

5. The mechanism of the formation of triatomic molecules is considered on the basis of the Bohr atom. Stable molecules of hydrogen are perhaps dissociated into free atoms when an electron is removed in the process of ionization, and these atoms attach themselves to neighboring neutral molecules to form triatomic systems.

6. We desire cordially to acknowledge our gratitude for much assistance in this work: to the Director of the Ryerson Physical Laboratory of the University of Chicago for the use of indispensable alternating current and the privileges of that laboratory; to the Research Grant of the American Association for the Advancement of Science for the funds for the construction of the quartz spectrum tube for the Schumann ray investigation; to Professor Stuart Weller, of the University of Chicago, for the gift of an excellent crystal of clear transparent fluorite for the Schumann ray investigation, and to Mr. A. C. Grubb for much of the work on the corona discharge.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## THE ADSORPTION OF SULFUR DIOXIDE BY THE GEL OF SILICIC ACID.

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### Introduction.

Many investigations of the adsorption of vapors by porous bodies have been made without a satisfactory explanation of the phenomenon being found. The fact that the adsorbing material is not chemically definite but has adsorbent properties dependent upon its method of preparation is not the least of the reasons for apparent lack of agreement both in experimental results and theoretical conclusions. Again, the possibility, and in many cases, the great probability of chemical reaction occurring during the process bring in another factor which is hard to control.

In the investigations carried on in this laboratory during the war it was found necessary to test many types of adsorbents, both as to their specific action against poisonous war gases as well as to their susceptibility towards other vapors and gases. It was realized in the beginning that porous bodies—mere mechanical condensers so to speak—were going to play an important part. Charcoal was brought into use and its protective ability greatly increased by improved methods of preparation. This laboratory focused a good part of its attention upon colloidal substances and gels. The gel of silicic acid, having been previously shown to possess adsorptive properties, received first attention. The main difficulty was its large scale preparation. Up to this time the method

of dialysis, a long and tedious process had been used. This difficulty was overcome and a quick and simple method, of which more will be said later, was developed. A product of high adsorptive power resulted.

This gel is a hard, translucent, porous solid, chemically inert and with proper precautions can be reproduced with definite exactness. Hence it is an ideal substance by which the 2 objectionable features mentioned above might be eliminated. It is true that it always contains a certain amount of water, either combined or adsorbed, but this factor may be kept constant and thus will not interfere with the more important investigation.

Thomas Graham<sup>1</sup> gives the first account of the preparation of silicic acid gel and the fact that it possesses a power of adsorption has been known since that time. Nevertheless, it was not until 25 years later, when van Bemmelen<sup>2</sup> commenced his lengthy and important experiments, that this property was investigated more thoroughly. This author made an exhaustive study of the hydration and dehydration of the gel in all cases, showing that these two curves did not follow the same path. This hysteresis will be taken up further on in the paper.

Zsigmondy<sup>3</sup> became interested in this substance and has published several articles on its structure, data for which were obtained chiefly from ultramicroscopic investigations.

Anderson,<sup>4</sup> working in Zsigmondy's laboratory, studied the systems, gel-water, gel-alcohol, gel-benzene. That is, he determined the equilibrium weight of each substance adsorbed per gram of gel at points corresponding to different pressures of the material adsorbed. Like that of van Bemmelen, the curve obtained by emptying the pores did not coincide with that observed when they were being filled, although the difference between the 2 paths was by no means as great as in the earlier work. It may also be mentioned that while van Bemmelen worked entirely under normal atmospheric pressure Anderson, on the other hand, did his work under a vacuum produced by the means of a high grade oil pump.

Patrick<sup>5</sup> was the first investigator of gas adsorption by this substance. He measured the amount of carbon dioxide, sulfur dioxide and ammonia adsorbed by this gel at different pressures for a number of different temperatures. He did not attempt to study the reverse adsorption path, nor did he use samples of the material containing different water content.

<sup>1</sup> T. Graham, *Phil. Trans.*, 151, 183-224 (1861); also *Ann.*, 121, 1-77 (1862); *Proc. Roy. Soc.*, 1864.

<sup>2</sup> J. M. van Bemmelen, *Z. anorg. Chem.*, 13, 233-356 (1896); "Die Adsorption," p. 196 (1910).

<sup>3</sup> Zsigmondy, *Z. anorg. Chem.*, 71, 356 (1911).

<sup>4</sup> Anderson, "Inaugural Dissertation," Gottingen, 1914.

<sup>5</sup> W. A. Patrick, "Inaugural Dissertation," Goettingen, 1914. See also *Koll. Z.*, 13-14.

The purpose of the present work may now be stated more clearly: to investigate the effect of different water content of the gel upon its adsorptive powers; to obtain measurements where temperature control and complete exhaustion could be more rigidly maintained than heretofore; and by using an inert body to interpret, if possible, the mechanism by which this phenomenon adsorption occurs.

#### Apparatus.

The apparatus used in these measurements is shown in Fig. 1. In general outline it is similar to that used by Homfray<sup>1</sup> in her work on charcoal and later by Patrick, in the original investigation of gas adsorption by silica gel. The essential parts are the gas container A, the gas buret B, the adsorption bulb C and the manometer D. These parts were all sealed together and mounted inside of a constant temperature bath about which more will be said later. The gas container was a steel cylinder filled

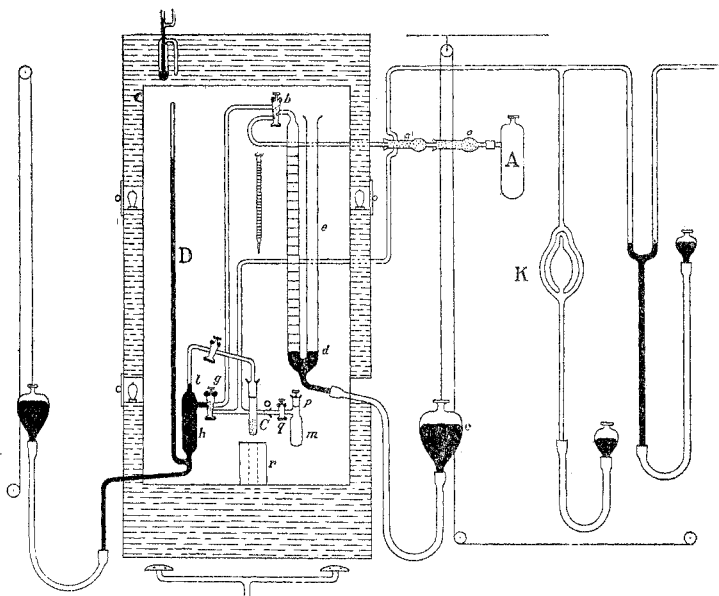


Fig. 1.

with liquid sulfur dioxide, the outlet of which was controlled by a sensitive valve. This was connected to the gas buret by means of drying tubes *a* and *a'*, containing calcium chloride and phosphorus pentoxide, respectively, and the 3-way mercury stopcock *b*. In order to fill the buret the stopcock *b* was opened to the adsorption apparatus and the mercury bulb *c* raised until all the air was forced out of the buret. The cock was then opened to the gas container and the mercury well *c* was lowered.

<sup>1</sup> *Z. phys. Chem.*, 74, 129 (1910).

Opening the cock *b* to the adsorption part of the mercury was again raised. This operation, repeated several times, removed a larger part of the air. To remove the last traces of air the bulb was lowered just so the mercury stood at the level *d* in the buret. The cock *b* was then opened to the gas container A and sulfur dioxide was allowed to sweep out the whole system for a considerable period of time. The exit tube from *b* was also swept out in a similar manner.

The gas buret B consisted of a graduated pipet connected by a U-joint to another tube, *e*, of the same bore, which served as an open manometer. This buret was recalibrated, mercury being used and the operation being carried out in a 30° constant temperature bath. As with most gases, all gas volumes were measured at this temperature, and if the temperature difference was less than 10°. no correction for glass expansion was deemed necessary. To determine the amount of gas introduced, the mercury in the two arms of the buret was leveled, this balance being adjusted by means of a very sensitive gear arrangement which enabled the reservoir C to be raised or lowered a small fraction of a millimeter, the correct position being ascertained by means of the cathetometer telescope. The reading of the cathetometer vernier, calibrated directly into 0.01 mm. divisions, was then taken. In like manner another reading was made after the gas introduction. By reference to the calibration curve these readings were transferred into cc. and were then corrected to standard conditions, 760 mm. and 0°. As the height of one mm. was equivalent to 0.19 cc. and as duplicate settings of the cathetometer could be made within 0.03 mm. the maximum error in reading gas volumes was 0.005 cc. As the adsorption proved to be considerable the cc. readings are given only to the second decimal place.

The gas buret was connected by a glass tube of small bore to the 3-way stopcock *g*, which in turn led to the expansion bulb *h*. This part of the apparatus had a capacity of approximately 100 cc. and served as a precaution against too hasty introduction of the gas.

The adsorption container C was connected to the expansion bulb by glass tubing and a ground glass joint protected by a mercury seal. The volume of this bulb together with that part of the connecting tube above the mark was obtained by introducing a known volume of dry air and measuring the pressure developed. Measurements with different volumes showed close agreement and a mean of these values was used for calculation purposes.

The manometer needs no special mention except that it was found desirable to have its bore identical with the bore at *l*. In the apparatus first used this was not the case and a constant correction for capillary depression was necessitated. Pressure readings were also made with the cathetom-

eter and hence all such readings are accurate to within 0.03 mm. The mercury well controlling the manometer was worked by a sensitive ratchet.

In order to study the curve formed while the pores were being emptied the bulb *m* was added by means of the ground glass joint *o*. This served as a holder for granulated soda lime which was introduced through the mercury-sealed ground glass joint *p*. The stopcock *q* maintained a vacuum in this vessel when removed from the apparatus for the purpose of weighing. The electric furnace *r*, previously calibrated, was used to heat the gel to the required temperature during evacuation.

The whole apparatus was enclosed in a completely water-jacketed air bath. Three gas burners under the bottom furnished rough heating adjustment, while a system of 8 carbon lamps, inserted in different sections of the water compartments and controlled by relays and a sensitive toluene-mercury regulator, procured very close temperature control. This bath was used by Morse and his co-workers in their measurement of osmotic pressure at high temperatures and hence is described elsewhere<sup>1</sup> in the literature. Suffice it to say that by means of this bath the temperature was maintained constant for any length of time with a maximum fluctuation of less than 0.05°.

In all of the work a vacuum was maintained by using in series a rotary oil pump and a Gaede high-vacuum mercury pump, both manufactured by E. Leybold. A MacLeod gage, K, served to determine when evacuation was complete, such being considered the case when the mercury threads in the gage became level.

#### Materials

All the mercury used in this investigation, that for traps, buret, manometer and gage, was thoroughly cleaned and purified. This was accomplished by first allowing it, in a state of very fine subdivision, to fall through 2.4 meters of dil. nitric acid for 5 or 6 times, washing with distilled water, then caustic soda, and finally with distilled water. After drying it was redistilled *in vacuo*.

The rubber tubing used to connect the mercury wells to the remaining part of the apparatus was soaked for 24 hours in dil. sodium hydroxide solution in order to remove sulfur present. This precaution prevented premature fouling of the mercury.

The sulfur dioxide used was that found in the trade and was taken directly from its metal cylinder—a method recommended by Travers in his careful work on purification of gases. Of course its purity was first tested. This was done by immersing a 100 cc. inverted buret filled with sodium hydroxide in a sodium hydroxide solution. The buret was now filled with sulfur dioxide from the cylinder, and after a short time was completely absorbed without the appearance of any gas bubble at the top

<sup>1</sup> *Am. Chem. J.*, 48, 29 (1912).

of the buret. Several experiments were also made from a sample obtained from the same cylinder which had been redistilled. No different results were observed. A further check on the purity of this substance was obtained from vapor-pressure measurements. No change in pressure being noticed, no matter how large a volume of gas was introduced. Hence the possibility of presence of oxygen, nitrogen and carbon dioxide, the most likely impurities, was eliminated.

All of the gel used in this investigation was made by the Davis, Patrick and McGavack<sup>1</sup> process. In general this consists in allowing an acid solution and a solution of sodium silicate, both solutions being kept at the proper concentration, to mix under violent agitation. The hydrosol "sets" in 1 to 18 hours, depending upon the temperature and concentration of the solution. When the desired state of firmness is reached the material was washed with city water, the washing being continued until no trace of electrolyte could be detected in the wash water. The material was then dried at 110° *in vacuo* until the water content was reduced to 7 or 8%. By this method a large amount of material was prepared.

The best grade of sodium silicate solution (water glass) furnished by the Philadelphia Quartz Company was used. C. P. hydrochloric was the acid used.

In order to remove dust particles and possible metal impurities the gel was subjected to still more drastic treatment. This was accomplished by saturating it with nitric acid fumes and refluxing with C. P. conc. nitric acid for 12 hours. The material was then washed thoroughly by decantation from distilled water over a period of 4 days. This part of the operation cannot be hurried or accelerated by increasing the amount of water as the rate of diffusion from the pores of the gel is very slow. The material was then dried in an air bath at 110°.

As even at 110° a large amount of water (16-24%) still remained in the gel, and as uniform samples of different water content were desired, some arbitrary process had to be employed to standardize the water content. This was accomplished by heating a mass of gel for different periods of time under a vacuum at different temperatures. For instance, Sample *c* was prepared by heating for one hour at 100-120° and for 3 hours at 300°. Sample *d* was heated for one hour at 100-120°, one hour at 300°, and finally 2 hours at 500°—a vacuum of 1 to 5 mm. being maintained in each case during the whole time. This treatment was rigidly held to in the preparation of all samples. The samples were then put in glass-stoppered bottles and these in a sulfuric acid desiccator.

All water determinations were made by heating the gel in a platinum crucible with a blast lamp. This method was applicable, as water was

<sup>1</sup> Reports submitted to the Chemical Warfare Service, a résumé of which will be published in the near future.

the only volatile component. The usual method for obtaining the density of an insoluble (in water) solid was employed, especial care being used to see that all adsorbed air bubbles were removed. Table I gives the experimental results.

TABLE I.—WATER CONTENT AND DENSITY OF DIFFERENT SAMPLES.

Sample	c.		d.		g.		f.	
	Water, %.	Density.	Water, %.	Density.	Water, %.	Density.	Water, %.	Density.
	4.79	2.1693	3.53	2.244	2.36	2.25 <sup>a</sup>	7.92	2.123 <sup>a</sup>
	4.82	2.1604	3.49	2.236	2.26	...	8.03	...
	4.90	....	....	...	....	....	8.07	...
Mean:								
	4.87	2.1648	3.51	2.240	2.31	....	8.01	...

<sup>a</sup> Calculated from values obtained from *c* and *d*.

Isotherms were made at  $-80^{\circ}$ ,  $-54^{\circ}$ ,  $-34.4^{\circ}$ ,  $-33.4^{\circ}$ ,  $0^{\circ}$ ,  $30^{\circ}$ ,  $40^{\circ}$ ,  $57^{\circ}$ ,  $80^{\circ}$  and  $100^{\circ}$ . For  $+30^{\circ}$  and  $+40^{\circ}$  the constant temperature both surrounding the apparatus was used. Solid carbon dioxide contained in a Dewar bulb served for  $-80^{\circ}$ . Liquid ammonia also contained in a Dewar bulb and with an arrangement for variable pressure served for the other low temperatures. The freezing and boiling points of water were used for  $0^{\circ}$  and  $100^{\circ}$ , respectively. The vapor of boiling acetone and benzene gave the points  $57^{\circ}$  and  $80^{\circ}$ . In no case was the adsorption bulb allowed to dip in the boiling liquid itself but was completely bathed with its vapor. The flask containing this liquid fitted tightly at the top around the adsorption bulb and had openings for a thermometer and also a long glass condenser which avoided the necessity of continually adding liquid. In all cases the remaining part of the apparatus was kept at a constant temperature by means of the constant temperature bath.

The actual temperature points of the 2 low degree experiments were fixed by the aid of the vapor-pressure measurements made on sulfur dioxide by Steele and Bagster.<sup>1</sup> These investigators furnish the only measurements of this constant at low temperatures ( $-73^{\circ}$  to  $-36^{\circ}$ ) and when the logarithms of these pressures are plotted against the absolute temperature a fairly straight line results. In the other low temperature runs (Expts. XXVIII and XXIX) a xylene thermometer, calibrated recently (1919) by the U. S. Bureau of Standards, was used. The corrected readings on this thermometer were  $-33.4^{\circ}$  for Expt. XXVIII and  $-34.4^{\circ}$  for Expt. XXIX. The vapor pressures observed in these runs correspond to temperatures  $-37.8^{\circ}$  and  $-38.8^{\circ}$  with reference to the Steele and Bagster results. Regnault,<sup>2</sup> Pictet<sup>2</sup> and Sajot,<sup>2</sup> however, have measured the vapor pressure of sulfur dioxide from  $-30$  to  $+100^{\circ}$ . Their results are in good agreement with each other and it is interesting to note that the logarithmic curve plotted

<sup>1</sup> Steele and Bagster, *J. Chem. Soc.*, [2] 97, 2613 (1910).

<sup>2</sup> Results tabulated in Landolt-Börnstein "Tabellen."

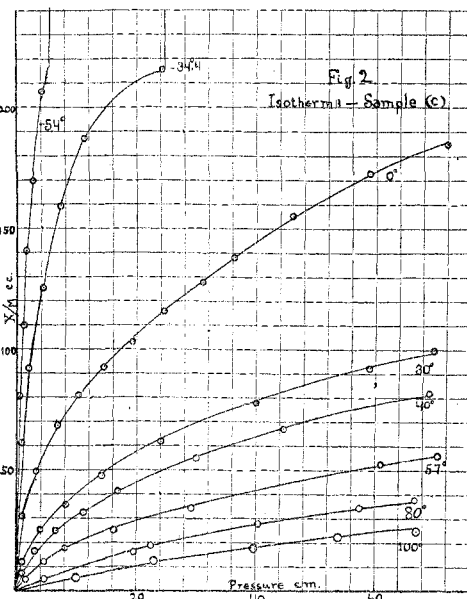
from them when extended fixes the temperatures in question at  $-34^{\circ}$  and  $-35^{\circ}$ , respectively, values which seem to be the true ones.

**Procedure.**

The gel was weighed directly into the adsorption bulb which was then attached to the apparatus. The furnace was put in position and heating and evacuation were commenced at the same time. The temperature and length of heating were governed primarily by a consideration of the water content of the gel. A temperature higher than that used in the preparation of the gel was never employed—this was done so as not to change the amount of water present. The evacuation was continued until the MacLeod gage indicated no pressure. The adsorption bulb was then allowed to come to the temperature desired and the first introduction of gas was made. Amounts of gas such that points might be obtained at 2, 5, 10, 20, 30, 50, 60 and 70 cm. were introduced. After introduction, the mercury level was brought to point *l* (see Fig. 1), and by reading this height and also that on the manometer itself, the point where equilibrium was reached could be ascertained easily.

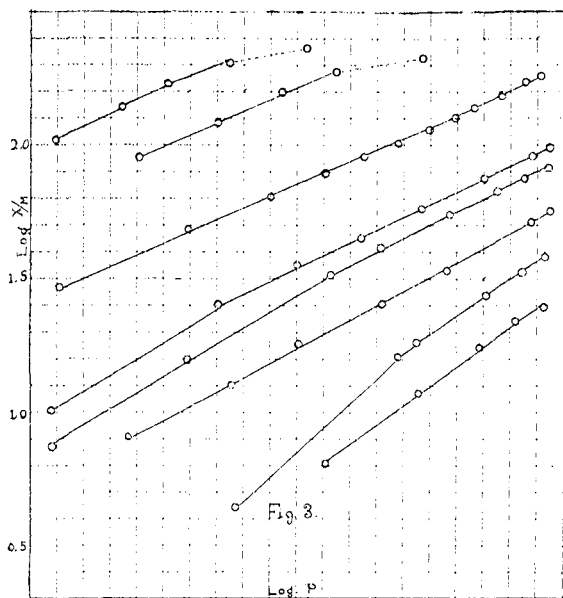
The difference between these 2 readings gave the pressure of the system. In the same manner another quantity of gas was introduced and its equilibrium pressure measured. This was continued until atmospheric pressure was reached.

For points on the reverse curves the following method was used. The bulb *m* was partially filled with soda lime granules, Stopcock *q* opened and the whole system thoroughly evacuated. After removing and weighing, the bulb was again attached and the system thoroughly evacuated. The mercury controlling the MacLeod gage was now raised to a point sufficient to cut off its large bulb. Then lowering the mercury in the expansion chamber, *h*, the stopcocks *g* and *q* were opened and gas was given off from the gel. When sufficient had escaped the cock *g* was closed and the mercury in *h* raised to *l*. The pressure gage showed almost instant adsorption by the soda lime, but to avoid any error *q* was left open for an hour in order not to miss the last traces of the gas. It was then closed





and the bulb removed and weighed. The same process was repeated for every point desired. Of course pressure readings were made for every point determined.



All pressure readings were corrected to  $0^{\circ}$  and all gas volumes to 760 mm. and  $0^{\circ}$ . The volume of the gas above the gel was calculated each time and subtracted from the amount introduced. Knowing the volume of the bulb C to the mark *l*, also the temperature and pressure, this value was easily calculated from the gas laws. When the bulb and the remaining part of the apparatus were at different temperatures the volume and tem-

perature of each part were considered in the calculation.

### Experimental.

The results for Sample *c* of the gel are given below. Figs. 2 and 3 show these facts graphically.

#### Expt. XII.

2.4256 g., (c).					100°.	<i>a</i> 1.125.	$1/n = 0.745.$
<i>P.</i>	<i>V</i> <sub>0</sub> .	<i>V</i> <sub>1</sub> .	<i>X.</i>	<i>X/M.</i>	log <i>P.</i>	log <i>X/M.</i>	<i>X/M</i> calc.
105.88	18.24	2.18	16.06	6.62	1.02478	0.82086	6.50
229.93	33.94	4.74	29.20	12.04	1.36159	1.08063	11.62
397.00	51.32	8.19	43.13	17.78	1.59879	1.24993	17.43
544.20	64.57	11.23	53.34	21.99	1.73576	1.34223	22.08
671.50	73.65	13.85	59.80	24.65	1.82705	1.39182	25.83

#### Expt. XIX.

2.6000 g. (c).					80°.	<i>a</i> 2.239.	$1/n = 0.662.$
<i>P.</i>	<i>V</i> <sub>0</sub> .	<i>V</i> <sub>1</sub> .	<i>X.</i>	<i>X/M.</i>	log <i>P.</i>	log <i>X/M.</i>	$1/n.$
47.00	12.66	1.00	11.66	4.48	0.67210	0.65128	0.448
192.19	47.60	4.09	43.57	16.73	1.28373	1.22350	0.680
224.73	53.30	4.78	48.52	18.66	1.35166	1.27091	0.681
407.88	80.73	8.70	72.03	27.70	1.61053	1.44248	0.678
575.32	101.09	12.24	88.85	34.17	1.75991	1.53364	0.672
671.95	111.56	14.29	97.27	37.41	1.82733	1.57299	0.669

Expt. XX.

2.6500 g. (c).		57°.			a 5.755.	1/n=0.533.	
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.
18.97	17.92	0.42	17.50	7.50	0.27807	0.91954	...
46.16	34.76	1.03	33.73	12.73	0.66427	1.10483	0.534
81.70	50.42	1.82	48.60	18.34	0.91222	1.26340	0.552
158.84	72.83	3.75	69.08	26.07	1.22747	1.41614	0.534
290.14	97.38	6.45	90.93	34.31	1.46261	1.53542	0.530
615.65	151.75	13.68	138.06	52.10	1.78933	1.71684	0.534
713.50	164.51	15.86	148.65	56.09	1.85339	1.74889	0.533

Expt. XVIII.

2.600 g. (c).		40°.			a 9.755.	1/n=0.50647.	
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.
9.44	19.72	0.22	19.50	7.50	1.97497	0.87506	0.4560
31.37	43.63	0.72	42.91	16.50	0.49651	1.21748	0.4596
64.77	67.14	1.49	65.65	25.25	0.81137	1.40226	0.5090
110.00	90.05	2.54	87.51	33.66	1.04139	1.52711	0.5165
189.13	112.80	3.90	108.90	41.88	1.22822	1.62201	0.5152
299.78	151.28	6.88	144.40	55.54	1.47680	1.74461	0.5114
448.60	184.95	10.30	174.65	67.17	1.65186	1.82718	0.5072
567.52	208.22	13.04	195.18	75.07	1.75398	1.87547	0.5053
692.20	229.51	15.88	213.63	82.16	1.84023	1.91466	0.5028

Expt. XXIII.

1.7600 g. (c).		30°.			a 12.93.	1/n=0.485.	
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	X/M calc.
9.50	21.09	0.23	20.86	11.85	1.97772	1.01372	...
40.56	46.24	0.98	45.26	25.72	0.60810	1.41027	25.32
82.32	66.25	1.99	64.26	36.51	0.91551	1.56241	35.94
141.46	87.50	3.42	84.08	47.77	1.15063	1.67916	46.74
241.77	113.78	5.84	107.94	61.33	1.38340	1.78767	60.61
408.02	146.29	9.86	136.43	77.52	1.61068	1.88941	78.10
592.10	175.60	14.29	161.31	91.65	1.77240	1.96213	93.59
702.40	191.72	16.97	174.75	99.29	1.84650	1.99691	101.60

Expt. XV.

2.1422 g. (c).		0°.			a 29.14.	1/n=0.43207.	
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.
17.67	80.58	0.44	80.14	37.41	0.24724	1.57299	0.4387
34.92	109.40	0.87	108.53	50.66	0.54307	1.70467	0.4422
59.32	137.74	1.48	136.26	63.61	0.77320	1.80353	0.4384
88.16	161.65	2.21	159.44	74.43	0.94527	1.87175	0.4307
129.25	190.26	3.23	187.03	87.31	1.11143	1.94106	0.4287
179.46	218.28	4.49	213.79	99.80	1.25396	1.99913	0.4263
225.21	242.18	5.64	236.54	110.42	1.35259	2.04305	0.4277
317.51	283.25	7.95	275.30	128.51	1.50175	2.10893	0.4291
408.48	321.18	10.23	310.95	145.15	1.61117	2.16182	0.4327
522.41	363.63	13.08	350.55	163.64	1.71801	2.21389	0.4361
652.13	397.64	16.33	381.31	178.00	1.81433	2.25042	0.4331

1.5440 g. (c).		Expt. XVI.			0°.	
P.	V <sub>o</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.
8.40	39.08	0.22	25.86	25.57	1.92428	1.40773
36.50	78.98	0.94	78.04	50.54	0.56229	1.70364
61.54	98.15	1.59	96.56	62.54	0.78916	1.79616
80.47	111.19	2.08	109.11	70.66	0.90563	1.84917
106.11	125.35	2.74	122.61	79.41	1.02576	1.89988
145.39	143.59	3.76	139.83	90.56	1.16254	1.95694
187.02	160.58	4.84	155.74	100.86	1.27189	2.00372
258.17	186.42	6.68	179.74	116.41	1.41185	2.06599
341.23	214.29	8.83	205.46	133.06	1.53305	2.12405
422.16	240.04	10.92	229.12	148.39	1.62548	2.17138
569.86	280.79	14.75	266.04	172.30	1.75577	2.23629
639.09	297.98	16.54	281.44	182.27	1.80556	2.26071

2.2224 g. (c).		Expt. XXIV.			29.89.		1/n = 0.4279.	
P.	V <sub>o</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.	
10.43	70.19	0.26	69.93	31.47	0.01828	1.49790	1.2248	
31.83	111.04	0.80	110.24	49.60	0.50285	1.69548	0.4374	
67.47	152.69	1.70	150.99	67.94	0.82911	1.93213	0.4301	
105.35	182.47	2.66	179.81	80.91	1.02263	1.90800	0.4248	
147.05	210.16	3.71	206.45	92.89	1.16747	1.96797	0.4218	
190.59	234.94	4.81	230.13	103.55	1.28010	2.01515	0.4215	
245.57	265.34	6.20	259.14	116.60	1.39017	2.06670	0.4252	
310.58	293.37	7.85	285.52	128.47	1.49217	2.10880	0.4244	
366.57	318.20	9.23	308.97	139.03	1.56415	2.14311	0.4268	
467.79	360.28	11.82	348.46	156.79	1.67005	2.19532	0.4310	
585.96	401.09	14.80	386.29	173.82	1.76787	2.24010	0.4324	
720.15	429.74	18.18	411.56	185.18	1.85742	2.26759	0.4264	

1.4310 g. (c).		Expt. XXVIII.			33.4°.		a 76.32°.		1/n = 0.3471 <sup>a</sup> .	
P.	V <sub>o</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.			
6.00	88.07	0.11	87.96	61.47	1.77815	1.71866	0.4234			
20.40	132.28	0.31	131.91	92.18	0.30963	1.96484	0.2657			
41.07	180.24	0.76	179.48	125.42	0.61352	2.09844	0.3355			
72.00	229.43	1.29	228.14	159.42	0.85733	2.20254	0.3735			
113.38	270.82	2.04	268.78	187.82	1.05453	2.27375	0.3709			
242.00	313.54	4.35	309.19	216.06	1.38382	2.33457	0.3266			
243.00	364.94	4.37	360.57	251.97	1.38561	2.40138	....			
243.01	455.54	4.37	451.17	351.28	1.38562	2.49869	....			

<sup>a</sup> These constants were calculated from all points; hence the slope of the curve is slightly less than indicated from the majority of the observations.

1.6660 g. (c).		Expt. XXIX.			-34.4°.		a 72.33°.		1/n = 0.3794.	
P.	V <sub>o</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.			
4.22	88.89	0.07	88.82	53.31	1.52531	1.72681	0.3536			
13.85	136.00	0.22	135.78	81.50	0.14145	1.91116	0.3665			
29.02	180.70	0.47	180.23	108.18	0.46270	2.03415	0.3778			
50.07	229.31	0.79	228.52	137.17	0.69958	1.13726	0.3973			
73.45	272.07	1.18	270.89	162.60	0.86599	2.21112	0.4051			
116.62	321.86	1.88	319.98	192.06	1.06677	2.28344	0.3975			
205.59	347.35	3.32	344.03	206.50	1.31300	2.31492	0.3470			
232.66	426.30	3.75	432.55	260.00	1.36672	2.41497	....			

Expt. XXVI.

1.2876 g. (c).  $-34^{\circ}$ .  $a$   $112.7^{\circ}$ .  $1/n = 0.405^a$ .

P.	$V_0$ .	$V_1$ .	X.	$X/M$ .	log P.	log $X/M$ .
0.40	40.17	0.00	40.17	31.19	$\bar{2}.60206$	1.49402
4.16	103.07	0.06	103.01	80.00	$\bar{1}.61909$	1.90309
9.85	142.41	0.16	142.25	110.47	$\bar{1}.99344$	2.04324
17.55	184.65	0.28	184.37	143.19	0.24728	2.15591
27.50	220.53	0.44	220.09	170.93	0.43933	2.23282
44.70	268.31	0.63	267.68	207.89	0.65031	2.31783
89.00	313.50	1.44	312.06	242.36	0.94596	2.38435
88.05	352.39	1.44	350.95	281.44	.....	.....
88.35	396.39	1.44	394.95	307.85	.....	.....

<sup>a</sup> Constant obtained by neglecting that point when saturation was nearly reached. For this reason  $1/n$  is slightly larger than is the case in Expts. XXVIII and XXIX.

Expt. XXV.

1.6892 g. (c).  $-80^{\circ}$ .  $a^b$ .

B.	$V_0$ .	$X/M$ .	log P.	log $X/M$ .	$1/n^a$ .
0.13	84.97	50.30	$\bar{2}.11394$	1.70157	.....
0.58	166.92	98.82	$\bar{2}.76343$	1.99484	.....
1.65	249.71	147.82	$\bar{1}.21748$	2.16973	.....
3.05	307.17	181.84	$\bar{1}.48430$	2.25969	.....
4.60	349.11	206.67	$\bar{1}.66276$	2.31528	.....
8.30	388.23	229.83	$\bar{1}.91908$	2.36138	.....
8.85	433.54	256.65	$\bar{1}.94694$	2.40934	.....
8.80	470.90	278.77	$\bar{1}.94448$	2.44526	.....
8.85	512.35	303.31	$\bar{1}.94694$	2.48187	.....

<sup>a</sup>  $V_1$  correction negligible; <sup>b</sup> not calculated as saturation pressure is less than 1 cm. and hence no comparable values would be obtained.

In order to make clear how each calculation was obtained from the actual results, and exact reproduction of Expt. XXIII, a typical example of all runs, is given below.

The table is almost self-explanatory. The meaning of the symbols being as follows:

$B$  = barometer reading in mm.

Buret = readings of the gas buret in mm. obtained from the cathetometer settings.

$V_2$  = buret readings transformed into cc. by aid of the calibration curve.

$V_2$  =  $V_2$  corrected to standard conditions,  $0^{\circ}$  and 760 mm.

$V_0$  = difference between the  $V_3$  readings, or, the total volume of gas introduced in cc. and under standard conditions.

$V_1$  = volume of gas in the vapor phase above the gel. in cc. and under standard conditions.

$X$  =  $V_0 - V_1$  total volume of gas adsorbed in cc.

$M$  = weight of the gel. in g.

$X/M$  = volume (cc.) adsorbed per g. of gel.

Time—In this column is given the time of introduction of the gas and also when pressure readings were made.

$p_1 - p_2$  = uncorrected pressure of the system in mm. of mercury.

$P$  = pressure of system in mm. of mercury corrected to  $0^{\circ}$  and for capillary depression.

$D$  = density of the gel.

$T$  = temperature of the constant temperature bath.

$T_1$  = temperature of adsorption bulb. At  $+30^\circ$  and  $+40^\circ$   $T = T_1$ .

$T_2$  = weighted mean of adsorption bulb temperature and that of the remaining apparatus. In runs at  $+30^\circ$  and  $+40^\circ$   $T_2 = T_1 = T$ .

$V_4$  = volume (cc.) of the adsorption bulb to point 1 (see Fig. 1).  $V_3$  and  $V_1$  were obtained by use of the following equations:

$$V_2 = \frac{V_2 \times B \times 273}{760 \times T} \text{ and } V_1 = \frac{(V_4 - M/D)P \times 273}{760 \times T_2}$$

#### Expt. XXIII.

Weight of bulb and gel 17.6478 g. SO<sub>2</sub> 30° Cap. Depression = 7.0000 mm.

Weight of bulb 15.8878 g.  $D = 2.1648$

Weight of gel (grams) 1.7600  $V = 21.08$  cc.

B.	Buret.	V <sub>2</sub>	V <sub>3</sub>	V <sub>0</sub>	V <sub>1</sub>	X.	X/M.	Time.	P <sub>1</sub> .	P <sub>2</sub> .	P <sub>1</sub> -P <sub>2</sub> .
766.10	182.30	97.02	88.12	21.09	0.23	20.86	11.85	12.15	.....	.....	.....
765.30	312.80	73.88	67.03	.....	.....	.....	.....	1.00	201.70	185.34	16.36
.....	.....	.....	.....	.....	.....	.....	.....	2.30	200.95	184.45	16.50
.....	.....	.....	.....	.....	.....	.....	.....	3.15	200.65	184.10	16.55
765.30	312.80	73.88	67.03	25.15	0.98	45.26	25.72	3.15	.....	.....	.....
765.00	471.20	46.18	41.88	46.24	.....	.....	.....	4.00	252.90	205.15	47.75
.....	.....	.....	.....	.....	.....	.....	.....	4.50	252.82	205.05	47.77
765.00	471.20	46.18	41.88	20.01	1.99	64.26	36.51	5.00	.....	.....	.....
764.70	595.33	24.12	21.87	66.25	.....	.....	.....	5.40	277.85	188.10	89.75
.....	.....	.....	.....	.....	.....	.....	.....	8.00	278.25	188.60	89.75
764.70	595.33	24.12	21.87	21.25	3.42	84.08	47.77	8.10	.....	.....	.....
764.95	726.88	0.68	0.62	87.50	.....	.....	.....	8.30	339.90	190.70	149.20
.....	.....	.....	.....	.....	.....	.....	.....	9.45	339.90	190.70	149.20
766.00	177.30	97.90	88.90	26.28	5.84	107.94	61.33	9.45	.....	.....	.....
766.00	342.00	68.96	62.62	113.78	.....	.....	.....	10.45	439.75	190.95	248.80
.....	.....	.....	.....	.....	.....	.....	.....	11.30	439.70	189.90	249.80
.....	.....	.....	.....	.....	.....	.....	.....	12.30	439.10	189.07	250.03
.....	.....	.....	.....	.....	.....	.....	.....	1.00	438.95	188.92	250.03
766.00	342.00	68.96	62.62	32.51	9.86	136.43	77.52	1.10	.....	.....	.....
765.00	544.65	33.20	30.11	146.29	.....	.....	.....	3.15	622.50	205.40	417.10
.....	.....	.....	.....	.....	.....	.....	.....	4.00	622.20	205.05	417.15
765.00	544.65	33.20	30.11	29.31	14.29	161.31	91.65	4.05	.....	.....	.....
763.85	725.75	0.88	0.80	175.60	.....	.....	.....	5.05	785.72	181.95	603.77
.....	.....	.....	.....	.....	.....	.....	.....	5.50	785.60	181.70	603.90
.....	.....	.....	.....	.....	.....	.....	.....	8.15	785.60	183.50	602.10
.....	.....	.....	.....	.....	.....	.....	.....	8.45	785.80	184.00	601.80
763.85	180.20	97.38	88.18	16.12	16.97	174.75	99.29	9.00	.....	.....	.....
763.15	281.00	79.65	72.06	191.72	16.97	.....	.....	9.45	887.40	176.80	710.60
.....	.....	.....	.....	.....	.....	.....	.....	10.30	887.10	174.05	713.05
.....	.....	.....	.....	.....	.....	.....	.....	11.00	887.10	174.05	713.05

#### Water Content and Adsorption.

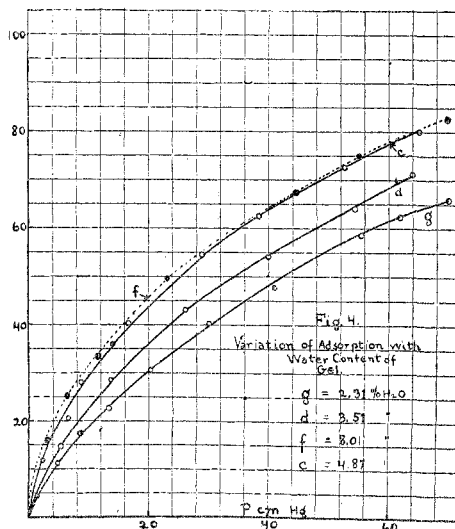
It was known from previous work<sup>1</sup> that, generally speaking, the adsorption of any gas was dependent upon the water content of the gel used. The fact that the gas or liquid was soluble or insoluble in water seemed

<sup>1</sup> Chemical Warfare Service paper, *loc. cit.*

to make no difference. It was also pointed out in this paper that a gel containing from 6 to 9% water seemed to be the most active. Such observations made it desirable to make measurements with gels of different water content.

As our method of treatment was static and its accuracy depended to a very great extent upon complete removal of all air before the run was started, we were limited to gels of very low water content, as lengthy evacuation and high temperatures were necessary to obtain air-free material. Gels with 2.31, 3.51, 4.86 and 7.97% water were used. The results are given below and are also shown graphically in Fig. 4. The sample containing 2.23% water is practically the lower limit, it being impossible to prepare a sample containing a smaller amount of water and at the same time preserve the structure of the gel. This fact may be used as an argument that a small amount of the water in the gel of silicic acid is not mechanically held, but is in some way intimately connected, chemically perhaps, with the silica network. A gel containing about 8% water was the upper limit, as with this amount at room temperature the gel has no vapor pressure and hence fairly good evacuation without any appreciable loss of water could be accomplished. The curves speak for themselves, the isotherms with 9.97 and 4.85% lie practically on the same line, indicating that the maximum value of adsorption would be possessed by a gel containing an amount of water lying between these 2 values. This further confirms the statement made in the paper previously mentioned.

The fact that sulfur dioxide is very soluble in water suggests the idea of solubility, that is, increased water content should cause increased adsorption. This idea, although plausible, is contradictory to some of the observations, for it has been shown that there is a maximum water content above which adsorption decreases and does not increase. Furthermore, even in those cases where adsorption does increase with greater water content: the increase is entirely too large to be accounted for by solubility. For instance, the average difference in  $X/M$  for Samples  $g$  and  $d$  was 7 cc. The actual difference in the amount of water was



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0.0120 g., which would adsorb at 40° about 0.5 cc. of sulfur dioxide, a value far too low for the difference actually observed.

It is believed that this difference in adsorption with small changes in water content might be due to the change caused in the size of the pores. If the water content is too low we have the pores too large and hence the capillary forces acting are enormously diminished and cause low values for adsorption. On the other hand, if the water content is too high we have the smaller capillaries partially filled and hence the space available for the gas is decreased. An adjustment of these 2 factors must be made to produce the best results.

## Expt. XVII.

2.4118 g. (g).		2.31% H <sub>2</sub> O.		40°.	$a = 3.936.$	$1/n = 0.678.$
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log X/M.	log P.
14.60	10.93	0.34	10.59	4.39	.....	.....
51.35	28.96	1.19	27.77	11.51	1.06108	0.71054
90.53	44.28	2.09	42.19	17.49	1.24279	0.95679
134.10	59.04	3.10	55.94	23.19	1.36530	1.12743
204.85	79.35	4.73	74.62	30.94	1.49052	1.31143
304.42	103.66	7.03	96.63	40.06	1.60271	1.48347
409.16	125.37	9.45	115.92	48.06	1.68178	1.61189
552.77	153.17	12.77	140.40	58.21	1.76507	1.74235
626.57	165.65	14.47	151.18	62.68	1.79713	1.79696
701.50	177.29	16.21	161.08	66.79	1.82471	1.84603

## Expt. X.

1.8921 g. (d).		3.51% H <sub>2</sub> O.		40°.	$a = 5.821.$	$1/n = 0.600.$
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.
45.76	27.68	1.06	26.62	14.07	1.63049	1.14829
137.34	57.73	3.20	54.53	28.82	1.13780	1.45969
263.77	87.62	6.14	81.48	43.06	1.42111	1.63407
400.32	112.75	9.33	103.42	54.66	1.60241	1.73767
549.71	134.41	12.81	121.60	64.37	1.74014	1.80868
644.89	150.05	15.03	135.02	71.36	1.80946	1.85345

## Expt. XIV.

2.9980 g. (f).		8.01% H <sub>2</sub> O.		40°.	$a = 8.129.$	$1/n = 0.555.$
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log X/M.	log P.
8.68	17.49	0.19	17.23	5.74	.....	.....
25.25	37.02	0.57	36.45	12.16	1.08493	0.40226
65.55	64.00	1.49	62.51	20.85	1.31911	0.81657
88.20	85.61	2.00	83.61	27.89	1.44545	0.94547
143.57	114.06	3.26	110.80	36.95	1.56761	1.15706
232.02	154.21	5.27	148.94	49.68	1.69618	1.36551
294.44	170.36	6.69	163.47	54.52	1.73656	1.46907
388.54	196.24	8.83	187.41	62.51	1.79595	1.58943
533.13	230.77	12.11	218.66	72.93	1.86291	1.72683
651.00	254.91	14.79	240.12	80.09	1.90358	1.81358

It was noticed that when the same charge was used for another run the amount adsorbed was distinctly less than in the original run. This

was due, without doubt, to the fact that it required more drastic treatment, longer evacuation and higher temperature, to remove the sulfur dioxide than it did in the case of the air originally present. During this process a small amount of water was removed and the result followed along the lines we have just discussed, decreased adsorption. In agreement with this conclusion is the further fact that where the gel originally started with was of low water content there was less difference between the first and second run. The following examples will show this more clearly. Compare Expt. XI with X, and Expt. IX with XVIII.

Expt. XI.

1.8921 g. <sup>a</sup>		30°.		
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.
32.43	22.28	0.75	21.53	11.37
89.93	43.44	2.08	41.36	21.85
166.08	64.58	4.31	60.27	31.85
265.11	85.21	6.20	79.01	41.75
407.48	110.13	9.48	100.65	53.19
572.81	134.95	13.35	131.60	64.27
672.04	147.22	15.66	131.56	69.53

<sup>a</sup> Previously used—originally (d) water content.

Expt. IX.

2.1985 g. <sup>a</sup> .		40°.		a = 8.727.		1/n = 0.5260.	
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.
20.90	27.64	0.50	27.14	12.34	0.32015	1.09132	0.4699
74.20	57.44	1.72	55.72	25.38	0.86451	1.40449	0.5362
152.00	85.68	3.55	82.13	37.31	1.18184	1.51183	0.5169
335.48	130.87	7.79	123.08	55.98	1.52566	1.74803	0.5290
574.74	173.34	13.33	160.01	72.78	1.75947	1.86201	0.5232

<sup>a</sup> Previously used—originally (c) water content.

### Adsorption Reversible.

All earlier work on the adsorption of vapors by silicic acid gel showed a marked difference in the amount adsorbed at the same pressure and temperature, depending upon whether the pores were being filled or emptied. The earlier work of van Bemmelen<sup>1</sup> with water and later that of Anderson<sup>2</sup> with water, alcohol and benzene, all showed this wide difference in the filling and emptying process. They explained this hysteresis from the known fact that a liquid in a capillary tube has a greater vapor pressure when being filled than when being emptied, as in the former case we have a diminution of the curvature of the liquid meniscus due to incomplete wetting. This is a very plausible explanation as well as an interesting example of capillary phenomena. So it was thought desirable to obtain isotherms where the sulfur dioxide was removed from the gel instead of being added.

As has been stated above, this was accomplished by opening a carefully

<sup>1</sup> *Z. anorg. Chem.*, 13, 233 (1897); 18, 98 (1898).

<sup>2</sup> *Loc. cit.*



evacuated soda-lime bulb to the system and when sufficient had been taken up removing the same and weighing. The weight was then changed to cc. at standard conditions by using the proper conversion factor.<sup>1</sup> All reversible measurements were made at 0°, as here we have a very large adsorption and the difference, if any, would for that reason be magnified. Expts. XXXII and XXXIII were the first reversible runs made.

## Expt. XXXII.

1.1140 g. (c).		0°.		$a = 32.95.$		$1/n = 0.4116.$	
Filling Pores.							
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.
19.05	44.27	0.54	43.73	39.25	0.27989	1.59074	0.2716
52.10	78.16	1.18	76.98	69.10	0.71684	1.83048	0.4487
102.40	100.54	2.32	98.22	88.17	1.01030	1.94532	0.4231
188.40	127.13	4.28	122.85	110.28	1.27508	2.04250	0.4115
291.00	153.32	6.59	146.73	131.71	1.46389	2.11962	0.4111
453.50	189.12	10.27	178.85	160.10	1.65658	2.20439	0.4144
704.80	225.25	15.96	209.29	187.87	1.84807	2.27387	0.4091

## Emptying Pores.

$a = 37.13.$				$1/n = 0.38107.$			
P.	Wt. SO <sub>2</sub> .	Vol. SO <sub>2</sub> .	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	1/n.
704.80	0.0000	0.00	225.25	15.96	209.29	187.87	
445.76	0.1060	37.05	188.20	10.12	178.08	159.86	
286.70	0.2060	72.00	153.25	6.50	146.75	131.73	
149.96	0.3095	108.18	117.07	3.50	113.57	101.95	
77.49	0.3828	133.79	91.46	2.21	89.25	80.12	
19.00	0.4870	170.21	55.04	0.44	54.60	49.01	
4.25	0.5459	190.80	34.45	0.10	34.33	30.85	
P.	log P.		X/M.		1/n.		
704.80	1.84807		2.27387		0.3810		
445.76	1.64910		2.20374		0.3844		
286.70	1.45743		2.11969		0.3766		
149.96	1.17598		2.00838		0.3738		
77.49	0.88925		1.90374		0.3755		
19.00	0.27875		1.69028		0.4324		
4.25	1.62939		1.53593		....		

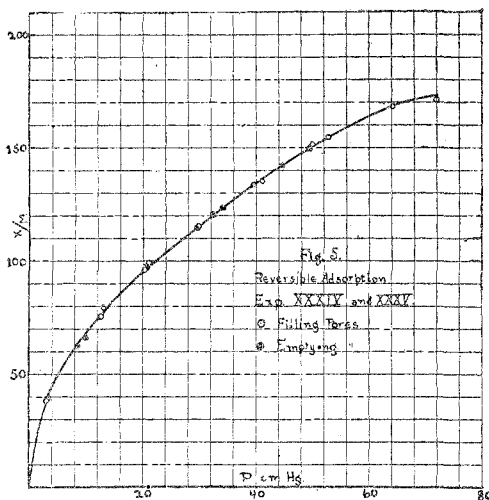
## Expt. XXXIII.

2.6005 g. (c).		0°.		$a = 29.222.$		$1/n = 0.4231.$	
Filling Pores.							
P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.
12.11	84.17	0.27	83.90	31.67	0.08422	1.50065	0.4166
63.87	171.11	1.39	169.72	65.26	0.80530	1.81465	0.4334
115.00	216.11	2.55	213.56	82.12	1.06070	1.91445	0.4232
176.40	258.33	3.75	254.58	97.90	1.24650	1.99078	0.4213
265.07	307.42	5.77	301.65	116.00	1.42336	2.06446	0.4207
349.26	349.64	7.61	342.03	131.52	1.54315	2.11899	0.4234
453.00	396.16	9.87	386.29	148.54	1.65610	2.17185	0.4265
561.44	437.18	12.23	424.95	163.42	1.74930	2.21330	0.4268
745.95	474.81	16.23	458.58	176.35	1.87792	2.24637	0.4157

<sup>1</sup> Landolt-Börnstein, "Tabellen," gives one liter of sulfur dioxide at sea-level, 760 mm. and 0°, weighs 2.8611 g.

$a = 30.605$		Emptying Pores.			$1/n = 0.4119.$	
P.	Wt. SO.	Vol. SO <sub>2</sub> .	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.
745.95	....	0.00	474.81	16.23	458.58	176.35
545.70	0.1062	33.12	437.69	11.85	425.84	163.75
338.91	0.3614	126.32	348.49	7.38	341.11	131.17
163.55	0.6386	223.20	251.61	3.56	248.05	95.39
50.17	0.9106	318.27	156.54	1.09	155.45	59.78
P.	log P.		log X/M.	1/n.		(X/M) <sub>F</sub> .
745.95	1.87792		2.24637	0.4050		...
545.70	1.73695		2.21418	0.4191		161.10
338.91	1.53008		2.21783	0.4130		130.00
163.55	1.21365		1.97950	0.4068		94.40
50.17	0.70044		1.77656	0.3985		67.50

In the last column, marked  $(X/M)_F$ , is given the amount adsorbed on filling for the same pressure values observed for the emptying process. In every case the former is the smaller value. Although this difference is small, nevertheless it is real. Doubt was at once raised whether all the air could be removed by the treatment used. If not, the first introduction of sulfur dioxide would liberate the air present and thus cause an increased pressure. On the first exposure to the soda-lime bulb practically all of the air would rush out and hence the pressure due to the air on the ascending curve would be eliminated and a greater adsorption at the same pressure would be observed. As a matter of fact, after the first exposure the MacLeod gage, used to indicate when all gas had been adsorbed, never showed a vacuum, but indicated the presence of 0.1-0.2 cc. of gas. This was not noticeable, or if so, very slightly after the first exposure.



It was now decided to prepare an absolutely air-free sample even at the expense of making a gel of only approximately known water content. This was accomplished by allowing the gel to stand in equilibrium with sulfur dioxide at about 70 cm. pressure overnight and then pumping it off and repeating the process. This was done 4 times and it is safe to say that the gel was completely freed from air. Two experiments were run with a sample thus prepared. The results are given on p. 964 and are shown graphically in Fig. 5.

## Expt. XXXIV.

2.3200 g.<sup>a</sup>      0°.       $a = 21.943.$        $1/n = 0.4910.$ 

## Filling Pores.

P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.
33.37	93.12	0.73	92.39	39.82	0.52336	1.60010	0.4944
131.14	182.60	2.87	179.73	79.27	1.11773	1.89911	0.4990
215.79	232.01	4.72	227.29	97.93	1.33403	1.99092	0.4869
305.14	276.46	6.68	269.78	116.28	1.48450	2.06551	0.4878
413.20	324.66	9.04	315.62	136.04	1.61616	2.13366	0.4902
529.44	369.68	11.58	358.10	154.35	1.72382	2.18851	0.4914
722.77	412.46	15.82	396.64	170.96	1.85900	2.23290	0.4790

## Emptying Pores.

 $a = 21.943.$  $1/n = 0.4910.$ 

P.	Wt. SO <sub>2</sub> .	Vol. SO <sub>2</sub> .	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.
722.77	....	....	412.46	15.82	396.64	170.96
498.27	0.1554	54.31	358.15	10.90	347.15	149.68
341.10	0.3399	118.80	293.66	7.47	286.19	123.36
209.71	0.5219	182.41	230.05	4.70	225.35	97.13
85.25	0.7559	264.20	148.26	1.86	146.40	63.10

P.	log P.	log X/M.	1/n.
722.77	1.85900	2.23290	0.4790
498.27	1.69747	2.17517	0.4913
341.10	1.53288	2.09118	0.4957
209.71	1.32162	1.98735	0.4888
95.25	0.93069	1.80003	0.4928

<sup>a</sup> Sample (c) repeatedly evacuated.

## Expt. XXXV.

2.3200 g.<sup>a</sup>      0°.       $a = 21.49.$        $1/n = 0.4966.$ 

## Filling Pores.

P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.	1/n.	X/M calc.
31.61	90.11	0.67	89.44	38.55	0.49982	1.58602	0.5078	38.06
130.54	183.00	2.94	180.06	76.07	1.11574	1.88121	0.4913	75.21
205.28	227.85	4.35	223.50	96.34	1.31235	1.98381	0.4966	96.37
296.21	274.51	6.28	268.23	115.62	1.47160	2.06303	0.4965	115.62
397.70	320.47	8.43	312.04	134.51	1.59956	2.12879	0.4977	133.83
508.66	363.98	10.78	353.20	152.24	1.70643	2.18253	0.4983	151.23
648.57	405.53	14.19	391.34	168.67	1.81196	2.22704	0.4944	170.62

## Emptying Pores.

 $a = 21.943.$  $1/n = 0.4910.$ 

P.	Wt. SO <sub>2</sub> .	Vol. SO <sub>2</sub> .	V.	V.	X.	X/M.
648.57	....	....	405.53	14.19	391.34	168.67
445.34	0.1878	65.64	339.89	9.43	330.46	142.44
323.00	0.3381	118.17	287.36	6.63	280.73	121.00
201.84	0.5128	179.23	226.30	4.27	222.03	95.70
96.46	0.7118	248.79	157.74	2.04	155.70	67.11
30.89	0.9058	316.59	88.94	0.65	88.29	38.06

$P$ .	$\log P$ .	$\log X/M$ .	$1/n$ .	$(X/M)^F$ .
648.57	1.81195	2.22704	0.4888	....
445.34	1.64869	2.15363	0.4926	143.00
323.00	1.50920	2.08279	0.4912	121.20
201.84	1.30501	1.98091	0.4901	95.80
96.46	0.98435	1.82679	0.4981	66.60
30.89	0.48982	1.58047	0.4881	37.80

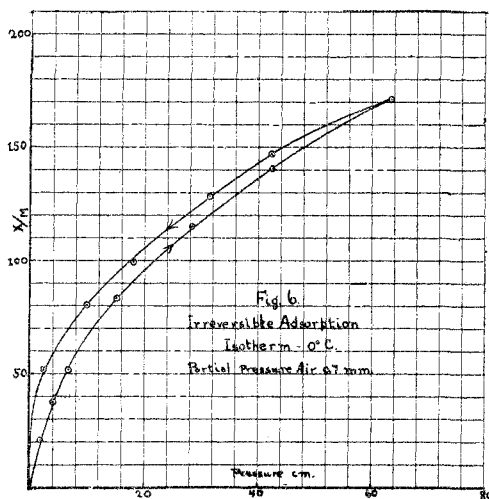
<sup>a</sup> Charge of Experiment XXXIV evacuated.

The agreement is well within the limit of experimental error. In other words, the adsorption of sulfur dioxide by silicic acid gel is a reversible process.

It will also be noticed that the absorption values do not agree with those previously made at this temperature. The reason for this may be found in the discussion given under the head of water content and adsorption. Here it was shown that by repeated exhaustion of the gel the water content of the gel is decreased and hence its adsorptive power (in this case) is at the same time lowered.

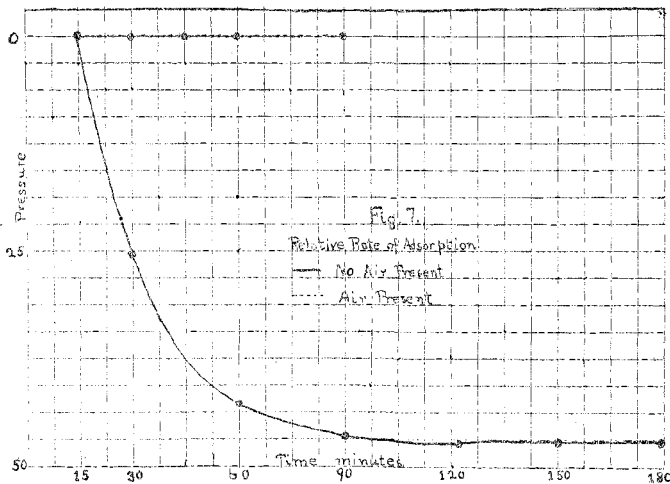
In order to prove more conclusively that minute traces of air were responsible for the lack of reversibility a sample was run where there was a definite amount of air present. This was done by evacuating the bulb but a short space of time. To be exact, there was at the beginning of the run a partial pressure of air of 0.7 mm. The experiment was carried out in exactly the same manner as previous reversible runs.

The experimental facts are given in Table II and Expt. XXXVII. They are also shown graphically in Fig. 6. Table II is given to show the large effect of small amounts of air upon the rate of adsorption. With air present, as may be seen, it is a question of hours before equilibrium is reached, while under conditions of a perfect vacuum equilibrium is reached in a very few minutes. The fact that there is an appreciable time



factor at all in the latter case is caused chiefly by the time necessary for the dissipation of the heat evolved during adsorption. In Fig. 7 are plotted the rates of adsorption in the form of  $dp/dt$  for two points, one obtained in the presence of air and the other in the absence of air. This gives another strong evidence of what important role air plays in adsorption

phenomena. The presence of this substance is suggested as a possible reason for the hysteresis observed by previous workers on reversible adsorption isotherms.



Expt. XXXVII.<sup>a</sup>

2.7430 g. (c).

0°.

$1/n = 0.4569$ .

Filling Pores.

P.	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.	log P.	log X/M.
25.28	56.97	0.54	56.43	20.57	0.40278	1.31323
46.05	104.32	0.99	103.33	37.60	0.66323	1.57519
69.20	148.09	1.49	146.60	53.44	0.84011	1.72787
148.37	230.27	3.19	227.08	82.78	1.17135	1.91793
284.86	320.64	6.13	314.51	114.66	1.45463	2.05941
424.55	396.48	9.12	387.36	141.22	1.62793	2.14989
636.35	487.38	13.67	473.71	172.70	1.80369	2.23729

Emptying Pores.

$1/n = 0.4012$ .

P.	Wt. SO <sub>2</sub> .	Vol. SO <sub>2</sub> .	V <sub>0</sub> .	V <sub>1</sub> .	X.	X/M.
636.35	0.0000	0.00	487.38	13.67	473.71	172.70
425.50	0.2114	73.89	413.49	9.15	404.34	147.41
318.13	0.3711	129.71	357.67	6.68	350.99	127.96
181.71	0.5999	209.67	277.71	3.90	273.81	99.82
107.64	0.7571	264.62	223.76	2.31	221.45	80.73
27.66	0.9818	343.15	144.23	0.58	143.65	52.37

P.	log P.	log X/M.	(X/M) <sub>F</sub> .
636.35	1.80369	2.23729	...
425.50	1.62890	2.16853	141.50
318.13	1.50264	2.10707	122.00
181.71	1.25937	1.99922	92.50
107.64	1.02197	1.90703	72.00
27.66	0.44185	1.71908	25.00

<sup>a</sup> Partial pressure of air at beginning of experiment of 0.7 mm. of Hg.

TABLE II.

<i>X/M.</i>	Time (min.).	Pressure (mm.).
20.57.....	40	30.60
	115	26.40
	145	25.80
	185	25.30
	215	25.30
37.60.....	40	51.50
	70	47.70
	100	46.75
	130	46.25
	205	46.20
53.44.....	15	93.90
	45	75.95
	75	71.00
	105	69.80
	135	69.65
	165	69.40
82.78.....	195	69.45
	15	195.99
	30	170.50
	60	153.10
	90	149.35
	125	148.70
	150	148.85
180	148.85	
114.66.....	15	343.65
	45	308.20
	75	291.05
	250	285.75
	280	285.80
141.22.....	15	500.10
	30	461.40
	125	428.40
	155	425.00
	185	426.05
	215	425.95
172.70.....	85	656.60
	150	640.17
	215	638.50
	255	638.45
Total time.....	25 hours, 45 minutes.	

**Discussion.**

Certainly there must be a mathematical interpretation possible and from the well defined regularity and similarity of the curves this appears to be far from complicated. A brief review of those equations in general use is certainly appropriate.

Many adsorption formulas have been proposed. That of Arrhenius,<sup>1</sup> later amplified by Schmidt,<sup>2</sup> is certainly logical and has been used over a wide range of cases. It has the following form when applied to gases:

$$pS = ke^{A(S-x)/S}$$

where  $p$  is the pressure of the gas,  $S$  the amount adsorbed at saturation per gram of substance,  $x$  the amount adsorbed at the different pressure intervals,  $K$  and  $A$  are constants and  $e$  has its usual value. Changing this somewhat, we may write

$$x = \frac{pS}{ke^{A(S-x)/S}},$$

which states that the amount adsorbed is equal to the product of the pressure, the saturation value and a constant, itself a function of the temperature, which fact is expressed by the power  $\frac{A(S-x)}{S}$  to which  $e$  is raised. Written in the logarithmic form,

$$\log p - \log S = \log K - \log x - \frac{A(S-x)}{S} \log e,$$

since  $\log e$ ,  $A$  and  $S$  are constants, and, as Schmidt has shown,  $\log K = k - \log S$ , the expression is simplified, giving

$$\log p - \log x - B(S-x) = k.$$

This gives an equation well suited for calculation purposes. The results of adsorption of sulfur dioxide by silica gel fits excellently this equation when the isotherms at the higher temperatures are used, those above 0°. Even those at the lower temperatures give fairly satisfactory results if proper manipulation of the constant  $B$  is made. The value of  $k$  increases with the temperature while there is a tendency for  $B$  to remain constant, although this also seems to increase with temperature. Theoretically  $B$  should remain unchanged throughout the temperature range.

A great drawback to this equation, as has been pointed out before by Marc,<sup>3</sup> is that it is too pliable. For instance, fixing arbitrarily the value of  $S$  the constant  $B$  may vary through wide limits and still fit the observations. Also, the value  $S$  can be changed at will and by slight changes in  $B$  and  $k$  the observations are again correlated. Another objection is the fact that  $S$  is not a constant through a wide temperature range. It is logical to believe that it must vary with the density of the condensed gas. This correction would be considerable and would give another variable to contend with in the Schmidt equation.

The adsorption ideas of Langmuir<sup>4</sup> in their present form are not applica-

<sup>1</sup> S. Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, 7 (1911).

<sup>2</sup> G. C. Schmidt, *Z. Phys. Chem.*, **78**, 667 (1912).

<sup>3</sup> Marc, *ibid.*, **81**, 679 (1913).

<sup>4</sup> THIS JOURNAL, **39**, 1848 (1917); **40**, 1361 (1918).

ble to the measurements of adsorption by porous bodies. The stray field of force, emanating from the surface of the adsorbent, it is believed, reaches out, attracts and holds those molecules of the gas that approach its surface. The maximum adsorption is reached when this surface is covered by a film of the adsorbed substance which is but a molecule in thickness. Hence, from this theory, other factors being equal, adsorption is dependent primarily upon the amount of surface exposed. The fact that the pressure of the gas phase changes gradually is ascribed to the difference in the strength of the individual lines of force given off from the surface. Much evidence is brought forth to support this conception. Thus, in order to apply the formula to porous bodies a measure of the internal surface would be necessary. The difficulty of such an undertaking is easily seen. It is true that a rough approximation might be arrived at by making ultramicroscopic measurements of the size of the pores, such as Zsigmondy<sup>1</sup> has done in the case of silicic acid gel, and combining this value with that number representing the internal volume of a definite mass of the substance. This, at least, would give an idea of the internal surface. Yet, granting that a fairly accurate estimation were possible, it certainly must be admitted that forces other than residual valence come into play, especially so when the pores themselves approach the vicinity of molecular dimensions. This fact Langmuir recognizes and suggests that true adsorption should deal with plane or smooth surfaces only. It is thus evident that the observations made in this investigation cannot be expressed by the Langmuir equation in its present form.

The simplest and most widely used adsorption equation is that proposed by Freundlich. This is purely an empirical relation, but one that is very elastic and easy of manipulation. If  $x$  is the amount adsorbed,  $m$  the mass of the gel,  $p$  the pressure of the gas,  $a$  and  $1/n$  constants, the equation is expressed as follows:

$$x/m = ap^{1/n},$$

or writing in the logarithmic form,

$$\log x/m = \log a + 1/n \log p.$$

This is an equation of a straight line and hence the constants  $a$  and  $1/n$  are easily interpreted— $a$  being the amount adsorbed when the pressure is unity, and  $1/n$  representing the slope of the line. It is readily seen that the constants change with a change from one temperature to another. So in order to make a perfect general equation this change must be expressed.

An inspection of Figs. 2 and 3 will show that the results obtained with silica gel and sulfur dioxide are very well represented by the Freundlich equation. For this reason the constants  $a$  and  $1/n$  have been given in

<sup>1</sup> *Loc. cit.*



the tables containing the data. The value of  $1/n$  given at the head of each experiment was obtained by the method of mean errors and from that the value of  $a$  was found by substitution in one of the equations. This value of  $a$ , you will notice, corresponds very closely to what would be read from the graph shown in Fig. 3.

A very exhaustive treatment of this equation and its relation to temperature is given by Freundlich<sup>1</sup> and for this reason it is not necessary to carry through the somewhat extended proof for the validity of the general equation, which takes into consideration all the variables—pressure, temperature and amount adsorbed. It has the following form:

$$\log (x/m)_t = \log (x/m)_0 - (z - \gamma \log p)t,$$

where  $z = -\frac{d \log a}{dt}$  and  $\gamma = \frac{d 1/n}{dt}$ . These values  $\gamma$  and  $z$  should be constants and although the experimental results do not strictly bear this out, yet there is sufficient constancy to make calculations that give good approximate agreement. Table III gives the observed values and those calculated from the equation above, using the observations made in Expts. XVIII and XIX. For this particular sample of gel  $z = -0.0146$  and  $\gamma = 0.0035$ , values obtained by taking a weighted mean of these differentials actually observed at the temperatures from  $0^\circ$  to  $100^\circ$ .

TABLE III.

Expt. XVIII (c) $40^\circ$ .			Expt. XIX (c) $80^\circ$ .		
P.	X/M obs.	X/M calc.	P.	X/M obs.	X/M calc.
9.44	7.50	...	47.00	4.48	6.20
31.37	16.50	14.45	192.19	16.73	16.75
64.77	25.25	22.62	224.73	18.66	18.70
110.00	33.66	30.73	407.88	27.70	28.99
169.13	41.88	39.01	575.32	34.17	37.05
299.78	55.54	53.91	671.95	37.41	41.20
448.60	67.17	67.99			
567.52	75.07	77.81			
692.20	82.16	84.36			

The objectionable feature of the Freundlich equation, as well as to most all other adsorption formulas yet proposed, is that isotherms at many different temperatures have to be made in order to obtain the proper value of the constants to be used for adsorption values at any pressure and at any temperature. There is no way of predicting or even roughly approximating what the adsorption would be at a temperature, say  $40^\circ$ , knowing the adsorption at some other temperature, say  $0^\circ$ . This means that a very large number of experiments must be made on every system before it can be properly disposed of and cataloged. This point will be taken up more fully in the latter part of the paper.

The accuracy of the measurements and the ease with which they can

<sup>1</sup> Freundlich, "Kapillarchemie," p. 101.

be reproduced is clearly shown by Expts. XV, XVI and XVII, which were carried out on different dates with 2.1422 g., 1.5440 g. and 2.224 g. of gel, respectively. The values of  $X/M$  at equal pressures were calculated by the aid of the Freundlich equation. These calculations are found in Table IV.

TABLE IV.  
 $X/M$  Calculated from  $1/n$  and  $a$  Values.

P. (Cm.).	Expt. XV. June 26.	Expt. XVI. July 4.	Expt. XXIV. Sept. 16.
5	58.45	56.70	59.36
10	78.68	77.33	79.86
15	93.63	92.73	94.97
20	105.91	105.48	107.40
25	113.90	116.55	118.16
30	126.03	126.47	127.75
35	134.64	135.51	139.64
40	142.58	143.86	144.48
45	149.93	151.66	151.95
50	159.58	158.98	158.96
55	163.44	165.91	165.57
65	175.57	178.80	177.84

In Fig. 3 we have plotted  $\log X/M$  against  $\log p$ . If the equation held absolutely we would have a system of straight nearly parallel lines. This is not strictly true. There are deviations in both directions, but more noticeably so with those isotherms carried out at the extreme temperatures. This bending is concave towards the  $x$ -axis, and for high temperatures takes place at the extreme left, while at the lower temperatures it occurs at the extreme right. The first case is probably due to the slight pressure developed by the adsorbed air released on the introduction of the first amount of sulfur dioxide. This pressure, although extremely small in itself, is, in proportion to the pressure of sulfur dioxide relatively large at this part of the curve and hence would produce a noticeable effect. More will be said later in regard to this point. The bending in the case of the lower temperatures is easily accounted for. In that region the vapor pressure of the liquid is approached and deviations would not be surprising but expected. Others<sup>1</sup> have shown that where  $p/p_0$  approaches unity the Freundlich equation is not applicable.

The mere fact that a chemically inert substance like silica gel is found exhibiting such marked adsorptive properties is sufficient in itself to indicate that the cause of adsorption does not lie in the interaction of adsorbent and adsorbed substance. In making the above statement we do not mean to say that it covers all the cases of gas or vapor adsorption, for the fact of specific gas adsorbents would tend to disprove it, *e. g.*, palladium for hydrogen. Perhaps it would be better to confine ourselves to the ad-

<sup>1</sup> Titoff, *Z. physik. Chem.*, 74, 641 (1910); L. B. Richardson, *THIS JOURNAL*, 39, 1828 (1917).

sorption of vapors, although it will be seen that our analysis permits the extensions to regions that are ordinarily considered as gaseous. As an approximate line of division we might select the critical temperature and confine ourselves to a discussion of adsorption occurring below this temperature. It cannot be too strongly emphasized that we are dealing with phenomena that exhibit adsorption to a marked degree, and are not manifestations of layers of a few molecules deep.

It is our belief that the adsorption of gases or vapors, let us say at all temperatures below the critical temperature, may be predicted from a knowledge of the physical constants of the gas or vapor alone. Furthermore, the role of the adsorbent is simply that of a porous body, its chemical nature being a matter of indifference. (Cases of obvious chemical affinity are of course excluded.) Adsorbents differ in the extent of their total internal volume and also in the dimensions of the spaces, called pores for simplicity, that make up the internal volume. It is conceivable that 2 adsorbents may possess the same internal volume but show marked differences in the adsorption of the same vapor due to differences in the distribution of the pore sizes.

If this is true the form of the adsorption curve expresses the distribution of the internal volume as a function of the dimensions of the pores. An attempt was made to express this relation in terms of the Maxwell distribution law, but a moment's reflection will convince one that there is no reason to expect the pore sizes to be distributed according to the laws of probability. The pores in the silica gel exist as the result of the juxtaposition of colloidal particles which are approximately all of equal dimensions and are, therefore, probably V-shape in cross section, or at any rate may be designated as tapering.

It is at once evident that if the adsorption curve simply shows the manner in which the various sized pores are distributed that go to make up the internal volume of the adsorbent, then, instead of seeking a relation between weight of adsorbed gas and the equilibrium pressure we should at once turn to the volume occupied by the adsorbed gas. As a matter of fact, if we express our isotherms of sulfur dioxide adsorption with volume of liquid sulfur dioxide as ordinates instead of weight, the curves are brought closer together. Our next consideration is, of course, to express the abscissas of our isotherms not as simple equilibrium pressures but as corresponding condensation pressures.

It has long been known that the properties which determine the ease of condensation of a gas or vapor are closely connected with the physical constants of the gas or vapor which are of importance in determining the magnitude of the adsorption. It is well known that condensations of vapors occur with greater ease in capillary tubes than on a level surface, provided the liquid wets the capillary wall. This phenomenon

has been long studied and the lowering of the vapor pressure of a liquid in a capillary in terms of the ordinary vapor pressure of the liquid  $P_0$  is given by the following relation:

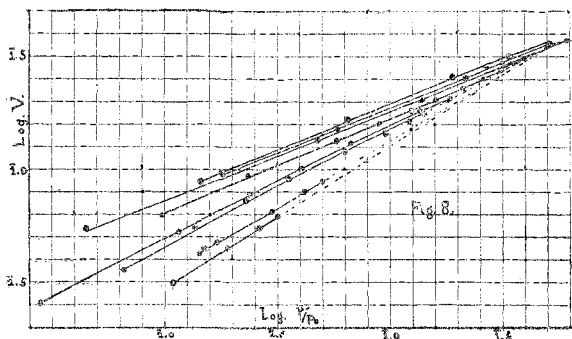
$$\ln P = \ln P_0 - \frac{2\sigma d}{DP_0 r},$$

where  $\sigma$  is the surface tension,  $d$  the density of the saturated vapor,  $D$  the density of the liquid and  $r$  the radius of the capillary. With the aid of this relationship we can readily derive the fact that the radius of the tube must be very small in order to have an appreciable effect on the vapor pressure of the liquid inside. It is not until we get to tubes of less than 0.001 mm. in diameter that we begin to affect the vapor pressure. From this it is clear that if we wish to account for the marked lowering of the vapor pressure in the case of adsorption, pores approaching molecular magnitude must be assumed. It is our feeling that such a wide extrapolation of the above formula is not justified and in the present analysis we shall not consider the question of absolute diameter of pores.

If we wish to compare the adsorption of a particular adsorbent for a gas or vapor at various temperatures, it is evident that the comparison must not be made at the same pressure, but rather at some corresponding pressure. As suggested by Williams and Donnan<sup>1</sup> the value of  $p/p_0$  may be selected for this purpose ( $p_0$  is the vapor pressure of the condensed vapor).

In Fig. 8 we have plotted the logarithms of the volumes of condensed sulfur dioxide (obtained by dividing the weight of sulfur dioxide by the density of liquid sulfur dioxide at the corresponding temperature) as ordinates against the values of logarithm  $p/p_0$  as abscissas. It will

be noted that greater volumes are taken up at lower temperatures at the same corresponding pressures. Furthermore, it is to be noted that all the adsorption isotherms are brought much closer together. When  $p/p_0$  equals unity the

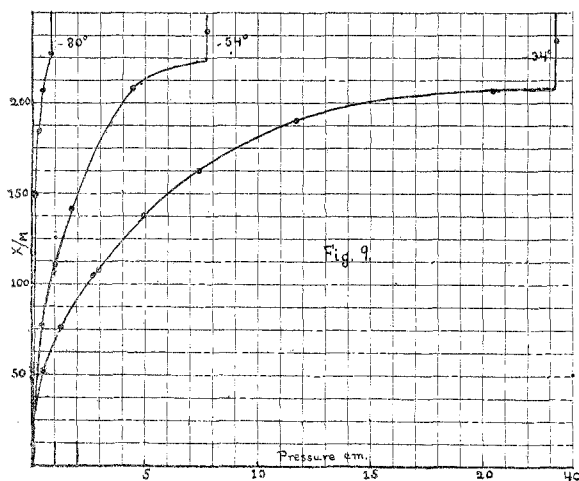


same volume of sulfur dioxide is taken up at all temperatures. At the higher temperature we were unable to work with pressures sufficiently great to enable us to realize the value of unity for  $p/p_0$ , however, the slope of the log curves is such as to bring all curves together at the point  $p/p_0 = 1$ .

An approximate idea of exactly what this volume is may be grasped by

<sup>1</sup> Williams and Donnan, *Trans. Faraday Soc.*, 10 (1914).

reference to Fig. 9. Here are plotted on a larger scale the results obtained at the lower temperatures, in fact those temperatures where the



saturation point was reached. This point is easily fixed by the very sharp break in the curve. Introducing density correction, these values become almost identical. Table V gives these results, corrected and uncorrected, as well as the saturation value of the isotherm at 0° calculated from the adsorption equation. The accuracy

of the Freundlich equation does not permit calculation of the saturation points at the higher temperatures as a wide deviation would be expected.

TABLE V.

Temperature.....	-80°	-54°	-34.0°	0°
Vol. gas phase, cc.....	232	228	216	209
Vol. liquid phase, cc. (or internal vol. of gel).	0.4073	0.4168	0.4039	0.4167

Similar results with silica gel were obtained by Bachmann.<sup>1</sup> This investigator showed that with the same sample of gel at the saturation pressure, that is the vapor pressure of the liquid at that temperature, the same volume of different liquids was taken up. Some experiments were carried out in which the liquid was introduced through the gas phase; others where the gel was introduced directly into the liquid. In this latter case the surface was carefully wiped with filter paper and possible errors from this source minimized. The author states that no correction for contraction or other volume change resulting from possible forces acting within the gel structure was considered in the calculation. A few determinations are given.<sup>2</sup>

Liquid.	Sample 2. Wt. absorbed. G.	0.3572 g. gel. Vol. per g. of gel. Cc.
H <sub>2</sub> O.....	0.2276	0.6210
C <sub>6</sub> H <sub>6</sub> .....	0.8791	0.6270
C <sub>2</sub> H <sub>2</sub> Br <sub>4</sub> .....	0.6720	0.6210

<sup>1</sup> W. Bachmann, *Z. anorg. Chem.*, **79**, 202 (1913).

<sup>2</sup> Other gel samples gave consistent although different values from the above. e. g., Sample 5—vol. = 0.3621 cc.; *loc. cit.*

The absolute value is not in agreement with that found in this investigation, but it must be remembered that the experimental method as well as the gel sample itself was different. The main point is that with the same gel sample there is an equal volume of the liquid adsorbed, no matter what the liquid or what the temperature.

Up to this point we have considered the lowering of the vapor pressure from the simple standpoint as being due to the rise in a capillary tube. Clearly, in our case the effect is not due to a difference in level, nor is it certain that we are dealing with tubes opened at both ends. For our purpose it is better to consider the lowering of the vapor pressure of the liquid in a pore as due to a negative tension exerted on the liquid around the meniscus. Thus this pull has its origin in the tendency of films which wet the walls to contract so as to expose as little of surface as possible. Looking at the adsorption of vapors in this light, it is seen that the condensed vapor is under a tension rather than a pressure. Furthermore, it is a simple matter to calculate the magnitude of this negative pressure. Using the well-known Gibbs relation,

$$\left(\frac{dp}{dP}\right)_T = \frac{V}{v},$$

where  $dp$  = change in the vapor pressure,  $dP$  = change in the hydrostatic pressure,  $V$  = volume of the condensed phase, and  $v$  = volume of the gas phase, expressing the variation of vapor pressure with the hydrostatic pressure, we can calculate that liquid sulfur dioxide at  $30^\circ$ , having a vapor pressure of 3496 mm., when in a capillary tube under a vapor pressure of 9.55 mm., is subject to a tension of about 530 atmospheres. When the pressure over the condensed liquid sulfur dioxide has risen to 706 mm. by the above relationship it can be shown that the negative pressure has fallen to 420 atmospheres. It is evident that we are in a position to calculate the negative pressure on any liquid provided we know the lowering of the vapor pressure, and the density of the condensed phase. (It is assumed that the vapor obeys the gas laws.)

If the liquid is in a closed tube this pull must occasion a dilation of the same to an extent that is proportional to the compressibility of the liquid. Worthington<sup>1</sup> has stated that the volume changes caused by negative pressure may be calculated with the aid of the compressibility coefficient. Unfortunately, we have no direct measurements of the compressibility of liquid sulfur dioxide and are, therefore, unable to evaluate quantitatively the volume change. It is known that in some cases<sup>2</sup> the relation

$$\beta\sigma^{1/2} = K$$

<sup>1</sup> Worthington, *Trans. Roy. Soc. (London)*, 183A, 355 (1892).

<sup>2</sup> Richards, *THIS JOURNAL*, 40, 59 (1919).

holds good, but it has only been tested over a narrow range of  $\sigma$  and many exceptions have been noted. We can, however, say that liquids of high surface tension have smaller compressibilities than liquids of low surface tension.

Here we have a possible explanation for the fact that the volume of sulfur dioxide at corresponding pressures are smaller at high than at low temperature. At the higher temperature the condensed phase is more compressible,  $\sigma$ , being smaller, and in addition the negative pressure is greater. In other words, we do not know the actual density of the condensed phase in the gel, but in all cases it is lower than the normal density which it approaches when  $p/p_0 = 1$ .

Expt. XII. 100°.			Expt. XXIII. 30°.		
$\sigma = 9.25, D = 1.111, p_0 = 2114.3 \text{ cm.}$			$\sigma = 22.75, D = 1.3556, p_0 = 349.6 \text{ cm.}$		
log V.	log $p/p_0$ .	log $p\sigma/p_0$ .	log V.	log $p/p_0$ .	log $p\sigma/p_0$ .
$\bar{2}.49183$	$\bar{2}.03643$	$\bar{1}.00257$	$\bar{2}.39811$	$\bar{3}.33415$	$\bar{2}.69113$
$\bar{2}.66113$	$\bar{2}.27363$	$\bar{1}.23977$	$\bar{2}.73466$	$\bar{2}.06453$	$\bar{1}.42151$
$\bar{2}.75343$	$\bar{2}.41060$	$\bar{1}.37674$	$\bar{2}.88680$	$\bar{2}.37194$	$\bar{1}.72892$
$\bar{2}.80302$	$\bar{2}.50189$	$\bar{1}.46803$	$\bar{1}.00355$	$\bar{2}.60706$	$\bar{1}.96404$
			$\bar{1}.11206$	$\bar{2}.83983$	$0.09681$
			$\bar{1}.21380$	$\bar{1}.06711$	$0.35698$
			$\bar{1}.28652$	$\bar{1}.22883$	$0.58581$
			$\bar{1}.32130$	$\bar{1}.30301$	$0.65999$

Expt. XVIII. 40°.			Expt. XIX. 80°.		
$\sigma = 21.0, D = 1.3111, p_0 = 471.2 \text{ cm.}$			$\sigma = 13.1, D = 1.192, p_0 = 1368 \text{ cm.}$		
log V.	log $p/p_0$ .	log $p\sigma/p_0$ .	log V.	log $p/p_0$ .	log $p\sigma/p_0$ .
$\bar{2}.21395$	$\bar{3}.30176$	$\bar{2}.62398$	$\bar{2}.60374$	$\bar{2}.14764$	$\bar{1}.26491$
$\bar{2}.55637$	$\bar{3}.82330$	$\bar{1}.14552$	$\bar{2}.65115$	$\bar{2}.21557$	$\bar{1}.33284$
$\bar{2}.74115$	$\bar{2}.13816$	$\bar{1}.46038$	$\bar{2}.82272$	$\bar{2}.47444$	$\bar{1}.59171$
$\bar{2}.86600$	$\bar{2}.36818$	$\bar{1}.69040$	$\bar{2}.91388$	$\bar{2}.62382$	$\bar{1}.74109$
$\bar{2}.96090$	$\bar{2}.55501$	$1.87723$	$\bar{2}.95323$	$\bar{2}.69124$	$\bar{1}.80851$
$\bar{1}.08350$	$\bar{2}.80359$	$0.12581$			
$\bar{1}.16607$	$\bar{2}.97865$	$0.30087$			
$\bar{1}.21436$	$\bar{1}.08077$	$0.40299$			
$\bar{1}.25355$	$\bar{1}.16702$	$0.48944$			

Expt. XXVI. -54°.			Expt. XXV. -80°.		
$\sigma = 39.0, D = 1.565, p_0 = 88.3 \text{ mm.}$			$D = 1.6295, \sigma = 44.5, p_0 = 8.8 \text{ mm.}$		
log V.	log $p/p_0$ .	log $p\sigma/p_0$ .	log V.	log $p/p_0$ .	log $p\sigma/p_0$ .
$\bar{2}.75603$	$3.65610$	$\bar{1}.24716$	$\bar{2}.94694$	$\bar{2}.16946$	$\bar{1}.81782$
$\bar{1}.16510$	$\bar{2}.67313$	$0.26419$	$\bar{1}.23931$	$\bar{2}.81895$	$0.46731$
$\bar{1}.30525$	$\bar{1}.04748$	$0.63854$	$\bar{1}.41420$	$\bar{1}.27300$	$0.92136$
$\bar{1}.41792$	$\bar{1}.29832$	$0.88938$	$\bar{1}.50416$	$\bar{1}.53982$	$1.18818$
$\bar{1}.49483$	$\bar{1}.49337$	$1.08443$	$\bar{1}.55975$	$\bar{1}.71728$	$1.36564$
$\bar{1}.57984$	$\bar{1}.70435$	$1.29541$	$\bar{1}.60585$	$\bar{1}.97460$	$1.62296$

Expt. XXIX.			Expt. XXIV.		
-34.4°.			0°.		
$\sigma = 36.2, D = 1.5302, p^{\circ} = 232.6 \text{ mm.}$			$\sigma = 28.5, D = 1.435, p^{\circ} = 116.2 \text{ cm.}$		
log V.	log $p/p_0$ .	log $p\sigma/p_0$ .	log V.	log $p/p_0$ .	log $p\sigma/p_0$ .
$\bar{2}.99858$	$\bar{2}.25870$	$\bar{1}.81741$	$\bar{2}.79757$	$\bar{3}.95307$	$\bar{1}.40755$
$\bar{1}.18293$	$\bar{2}.77484$	$0.33355$	$\bar{2}.99515$	$\bar{2}.44763$	$\bar{1}.90211$
$\bar{1}.30592$	$\bar{1}.09609$	$0.65480$	$\bar{1}.13180$	$\bar{2}.76370$	$0.21818$
$\bar{1}.40903$	$\bar{1}.33297$	$0.89168$	$\bar{1}.20767$	$\bar{2}.95742$	$0.41190$
$\bar{1}.48289$	$\bar{1}.49938$	$1.04809$	$\bar{1}.25764$	$\bar{1}.10226$	$0.55674$
$\bar{1}.55521$	$\bar{1}.70016$	$1.25887$	$\bar{1}.31482$	$\bar{1}.21489$	$0.66937$
$\bar{1}.58669$	$\bar{1}.94639$	$1.50510$	$\bar{1}.36637$	$\bar{1}.32496$	$0.77944$
			$\bar{1}.40847$	$\bar{1}.42696$	$0.88244$
			$\bar{1}.44278$	$\bar{1}.49994$	$0.95442$
			$\bar{1}.49499$	$\bar{1}.60484$	$1.05932$
			$\bar{1}.53977$	$\bar{1}.70266$	$1.15714$
			$\bar{1}.56726$	$\bar{1}.79221$	$1.24669$

As an empirical relationship, the result of dividing the volume of the condensed sulfur dioxide by the value of the surface tension raised to a fractional power was tried. Qualitatively, this produces a correction in the right direction. In order to take into consideration the constant that connects the value of the surface tension with the change of volume, we have thrown our relation into the following form:

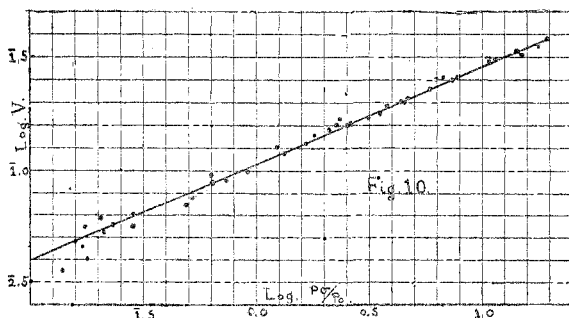
$$\frac{V}{\sigma^{1/n}} = k(P/P_0)^{1/n}$$

which, for calculation purposes, can be arranged thus

$$V = K \left( \frac{P\sigma}{P_0} \right)^{1/n}$$

assuming that the same value of  $1/n$  holds both for  $p/p_0$  and  $\sigma$ .

The preceding tables show the value of  $V$ ,  $p/p_0$  and  $P\sigma/p_0$ , all expressed as logs for convenience in plotting. Fig. 10 shows the contents of these tables when plotted with log  $V$  as abscissas and log of  $P\sigma/p_0$  as ordinates.



From this logarithm curve the value of the constant  $1/n$  and  $k$  are found to be 0.447 and 0.1038. In this case  $k$  has been taken as that



volume where  $\frac{P\sigma}{p_0} = 1$  and  $1/n$  has its usual significance—the slope of the curve. Hence our adsorption equation for the system silica gel—sulfur dioxide would be,

$$V = 0.1038 \left( \frac{P\sigma}{p_0} \right) 0.447,$$

where  $V$  is expressed in cubic centimeters,  $\sigma$  in dynes/cm., and  $p$  and  $p_0$  in the same unit of pressure. The close agreement is very striking and is strong evidence of our claim that the volume occupied by the adsorbed vapor is the same at the same value of the corresponding pressure  $p/p_0$ .

#### Summary.

1. The adsorption of sulfur dioxide by silica gel was measured at various temperatures between  $-80^\circ$  and  $+100^\circ$ .
2. The effect of the water content of the silica gel was studied. Maximum adsorption was shown by gels containing about 7% water.
3. The adsorption was shown to be reversible in the absence of air. In the presence of small amounts of air the rate of adsorption was greatly decreased and adsorption and desorption were irreversible.
4. The empirical equation of Freundlich was found to hold over almost the entire range studied—exceptions being at these points where the saturation pressure was approached.
5. The equation

$$\frac{V}{\sigma^{1/n}} = K(p/p_0)^{1/n},$$

is found to hold, where  $V$  = volume of condensed phase uncorrected,  $\sigma$  the surface tension,  $p$  the pressure of the gas phase,  $p_0$  the vapor pressure of the liquid,  $k$  and  $1/n$  constants dependent upon the physical properties of the adsorbent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

### A SURFACE CONDENSATION ERROR IN CERTAIN MEASUREMENTS OF VAPOR PRESSURE BY THE GAS CURRENT SATURATION METHOD.

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In the employment of the method referred to in the title, the possibility of condensation of the saturated vapor on surfaces earlier in the apparatus train than the weighed absorption tubes has been appreciated by some investigators but neglected by others. In order that the seriousness of this source of error in the case of water may be more fully understood, the writer proposes to illustrate its incidence in certain investigations