THE HEAT OF ADSORPTION OF HYDRATED SILICA GEL

THESIS FOR THE DEGREE OF M. S.

M. M. Nasif

1931

[redacted]

[redacted]

Silica gel

Chemistry

THE HEAT OF ADSORPTION
of
HYDRATED SILICA GEL

A Thesis
Submitted to the Faculty
of
MICHIGAN STATE COLLEGE

In Partial Fulfillment of the
Requirements for the Degree

of

Master of Science
Department of Chemistry

By

M. M. Nasif

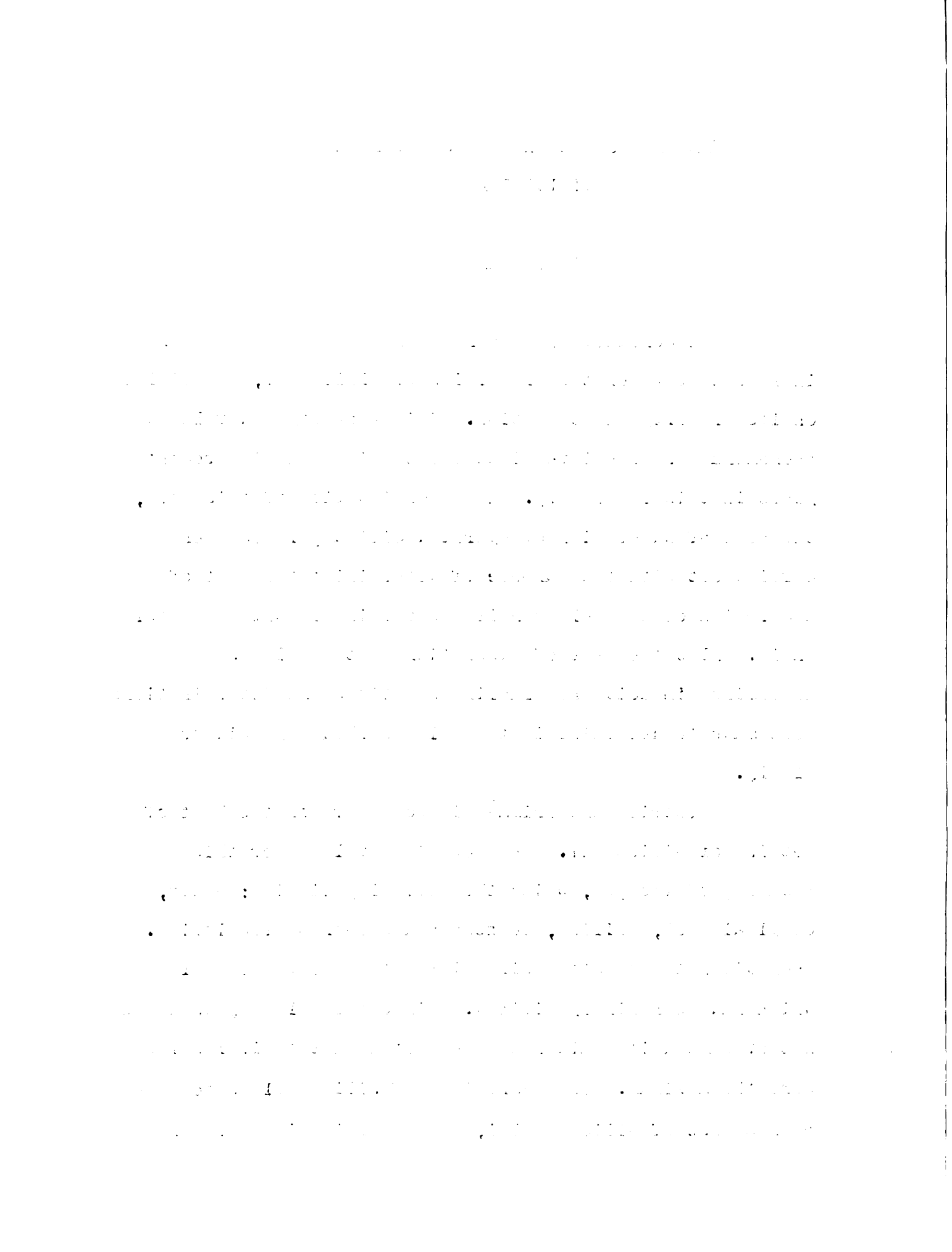
1931

THE HEAT OF ADSORPTION OF HYDRATED SILICA GEL

HISTORICAL

A considerable amount of research has been done in recent years on the properties of silica gel, especially on its property of adsorption. This property and related phenomena has been investigated extensively during recent years in this laboratory. As a continuation of this work, the heat of adsorption of hydrated silica gel has been carried out with the purpose of determining the heat of adsorption of the gel when it has varying amounts of water on it. Also the heat of adsorption of the gel was determined in acid and alkaline solutions and determinations were made to determine if the gel adsorbed any acid or alkaly.

Patrick and Grimm[1] did some work on the heat of wetting of silica gel. They obtained values for this property of the gel, using the following liquids: water, ethyl alcohol, aniline, benzene and carbon tetrachloride. They did not evacuate their gel and they also used gel which had been finely divided. Since the gel they used was not evacuated it would not be expected that their results were the maximum. They conceived of silica gel as to have been a mass of silica nuclei, each nuclei being surrounded



with a thin film of water. Having such a conception of silica gel they accounted for the heat of adsorption or wetting on the basis of surface energy changes that took place at the surface of each nuclei.

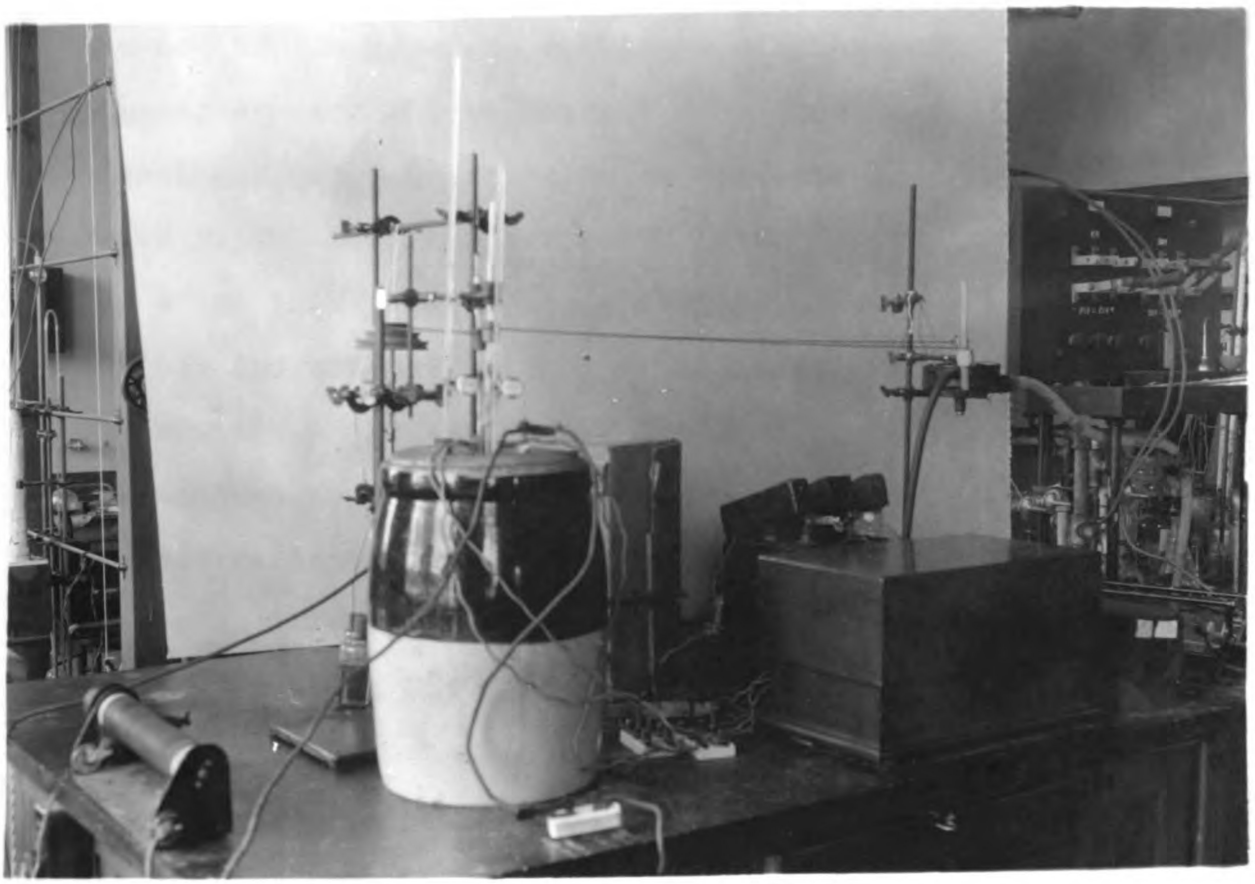
Much research has been done on the heat of adsorption of soils. Bouyoucos[2] says that in the case of soils the maximum is reached when the soil has been heated to 107°C. for 24 hours. He also states that the amount of water necessary to produce the heat is comparatively small. In an other article he says that the temperature rise of water by sudden compression amounts to 0.018°C. per 10 atmospheres, and that the force of compression rises to such large values as 156 atmospheres.

The heats of adsorption of some eleven organic liquids on charcoal were determined by Lamb and Coolidge[3]. They determined the heats of adsorption by the expression $h = mx^n$, where h represents the heat of adsorption per c.c. of vapor, x the number of c.c. of vapor adsorbed, and m and n characteristic constants of the vapor adsorbed.

APPARATUS AND MATERIAL

Calorimeter:- A great deal of time was spent in constructing a colorimeter that would be suitable for this work. Several different types were tried but the adiabatic type was the one finally used. The difference in temperature of the outer and inner container was never allowed to be greater than 0.05° and very often it was less, and the time during which this difference existed was very short. The time at which the two containers are at maximum difference in temperature is when the bulb containing the gel is broken and the temperature of the liquid in the inner container goes up suddenly. However, by means of a large resistance used as a heating element, the temperature of the outside vessel is brought up quickly so that there is no more than 0.05° difference between the two at any.time. All parts inside of the calorimeter were made of glass with the exception of the leads for the inside heating element. These were made of copper of such size as to produce no heat when the current was flowing thru them. These leads were also lacquered to prevent corrosion by the liquids. The heating element in the inside vessel was a piece of platinum about 5 cms. long soldered onto the copper leads.

The outside of the calorimeter was an earthen-



ware jar about 16 inches tall and 10 inches in diameter. Inside of this jar was an inverted bell-jar. The space between these two vessels was filled with saw-dust and the top of the saw-dust filling was covered with a coating of paraffin to prevent an air current. This vessel was covered with a round piece of one inch board which fitted over the top very tightly. Thru this cover was a two inch hole in the center to allow the stirrer and the thermometer of the inside container to project out of it. There was also a hole for the stirrer thermometer, and leads for the heating element. Inside of this container was an evacuated Dewar flask about 12 inches tall and 1 5/8 inches inside diameter. This was supported in the center of the inverted bell-jar and weighed down by means of a heavy lead weight. The space between the Dewar flask and the bell-jar is filled with distilled water.

Preparation of Gel:- The gel used was a product of The Silica Gel Corporation and was of good quality. All samples of gel were first freed of any particles that were brown or discolored in any way and also particles that were of a white color. Only the clear transparent particles being used.

Approximately 2.5 g. samples of the gel were used in all cases. The gel was treated under different

conditions with different experiments, the results being that the different samples under different conditions of treatment giving different values for the heat of adsorption. The samples of gel were placed in glass bulbs which were blown so that the walls became very thin, yet were strong enough to withstand being evacuated. These bulbs were then sealed off from the air with the gel in them.

One experiment was performed with several samples of gel just as the gel was received, that is, without being treated in any way, using water.

Other experiments were done using several samples of gel that had been (1) heated for 24 hours at 120°C., (2) for 4 hours at 250° and evacuated at the same time, and (3), evacuated for 1 hour without heating and combinations of heat and vacuum, the purpose being to get samples of gel with varying water content.

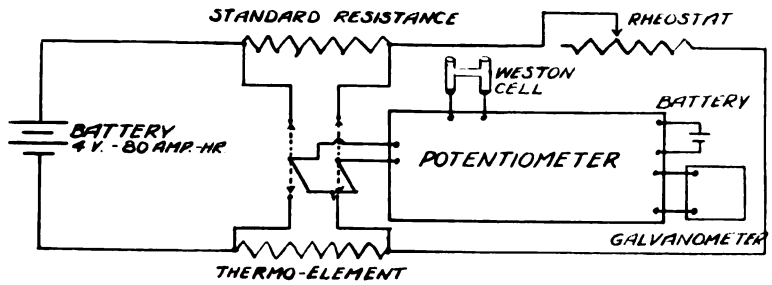
The above experiments were repeated using 0.2 N $H_2 SO_4$ solutions in place of water.

The water used was distilled laboratory water which had been redistilled, and the sulfuric acid solution was made of this water and C.P. $H_2 SO_4$.

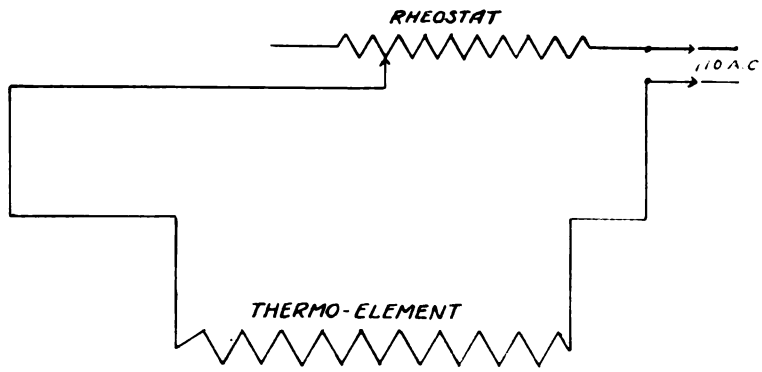
The thermometers used were Bureau of Standards thermometers. The one in the outside vessel being graduated to 0.1°, and the one used on the inside of the Dewar flask being graduated to 0.01°.

Method of Prodedure:- The liquid whose heat of adsorption was to be determined was put into the Dewar flask. Then the bulb containing the gel was put into the flask and the glass rod with a loop on the end of it was placed over the bulb to hold it down and keep it from getting in the way of the stirrer. Then the stopper with the thermometer, stirrer and thermo-element sealed in it was put into the flask. The flask was then put into the outside bath. The temperature was brought to the temperature of the liquid in the flask either by cooling or heating, as the case may be, during which operation the stirrers in both vessels being in motion. The temperature of the liquid in the flask was then noted and recorded. Then the bulb was broken and the temperature was noted every five seconds by means of a stop-watch until a constant temperature was attained. The time required for this rise in temperature was noted. Then enough heat was introduced into the system to produce the same rise in temperature in the same length of time. This was accomplished by allowing a current from a 4 volt lead storage cell to pass thru a rheostat, a standard resistance and the thermo-element. The current was so adjusted that it would produce the same rise in temperature in the same length of time that the gel did. In this way all losses were corrected. The current was measured

WIRING DIAGRAMS



INSIDE VESSEL



OUTSIDE VESSEL

by noting the potential drop across the standard resistance of 0.1 ohm by means of a type K polentiometer. Then the potential drop across the thermo-element was measured in the same way by throwing the switch in the other direction. Knowing the current and the potential drop, the resistance can be calculated.

Method of Calculating the heat of adsorption:- Joule's law states that

$$H \text{ (calories)} = \frac{i^2 r t}{4.18} \quad \text{or} \quad H = \frac{E I t}{4.18}$$

Knowing the current, potential drop and the time, the amount of heat introduced into the system can be calculated. Now this gives the number of calories produced by the current and which caused the liquid in the calorimeter to rise the same number of degrees in the same length of time as the gel did. It is necessary to use a current of such value that it will produce the same rise in temperature in the same length of time as the gel, so that losses due to conduction and radiation will be accounted for.

This heat is due to all the gel added. Now to obtain the heat due to one gram of gel or the heat of adsorption of the gel, it will be necessary to divide the total amount of heat by the number of grams of gel used.

$$\frac{H}{g} = \frac{E\,I\,t}{4.18g}$$

where g is the number of grams of gel added.

The results obtained are tabulated as follows:

TABLE I

GEL CONTAINS 6.2% WATER. WETTING WITH WATER

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel.
2.5009	22.135	22.510	.375	4.110	.2424	200	47.7	19.07
2.4997	22.160	22.530	.370	4.115	.24278	195	46.6	18.65
2.5003	22.015	22.395	.380	4.280	.2525	180	46.5	18.60
2.5008	22.240	22.830	.390	4.130	.24367	205	49.34	(19.73)
2.5004	22.425	22.802	.373	4.220	.2490	190	47.82	19.13
2.4992	22.557	22.935	.378	4.114	.2427	200	47.75	19.11
2.5002	22.512	22.532	.380	4.112	.2426	200	47.73	19.09
2.5033	22.047	22.435	.388	4.095	.2416	210	48.45	19.35
2.5001	22.725	23.092	.367	4.095	.2416	190	44.95	(17.98)
						Average		19.00

TABLE II

GEL CONTAINS 4.2% WATER. WETTING WITH WATER

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.4997	22.460	22.893	.433	4.510	.2660	190	54.5	21.81
2.5007	22.600	23.032	.432	4.511	.2661	190	54.5	21.80
2.5021	22.305	22.745	.440	4.495	.2652	200	56.95	(22.76)
2.5002	23.085	23.510	.425	4.500	.2658	190	54.4	21.76
2.5013	22.655	23.090	.435	4.712	.2780	180	55.98	22.38
2.5008	22.497	22.931	.434	4.710	.2760	180	55.94	22.37
						Average		22.02

TABLE III

GEL CONTAINS 3.7% WATER. WETTING WITH WATER

2.4441	24.080	24.575	.490	4.971	.2985	165	55.89	22.87
2.4521	22.360	22.850	.490	5.101	.3121	150	55.2	22.50
						Average		22.68

TABLE IV

GEL CONTAINS NO WATER. WETTING WITH WATER

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.4297	22.690	23.250	.560	5.526	.3245	170	72.8	29.96
2.4368	21.970	22.560	.590	5.541	.3289	170	74.02	30.38
2.4005	21.200	21.760	.560	5.463	.3224	170	71.6	29.83
2.4132	21.300	21.875	.575	5.023	.2970	200	71.37	29.58
2.4349	21.305	21.870	.565	4.997	.29605	205	72.58	29.79
2.3944	21.850	22.435	.585	5.7075	.3310	160	72.54	30.21
2.3940	21.450	22.036	.586	4.788	.2831	240	74.55	(31.14)
2.3811	22.640	23.220	.58	5.675	.33305	160	73.11	(30.71)
						Average		29.96

TABLE V

GEL CONTAINS 15.5% WATER. WETTING WITH WATER

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.5006	23.133	23.318	.185	2.410	.1422	240	19.70	7.88
2.5038	23.007	23.185	.178	2.673	.1634	190	19.82	7.92
						Average		7.90

TABLE VI

GEL CONTAINS 12.5% WATER. WETTING WITH WATER

2.4406	22.055	22.280	.225	3.705	.2170	140	26.80	10.98
2.4284	22.207	22.430	.223	3.691	.21765	140	26.89	11.07
						Average		11.02

TABLE VII

GEL CONTAINS 12% WATER. WETTING WITH WATER

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.3983	23.910	24.138	.228	3.717	.2181	140	27.13	11.32
2.4002	23.170	23.401	.231	3.718	.2182	140	27.13	11.30
						Average		11.31

TABLE VIII

GEL CONTAINS 8.5% WATER. WETTING WITH WATER

2.3320	22.522	22.825	.313	4.519	.2638	150	42.70	18.29
2.2872	22.465	22.775	.310	4.578	.2652	140	42.53	18.60
						Average		18.24

TABLE IX

GEL CONTAINS 3% WATER. WETTING WITH WATER

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.2339	22.500	22.890	.390	4.483	.2629	150	42.21	18.90
2.2366	22.520	22.913	.393	4.489	.2632	150	42.40	18.96
						Average		18.93

TABLE X

GEL CONTAINS 1% WATER. WETTING WITH WATER

2.1418	22.340	22.832	.492	5.401	.2993	130	50.10	23.40
2.1459	22.503	22.994	.491	5.410	.33001	120	51.10	23.81
						Average		23.60

TABLE XI

GEL CONTAINS NO WATER. WETTING WITH WATER

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.3964	23.288	23.880	.592	4.788	.28615	210	71.12	29.66
2.3980	22.235	22.835	.600	4.785	.2855	220	71.53	29.85
						Average		29.75

TABLE XII

Comparison of Heat of wetting with % Water

Gel + Water Percent water	W_H Cal.
None	29.75
1%	23.60
3%	18.93
8.5%	18.24
12%	11.31
12.5%	11.02
15.5%	7.90

TABLE XIII

GEL CONTAINS 15.5% WATER. WETTING WITH .2N H_2SO_4

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.4997	21.925	22.108	.183	3.986	.1790	170	21.72	8.71
2.5022	21.105	21.295	.190	4.500	.2699	75	21.71	8.69
						Average		8.70

TABLE XIV

GEL CONTAINS 8% WATER. WETTING WITH .2N H_2SO_4

2.2647	22.480	22.800	.320	3.896	.2272	190	40.23	17.77
2.2939	22.816	23.119	.303	4.495	.2608	150	39.18	17.10
						Average		17.43

TABLE XV

GEL CONTAINS NO WATER. WETTING WITH .2N H_2SO_4

Wt. of gel used	Initial Temp.	Final Temp.	Rise in Temp.	Current	Voltage	Time Sec.	Total heat	Heat per gr. of gel
2.4131	23.150	23.710	.56	4.772	.2850	210	68.20	28.30
2.3776	22.340	22.920	.58	5.047	.3006	200	72.58	28.80
						Average		28.55

DISCUSSION

It is a well established fact that water adsorbed on the surface of a solid, such as silica gel, has undergone a thermodynamic change in state and is held on the surface by an enormous force. Some of the early investigators to advance this theory are Jungh[4], Rose[5], and Parks[6]. This has been more recently confirmed by Patrick and Grimm[1] and Lamb and Coolidge[3] by their data on the heat of adsorption of water.

It is quite apparent that the heat of adsorption is due to a change of concentration of the molecules of the liquid at the surface or in the pores of the gel. This has been recently confirmed by Ewing and Spurway[7] in their determination of the density of water adsorbed on silica gel. They found that the density of water increased when adsorbed on silica gel up to the value 1.6869 g. of water. They noticed that heat was liberated when the gel was allowed to absorb water, but they did not make any measurements on it. They found a close correlation between the density values for 1.6867 g. and 0.6357 g. of adsorbed water which, they said, indicated one phase of water on the gel. The mean density values for the two larger quantities of adsorbed water are less than the density of liquid water at the operating

temperature, indicating the presence of three phases of water: compressed water, liquid water, and water vapor. This water vapor, they said, exerts only a low vapor pressure; hence, all three forms of water are held on the gel under pressure.

Then by calculations based upon the volume of the adsorbed water in the runs where the silica gel contained 1.6867 g. or 0.6357 g. of water, and a correlation of Bridgeman's compressibility data, it was shown that in these cases the pressure on the adsorbed water was of the magnitude of 750 atmospheres.

Thus, when the molecules of water are compressed at the surface or in the pores of the gel, there is a decrease in the kinetic energy of the molecules. In order to have a decrease in the kinetic energy, heat is liberated which is an increase in the potential energy of the molecules. This is the opposite of such phenomena as latent heat of vaporisation, in which case the molecules are driven farther apart due to the addition of heat to the system and the heat being transformed into kinetic energy of the molecules. The forces acting in this phenomena are the stray fields around the molecules of the wetting substance and the molecules of the substance being wetted. The greater these stray fields, the less the tendency to exhibit this phenomena.

The results given in Tables I to IV inclusive, were obtained with a gel that had a maximum water content of 6.2%. The results indicate that there is a general increase in the heat of adsorption as the water content of the gel is decreased. The results given in Tables V to XI inclusive, show somewhat the same thing. There is a decided increase in the heat of wetting between the gel containing 15.5% water and the gel containing 8.5% water. But there is a large difference in the heat of wetting of the gel with 8.5% and that with 3%. As the water content decreases below 3%, the heat of wetting again increases rapidly until the maximum value is reached. It is interesting to note that the largest rise in temperature took place very shortly after the gel was exposed to the liquid and that this initial rise in temperature was larger and took place more quickly with the gel that had the smaller amounts of water on it. We obtained more nearly a wetting of the gel by the liquid, as indicated by the results given in Tables IV and IX, because when the gel is heated and evacuated, the water is in the gaseous state, and a smaller quantity can be held, and is probably held, on the surface of the gel. Now, when the gel is again cooled, the water becomes liquid and occupies a much smaller volume than when in the gaseous state. This condensation of the gaseous water leaves a

large portion of the surface of the gel with nothing adsorbed on it. This free surface then absorbs the liquid with great rapidity and liberates a large amount of energy. The larger this free surface the greater the amount of energy liberated.

According to Patrick and Grimm[1], in order to get a heat of wetting of 19.22 Cal. per gram of gel it is necessary that the gel exhibit a surface of 6.9×10^7 cm.^{2} which is an enormously large surface. It is evident that the surface energy is therefore sufficient to explain the observed heat effects.

Lamb and Coolidge[3] in their determinations on the heat of adsorption of vapors on charcoal have calculated that the amount of carbon disulfide adsorbed on a gram of charcoal is 0.4 cc at atmospheric pressure and about 0.25 cc under a pressure of 37,000 atmospheres. The carbon disulfide was sufficient to fill all the capillaries which had a volume of 0.42 cc. Assuming the capillary area to be 100 square meters and that the thickness of a molecular layer is 1×10^{-8} cm., then the above amount of carbon disulfide if spread over the whole surface would have given a layer 40 molecules deep.

Lamb and Coolidge[3] regard the heat effect as due to two factors, the heat of liquefication of the gas and the heat effect due to further compression of the

liquid by the adhesive forces of the adsorbent. The latter or net heat of adsorption, is equal to the heat of wetting at the saturation pressure of the liquid.

Harkins and Ewing[8] have obtained direct experimental evidence of the compression of a layer of liquid adsorbed on a solid in the case of activated charcoal and organic liquids. The attractive forces between the charcoal and the various liquids are shown to be constant and of the order of 30 to 40 thousand atmospheres, in agreement with the findings of Lamb and Coolidge[3]. It is pointed out that experiments on the internal pressure of the liquids have not succeeded in demonstrating pressures higher than 72 atmospheres.

Harkins and Ewing derive the heat of adsorption of a liquid by a solid from surface energy considerations as follows: If we consider that the solid is immersed in the liquid against air, the net result is that the surface of the solid is replaced by a solid - liquid interface. The heat of adsorption, $-Qa$, is then equal to the total amount of energy given off in the process when carried out isothermally, Ea, or

$$-Qa = Ea = Es - Ei$$

Where Es and Ei are respectively the total

energies of the solid surface and of the interface. The heat of adsorption of a liquid on a solid has always been found to be positive, indicating that the total surface of the solid is greater than that of the interface.

Table XII is a summary of the results given in Tables V to IX inclusive.

In Tables XIII, XIV, and XV are given the results obtained by wetting the gel having the indicated water contents with approximately 0.2N sulfuric acid. These results agree very well with those obtained for water and gel having on it the same amount of water. This indicates that the presence of sulfuric acid does not effect the heat of wetting of the gel. The acid was analyzed before and after it was exposed to the gel, and it was found that the concentration increased from 0.19330 before exposure to 0.1986 after exposure. This indicates that water and not sulfuric acid was adsorbed by the gel.

Bartell and Miller[9] in their work on the adsorption by sugar charcoal of acid and basic dyes say that inorganic acids are but comparatively slightly adsorbed by charcoal because the inorganic onion replaces more feebly the OH_s^- ion. Inorganic bases are adsorbed scarcely at all, owing to the fact that metals less noble than H do not replace H^+ from Carbon.

Silica gel does not seem to have an affinity for acid radicals much the same as carbon.

An attempt was made to obtain the heat of wetting of silica gel with sodium hydroxide solution but no constant temperature could be obtained which indicated that the alkaly reacted with the gel.

SUMMARY

1. Some heats of wetting of silica gel with water were obtained with the gel containing varying amounts of water on it.

2. The heat of wetting increased more rapidly as the amount of water on the gel became smaller, that is, there was a very large increase in the heat of wetting between the gel that had 1% water on it and the gel that had very little or no water on it.

3. The heat of wetting of a 0.2N solution of sulfuric acid was obtained and found to be the same as for water along.

4. No value for the heat of wetting of sodium hydroxide was obtained because it was thought that the alkaly reacted with the gel.

REFERENCES

1. Patrick and Grimm

Jour. Am. Chem. Soc. 43,2144 (1921)

2. Bouyoucos

Technical Bulletin No. 42,

Soil Science, Vol. 17, No. 2, Feb. 1924,

Soil Science, Vol. 19, No. 2, 1925,

3. Lamb and Coolidge

Jour. Am. Chem. Soc. 42, 1146 (1920)

4. Jungh,

Ann. Phys. Chem. 125, 292 (1865)

5. Rose,

Ann. Phys. 73, 1 (1849)

6. Parks,

Phil. Mag. 4, 220 (1902); 5, 517 (1903)

8. Harkins and Ewing

Jour. Am. Chem. Soc. 43, 1795 (1921)

9. Bartell and Miller

Jour. Phys. Chem. 28, 992 - 1000 (1924)