a]	.01711	.0219	.257
20.6	.01814	.0200	.236	54.5	.01644	.0219	.257

[a] Desorption experiment.

Discussion

The data portray true reversible equilibria, because points on the curves obtained by sorption or by desorption are indistinguishable within the experimental error. The experiments were always sufficiently prolonged for this to be the case. Somewhat higher values, less affected by high pressures, would probably have been obtained had we taken even greater precautions in the preliminary evacuation of the charcoal.[14]

The first half of the total sorbed material is taken up at low pressures, almost infinitesimal in the cases of nitrous oxide and ethylene, but we are concerned here with the behavior in the higher regions of pressure. Here the buoyancy correction for the density of the gas or vapor becomes important. This was very clearly shown in the unabridged tables where neglect of the buoyancy correction causes the uncorrected values of the sorption x to pass through a maximum and then fall off with further increase of pressure. To evaluate the correction it is necessary to know the density of the charcoal. Unfortunately, this is a matter of extreme divergence of opinion, the bulk density, not allowing for pores, being far less than unity.

The density of diamond is 3.47–3.56,[15] and that of graphite is 2.25–2.26.[16] Polanyi,[17] like A. M. Williams,[18] considers that the density of active charcoal may be 1.5, and H. Briggs[19] assumes it to be only 1.33, whereas G. A. Hulett[20] concludes that it is 2.2, approximating that of graphite. The uncertainty arises from the divergent results obtained when the density is determined by immersing the charcoal in different liquids. The values for the density so derived range from 1.65 to 2.28. Two opposing explanations are current for this divergence. The first view is that the liquid sorbed is highly compressed and much denser than the surrounding liquid;

[14] J. W. McBain, *Nature*, **117**, 550 (1926), and other communications, *loc. cit.*

[15] "International Critical Tables," Vol. III, **1928**, p. 21.

[16] *Ibid.*, Vol. II, **1928**, p. 592.

[17] F. Goldmann and M. Polanyi, *Z. physik. Chem.*, **132**, 345 (1928).

[18] A. M. Williams, *Proc. Roy. Soc. Edinburgh*, **38**, 23 (1918); **39**, 48 (1919).

[19] H. Briggs, *Proc. Roy. Soc.* (London), **A100**, 88 (1922).

[20] H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, **28**, 1082 (1924).

hence it would displace less than its own weight of ordinary liquid and, therefore, must add to the apparent density of the charcoal. According to this, the charcoal must be less dense than is ever experimentally observed. The contrary interpretation is that the solid framework of the carbon is of high density, about 2.2, but that, owing to the extreme fineness of its porosity, it is not completely penetrated by liquids. When helium at atmospheric pressure and temperature is used as the fluid displaced by the carbon,[20] the result is unaccompanied by sorption and the density found is 2.2.

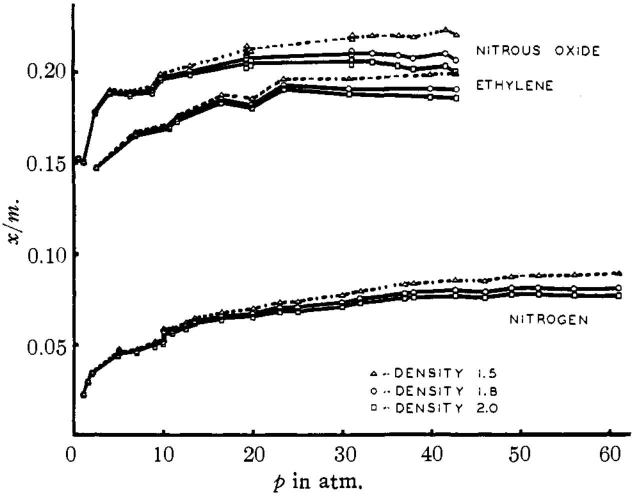

Fig. 8.—Sorption of nitrous oxide, ethylene and nitrogen at 20° assuming the density of charcoal as 1.5, 1.8 and 2.0, respectively. The data used are obtained from Tube III nitrous oxide, Tube III ethylene and Tube I nitrogen.

Although we do not know how completely nitrogen, nitrous oxide and ethylene are able to penetrate the finest porosities of the charcoal, the exact value of the density does not greatly affect the trend of our results. This is illustrated by typical data for all three substances in Fig. 8, which shows what the sorption would be if calculated assuming alternatively the densities 2.0 and 1.8, as well as the inadmissibly low value 1.5. For all three substances it is evident from Fig. 8 that the sorption becomes constant for all the higher pressures, irrespective of whether the density is taken as 1.8 or 2.0. These data, within the experimental error, exhibit a saturation value of sorption.

In Figs. 9, 10 and 11 the values for the sorption are plotted against pressure, being calculated as in the foregoing tables upon the assumed value of 1.8 for the effective density of the charcoal. A saturation value is found for all the experiments with nitrous oxide and ethylene, whereas with nitrogen the saturation value is observed only for the steam-activated charcoal.

However, the uppermost curve in Fig. 11, representing the highest values for sorption by air-activated charcoal at −77°, leads to an almost constant saturation value which would become unmistakable if any higher density were assumed for the charcoal.

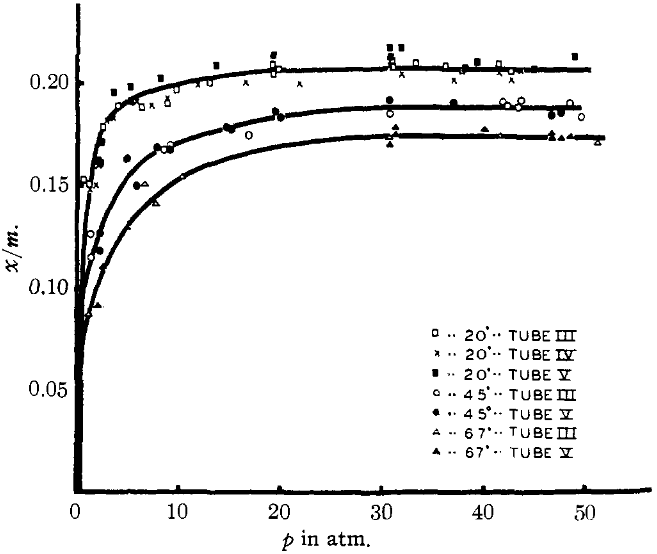

Fig. 9.—Sorption of nitrous oxide by "Steam D" charcoal.

For nitrogen with air-activated charcoal at 20° no saturation value is attained. This is not surprising when we compare the other saturation values corresponding to different temperatures and note that, although they definitely diminish with rising temperature, the highest values for the sorption of nitrogen at 20° are only half those of the corresponding saturation values at −77°. It is evident that appreciably more sorption must take place and much higher pressures must be employed before a saturation value at 20° could be reached.

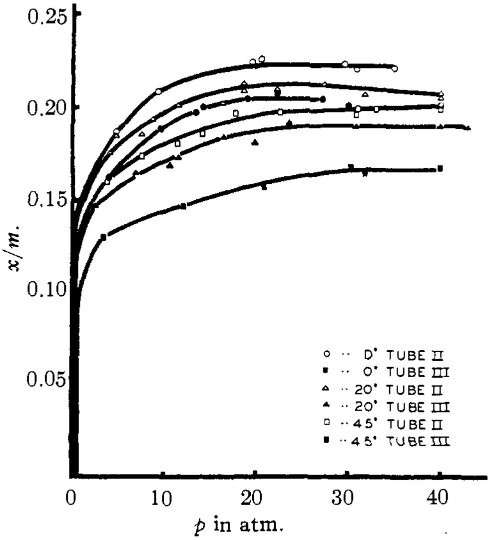

Fig. 10.—Sorption of ethylene by "Air C" charcoal.

Data exhibiting a saturation value cannot adequately be represented by the ordinary ''exponential'' isotherm, $x/m = kp^{1/n}$. Neither can they be represented by the exacting Williams–Henry formula, log $(x/m/p = k_1 - k_2 \times (x/m)$.

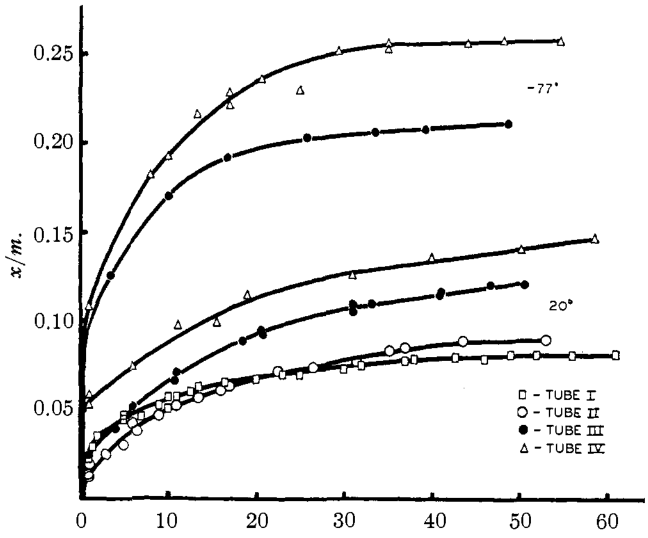

Fig. 11.—Sorption of nitrogen by charcoal. "Steam D" charcoal was used in Tubes I and II, and "Air C" in Tubes III and IV.

This formula cannot be legitimately applied where the sorption exceeds a fraction of the saturation value. The inadequacy of both formulas is illustrated in Figs. 12 and 13, where the respective formulas demand a straight line graph. A saturation value would be indicated by the Williams–Henry graph becoming vertical for that range of pressure. However, over a limited range either formula can be used to give a fair representation of the results.

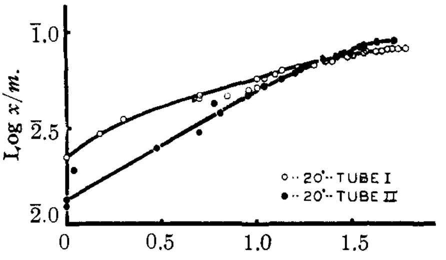

Fig. 12.—Sorption of nitrogen graphed according to the experimental formula, $x/m = kp^{1/n}$.

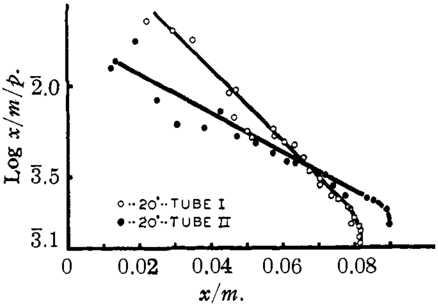

Fig. 13.—Sorption of nitrogen graphed according to the Williams–Henry formula, log $x/m/p = (k_1 - k_2) \times x/m$.

The question will be raised as to whether some buoyancy correction should not have been introduced for the sorbed gas or vapor itself. The answer is that no such correction is admissible if the classical conception of a compressed film of sorbed material is assumed (de Saussure 1814, Mitscherlich, Bunsen, etc., Polanyi 1917 and 1928). Sorption is defined, both practically and theoretically, as the excess of material in the neighborhood of the solid over that which would obtain if the surrounding atmosphere reached the surface quite unchanged in concentration.

Nevertheless, from the standpoint of chemosorption or of a monomolecular film, it is inevitable that one should seek to distinguish between molecules which are held by sorption and those of the atmosphere which they have displaced. Considering an extreme case such as a body of liquid in contact with a crystalline surface, where the concentration of the liquid is uniform right to the crystal face, by ordinary criteria no sorption would have taken place, yet, if the molecules touching the crystal were specially oriented, they should be regarded as a sorbed monomolecular layer which has displaced an equal bulk of liquid (neglecting here the probable occurrence of oriented chains of molecules reaching into the liquid from a monomolecular layer).[21]

Applying the foregoing considerations to the present cases, the attempt may be made to estimate what the correction would be for the atmosphere displaced by the sorbed material if it is directly attached to the carbon by primary or residual valences. The weight of sorbed material is about one-fifth of that of the carbon, but its volume is uncertain. The densities of solid nitrogen, of liquid nitrogen at −190°, of liquid ethylene at −102° and of nitrous oxide at −89° are 1.0, 0.8, 0.6 and 1.2, respectively. On account of expansion, these densities would be less at the temperatures employed, but this would be partly compensated by compression at the highest pressures. Taking 1.0 and 0.6 as fair limits and assuming for these small molecules that the true density of carbon is 2.2, the combined density of carbon plus sorbed material comes to 1.8 or 1.5. These are equal to the lower densities already considered in Fig. 8 with the important difference that saturation values might still appear with the lower density, owing to the great compressibility which would necessarily accompany so low a density of the sorbed material. The higher density is, moreover, more probable if each sorbed molecule is attached directly to carbon. In other words, the results as portrayed in the graphs are not misleading over the pressure ranges so far investigated even if the actual values might have to be slightly greater and a saturation value was not quite strictly attained. The Langmuir theory supposes that a limiting value for sorption is approached asymptotically with great increase of pressure.

[21] J. W. McBain and G. P. Davies, This Journal, **49**, 2230 (1927); Sir W. Hardy, *J. Gen. Physiol.*, **8**, 641 (1927); J. W. McBain, *Nature*, **120**, 362 (1927).

In Figs. 14, 15 and 16 the results are graphed in a form derived from the Langmuir equation for plane surfaces

$$\frac{x}{m} = \frac{abp}{1 + ap} \text{ or } \frac{p}{x/m} = \frac{1}{ab} + \frac{p}{b}$$

where if a and b are constants, the graphs should be straight lines. It is seen from the figures that this representation is in striking agreement with all the data. When the results for nitrogen at 20° were calculated with alternative densities, it was found that an assumed density of 1.5 did not yield a straight line but that 1.8 was satisfactory and 2.0 was even better. The intercepts of the straight lines with the ordinate on the left of the figures where $p = 0$ give a numerical value of $1/ab$, whereas the slopes of the straight lines give a numerical value of $1/b$.

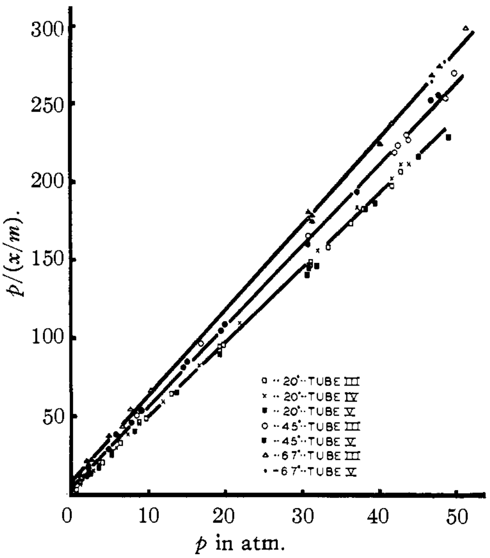

Fig. 14.—Sorption of nitrous oxide by "Steam D" charcoal graphed according to the Langmuir equation, $p/(x/m) = (1/ab) + (p/b)$.

The results for the sorption of nitrogen at room temperature, extending as they do up to 60 atmospheres pressure, appear to afford the opportunity for a crucial test of the classical de Saussure or Polanyi hypothesis that the sorbed gas is in the form of a compressed atmosphere obeying an ordinary equation of state such as that of van der Waals but under an excess compression due to the attractive forces of the solid. Knowing the actual behavior of nitrogen · under compression from the work of Amagat and others, we can consider 1 cc. of the sorption space, that is, the region within which the attractive forces of the solid are operative, and calculate directly what the density of the nitrogen in 1 cc. would be if the average pressure inside the sorption space exceeds that of the surrounding atmosphere by any specified amount.

For example, using Amagat's data for values of pv at 16° and various pressures as recorded in "International Critical Tables," the density of nitrogen at 1 atmosphere is 0.00118, and if there is an extra pressure of 1000 atmospheres in the sorption space, the density there would be that corresponding to 1001 atmospheres, namely, 0.5861. The difference in density would be attributed to sorption and would be 0.5849 for a gas pressure of 1 atmosphere. Now if the pressure of the body of the nitrogen were 60 atmospheres, with its density 0.07163, and the excess pressure in the sorption space were again 1000 atmospheres, making a total of 1060 atmospheres, the density then would be 0.5995. Once more the difference in density would be attributed to sorption, and this would amount to 0.5279 for a pressure of 60 atmospheres as compared with the 0.5849 for nitrogen under 1 atmosphere pressure.

In other words, it follows from the known behavior of nitrogen that if nitrogen in the sorption space is like nitrogen in the surrounding atmosphere, except for an extra compression of 1000 atmospheres in the sorption space, we must have observed a distinct decrease in the amount of sorption of nitrogen in our experiments at 60 atmospheres as compared with 1 atmosphere.

Actually, the behavior is wholly different. Instead of the sorption decreasing when the pressure of nitrogen is raised from 1 atmosphere to about 60 atmospheres, the sorption increases many fold. Hence our experiments at high pressures definitely disprove the assumption that the nitrogen in the sorption space is subject to an extra compressive force of the order of 1000 atmospheres.

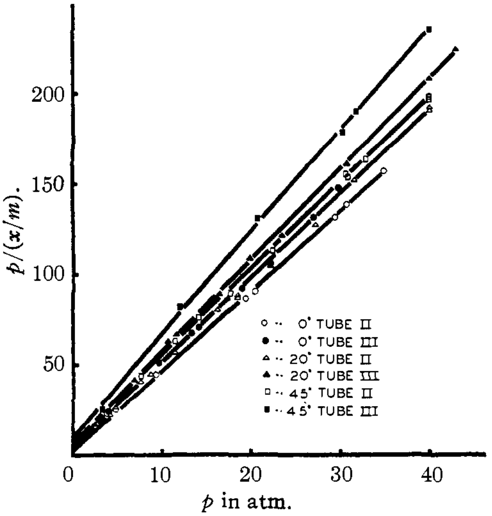

Fig. 15.—Sorption of ethylene by "Air C" charcoal graphed according to the Langmuir equation, $p/(x/m) = (1/ab) + (p/b)$.

The same test can be applied to a statement that the excess pressure in the sorption space exceeds that in the surrounding space by, say, 100 atmospheres. Here again a slight decrease is predicted in the amount of sorption at the higher pressure, in violent discord with the facts. This apparently conclusive disproof of a conception which has remained up to the present largely a matter of opinion which was held for over a century by almost all the men of science who concerned themselves with this subject, is of such importance that we repeat the experimental data for inspection in tabular form in Table XI to compare with the typical calculations exhibited in Table XII.

It is evident from a comparison of the facts in Table XI with the known behavior of nitrogen in Table XII that they are glaringly incompatible with the conception of a sorption film differing from the surrounding atmosphere merely through compression caused by the attractive forces of the solid. It is clear that of the nitrogen sorbed by charcoal, only a negligible propor-

TABLE XI

SORPTION OF NITROGEN AT 20° OBSERVED AT 1 ATMOSPHERE COMPARED WITH THAT OBSERVED AT A MUCH HIGHER PRESSURE

Tube no.	Pressure, atm.	x (uncorr.)	x (corr.)	Increase
I	1	0.002084	0.00215	3.5-fold
	61	.003636	.00784	
II	1	.001063	.00113	7-fold
	53	.004656	.00812	
III	1	.002255	.00233	5-fold
	50.6	.007692	.0114	
IV	1	.004897	.00496	2.5-fold
	58.5	.008918	.0125	
Wright V′	1.02	.0063	.0066	4-fold
	26.67	.0193	.0264	
Wright VI and VI′	1.02	.0059	.0061	3.5-fold
	31.97	.0152	.0210	

TABLE XII

CALCULATION, FROM AMAGAT'S DATA, OF THE EXCESS CONCENTRATION OR DENSITY OF NITROGEN AT 16° WHICH WOULD OBTAIN AT 1 ATMOSPHERE AS COMPARED WITH 60 ATMOSPHERES IF NITROGEN IN THE SORPTION REGION IS UNDER ANY STATED EXTRA COMPRESSIVE FORCE, F ATMOSPHERES. THE DENSITY OF NITROGEN AT 1 ATMOSPHERE IS 0.00118 AND AT 60 ATMOSPHERES IS 0.07163

F, atm.	Density at $1 + F$	Excess over density at 1 atm.	Density at $60 + F$	Excess over density at 60 atm.	Remarks
1000	0.5861	0.5849	0.5995	0.5279	Decrease[a]
100	.1199	.1187	.1849	.1133	Decrease[a]
10	.0130	.01182	.08353	.01190	Very slight increase[a]
5	.0071	.00592	.07759	.00596	
1	.0023	.00112	.0729	.00127	

[a] Experiment, on the contrary, shows a many fold increase.

tion can be in the compressed state envisaged in the de Saussure–Polanyi conception, even if this compression be estimated at only 1 atmosphere. Estimates by various advocates of the compressed film theory have ranged up to 37,000 atmospheres.

Clearly the Langmuir conception, which is the only alternative explanation ever put forward for the sorption of nitrogen by charcoal, is correct. Its essence is the assumption that only such molecules are sorbed as are in direct contact with the molecules holding them. The Langmuir conception includes the possibility that further molecules may be held by the primary monomolecular layer.[22] The results and calculations of the present paper disprove, moreover, a further alternative hypothesis introduced by Polanyi

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[22] This view was put forward by R. A. Smith in 1863 (see *Proc. Roy. Soc.* (London), **A112**, 301 (1928)). See also, A. B. Lamb, R. E. Wilson, and N. K. Chaney, *J. Ind. Eng. Chem.*, **11**, 424 (1919); I. Langmuir, *Trans. Faraday Soc.*, **17**, 614 (1921); E. K. Rideal [*Nature*, **117**, 627 (1926)] who compares such attraction of a magnet on a string of iron filings; F. G. Keyes and M. J. Marshall [THIS JOURNAL, **49**, 156 (1927)] who especially emphasize it.

in 1928 in an attempt to conform the compressed film concept with monomolecular adsorption by assuming a sideways compression of the adsorbed layer such that it would be the equivalent of a two-dimensional gas or at lower temperatures form islands of liquid.

Experiments with active charcoal do not suffice to disprove the possible existence of relatively weak forces of molecular attraction at distances greater than a molecular diameter. This is due to the extraordinarily complete development of the "porosity" of the charcoal. It must, from such data as ours, be regarded as comparable with that of an open space lattice such as dehydrated chabazite, which acts as a molecular sieve for separating large from small molecules.[23] The sorbed molecules of nitrogen must be so intimately surrounded by the atoms of carbon with which they are in contact that the designation "adsorption," which implies a surface, becomes a misnomer. There is very little difference in such a case between adsorption and absorption;[24] and if a precise word to describe sorption by charcoal were required, the new term "persorption" might be coined. Experiments on smooth surfaces, preferably crystal faces, are required to examine the residual effects which may occur at a greater distance from the surface.

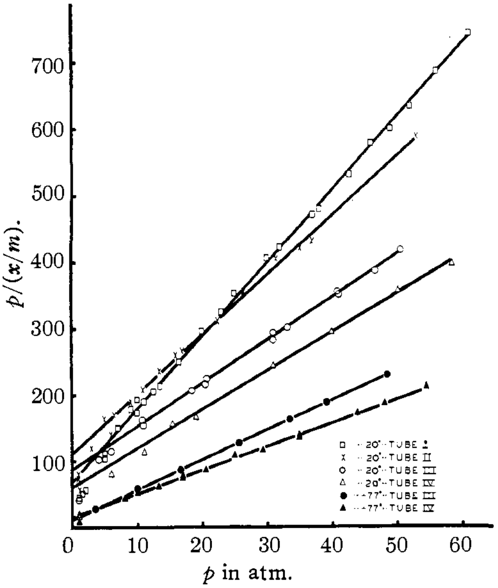

Fig. 16.—Sorption of nitrogen by charcoal graphed according to the Langmuir equation, $p/(x/m) = 1/ab + p/b$. "Steam D" charcoal was used in Tubes I and II, and "Air C" in Tubes III and IV.

[23] J. W. McBain, *Kolloid-Z.*, **40**, 1 (1926); "Colloid Symposium Monograph," Vol. IV, **1926**, p. 7; O. Weigel and E. Steinhoff, *Z. Krist.*, **61**, 125 (1924); O. Schmidt, *Ebenda*, **133**, 263 (1928); R. Seeliger, *Physik. Z.*, **22**, 563 (1921); F. Simon, *Z. physik. Chem.*, **132**, 456 (1928).

[24] J. W. McBain [*Trans. Faraday Soc.*, **14**, 202 (1919)] found that in experiments on the sorption of iodine extending over many years, during which the total sorption was doubled, the amounts taken up after the initial sorption conformed with a sorption isotherm rather than with a formula for true solution such as Henry's law, although the delay must have been conditioned by slow processes of diffusion. The solvent and other impurities have to diffuse out of the carbon while the solute is diffusing in and replacing them. Modern vacuum technique has not been applied in the study of sorption by solutions.

Although the preceding discussion has been confined to the gas nitrogen as a test case, the result, if recognized as valid, must extend to all cases of sorption by active charcoal.

The critical temperature and pressure of nitrous oxide are 36.5° and 71.7 atmospheres, respectively, those of ethylene 9.7° and 50.9 atmospheres and those of nitrogen $-147.1°$ and 33.5 atmospheres. Nitrogen, therefore, has been studied far above its critical temperature, while nitrous oxide and ethylene have been studied below and above their critical temperatures. The results are all very similar. There is no noticeable influence of this critical constant in the form or position of the sorption curves whether one compares the graphs above and below the critical temperature for one substance or compares the two vapors with nitrogen. This suffices to show that capillary condensation plays no role in such cases of sorption by charcoal.

Summary

1. Using the McBain–Bakr sorption balance, the sorption of nitrogen, nitrous oxide and ethylene has been measured at pressures up to 60 atmospheres.

2. The curves for gases and vapors are similar, and no special difference is noticed when studying nitrous oxide and ethylene above and below their critical temperatures.

3. The data appear to afford a crucial disproof of the classical conception of the sorbed film as a compressed fluid. This was suggested by de Saussure in 1814 and is currently associated with the name of Polanyi. The disproof extends equally to the modification introduced by Polanyi in 1928. The behavior predicted by such hypotheses is in flagrant contradiction with the known compressibility of nitrogen and the actual sorption at 60 atmospheres as compared with that at 1 atmosphere. Only a negligible proportion of the sorbed nitrogen can be in such a state; the remainder must be directly attached as postulated in the hypotheses of Langmuir. It is, therefore, shown that the terms adsorption and absorption are equally misnomers when applied to sorption by active carbon. The dissemination of the sorbed molecules between the carbon atoms is almost as intimate but is not as uniform as that of a true solid solution. On the other hand, owing to so much of the "porosity" of active charcoal being on an atomic or molecular scale, the conception of a surface disappears. The term "persorption" is proposed if a new term is required to describe such phenomena.

4. When the data are expressed according to the definition of Gibbs or of the compressed film conception as the excess in the neighborhood of the surface over the amount corresponding to the surrounding atmosphere, saturation values are obtained for all except some of the experiments with nitrogen. When expressed in absolute amounts, according to the Lang-

muir conception, the saturation values become doubtful, tending to show slight increase with further rise in pressure.

5. The data over the whole range of higher pressures are adequately represented by the Langmuir formula.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

TWO DELICATE TESTS FOR THE DETECTION OF COPPER AND SOME REMARKS ON THE RHODANINE TEST OF FEIGL FOR SILVER

BY I. M. KOLTHOFF

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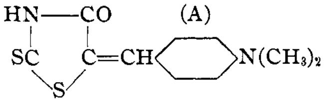

(A)

I. Recently, F. Feigl[1] has described a new and very delicate test for silver with *p*-dimethylaminobenzylidene-rhodanine as a reagent (A). According to Feigl, this reagent gives in weakly acid, neutral and ammoniacal solutions, a flocculent red precipitate with silver. In 5 cc. of a weakly acid solution, one part of silver in 5,000,000 of solvent could be detected. In working with 10 cc. of solution, to which 0.5 cc. of 4 *N* nitric acid and 0.3 cc. of a saturated solution of the rhodanine[2] in alcohol were added, the same sensitivity was found by the writer. A solution with 1 mg. of silver in a liter produces a distinct reddish brown color (10 cc. of solution, conditions as above); with 0.5 mg. of silver per liter a weakly reddish color was noticed; with 0.2 mg. per liter the solution showed a very weak pink color after ten minutes' standing, distinctly different from the blank, which was slightly yellow. In ammoniacal solution (10 cc. of solution +1 cc. of 6 *N* ammonia and 0.1 cc. of indicator) the color in the presence of silver is reddish-brown and in very dilute solutions orange-brown. The sensitivity in this case is about 2 mg. of silver in a liter.

In acid medium the reagent is so sensitive toward silver that it even cannot be used as an indicator for the titration of iodide with silver solution. A weakly acid solution of 0.01 *N* potassium iodide to which some reagent had been added gave a dark red precipitate after addition of a few drops of 0.01 *N* silver nitrate. Even the silver in the complex potassium silver cyanide reacts with the rhodanine. According to Feigl, the rhodanine is quite specific for silver. This, however, is not the case, as mercury and copper salts under the right conditions can react with it in a very sensitive

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[1] F. Feigl, *Z. anal. Chem.*, **74**, 380 (1928).

[2] The reagent was prepared in the organic division of this University, according to the procedure given by Feigl. It had the same properties as a sample kindly submitted by Dr. Feigl. Instead of using a 0.03% solution of the rhodanine in acetone as described by Feigl, a saturated solution in alcohol (about 0.02%) was taken.