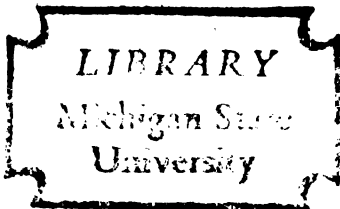A MAGNETOCHEMICAL INVESTIGATION
OF THE ADSORPTION OF PARAMAGNETIC
SALTS

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE

Robert Earle Vander Vennen

1951

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A MAGNETOCHEMICAL INVESTIGATION OF THE
ADSORPTION OF PARAMAGNETIC SALTS

By

Robert Earle Vander Vennen

AN ABSTRACT

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A MAGNETOCHEMICAL INVESTIGATION OF THE
ADSORPTION OF PARAMAGNETIC SALTS

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The purpose of this work has been to study the magnetic susceptibilities of some paramagnetic iron-group salts adsorbed from aqueous solution on charcoal and silica gel. Assuming the magnetic susceptibilities of the adsorbent and adsorbed salt to be additive functions, from knowledge of the amount of salt adsorbed the magnetic moment of the latter can be calculated. This observed value can be compared with the value for the salt in solution in order to determine whether or not the electronic structure of the salt has changed upon adsorption.

A review of the literature shows that little has been published on this type of work. An early paper reported that the adsorbed atoms lose their paramagnetism on charcoal but not on silica gel, but the work merited re-examination.

The Gouy method for determining magnetic susceptibilities was used. This requires measuring by a balance the apparent change in weight of the sample when placed in the magnetic field. The electromagnet constructed for this purpose is described, and calibration data for it are given.

Measurements were made over a range of field strengths from 8,000 to 13,500 oersteds. Between each measurement the circuit was broken and attempts made to eliminate residual field. Adsorption experiments were carried out by adding standard salt solution to known weights of dried charcoal and silica gel, and the amount of adsorption determined by the decrease in salt content of the solution.

The gram susceptibility of pure charcoal is found to be -0.462 x 10^{-6} e.g.s. units, and of silica gel -0.317 x 10^{-6}. Magnetic susceptibility values determined for the adsorbed paramagnetic ions are compared with the values obtained for the ions in solution and in the solid state. These results are recalculated and compared also in terms of "effective Bohr magneton numbers". The ions in the adsorbed state are found to have the same paramagnetism as they have under other conditions, except for an anomaly in the case of $Fe_2(SO_4)_3$.
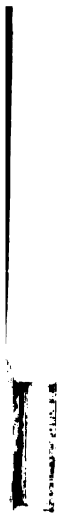
In order to interpret this work in terms of a mechanism of adsorption, a brief review is given of the work reported in the literature on adsorption of electrolytes from aqueous solution on charcoal. Factors having the greatest effects on the nature of adsorption are: impurities in the adsorbent, surface oxides, charge of aqueous suspensions, and activation of the adsorbent, including both the activating atmosphere and the temperature of activation. Electrolyte adsorption may be explained as due to "chemical" interaction with the surface, and to electrostatic attraction between the surface and dissolved ion.

The evidence presented points to the conclusion that, since the paramagnetism of the ion is apparently not disturbed upon adsorption, the ions are likely bound by electrostatic forces to oxygen atoms on the adsorbent surface.

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INTRODUCTION

I. INTRODUCTION

In spite of the great importance of adsorption and catalysis both in industry and from a theoretical point of view, very little is actually known about the nature of the forces which bind the adsorbate to the adsorbent. The method of magnetic susceptibilities has in a few cases been applied to this problem, and the results are particularly striking when the substance adsorbed has a large paramagnetism. The purpose of this investigation has been to study the magnetic susceptibilities of some paramagnetic iron-group salts adsorbed from aqueous solution on charcoal and silica gel. It was thought that using the Wiedemann additivity law to determine the susceptibility of the adsorbate, something could be learned about the type of forces binding the adsorbed salt to the adsorbent.

HISTORICAL BACKGROUND

II. HISTORICAL BACKGROUND

Although it is generally recognized that magnetic susceptibility values can be a powerful means of determining the types of binding between atoms, this method has been scarcely at all applied to the binding which exists in adsorption. Most extensively studied from the magnetic point of view seems to be adsorbed oxygen, which has been thoroughly studied by Juza and his associates (1). Their results show that the susceptibilities are not additive, assuming the oxygen to be molecularly adsorbed. Thus they can determine the relative amounts of oxygen adsorbed molecularly and of combined oxygen, since the latter is diamagnetic. Also studied magnetically are the adsorption of bromine (2), and of oxides of nitrogen (3).

Courty has investigated the additivity of water vapor on charcoal and porcelain (4), and has reached some interesting conclusions. He found that, except for pulverized activated charcoal and "clean" porcelain, the susceptibility of the adsorbed water was dependent upon the amount of water adsorbed. This was due presumably to incomplete displacement of the paramagnetically adsorbed air. He also found that when charcoal was increasingly pulverized and activated it became increasingly more paramagnetic. He explained this by saying that the charcoal with the greatest surface area held the most adsorbed air, and the air being paramagnetic gave an observed paramagnetism to the charcoal.

Some work has been done on the adsorption by paramagnetic palladium catalysts, particularly with regard to catalyst poisoning (5). The

paramagnetism of the palladium catalyst is found to be reduced upon adsorption.

Boutaric and Berthier investigated the additivity properties of $Fe(OH)_3$ and $FeCl_3$ (6). When $Fe(OH)_3$ and $FeCl_3$ were adsorbed on bentonite the susceptibility of the ferric ions appeared to increase. But when substances were adsorbed on sols of $Fe(OH)_3$ and of $FeCl_3$, the susceptibility was lower than that predicted on the basis of additivity.

Selwood has also done considerable work on the relationship between adsorption and magnetism (7), with particular emphasis on the effect the magnetism of the adsorbent has on adsorption.

But perhaps the earliest work of this kind, and that related most directly to the present investigation, was done by S. S. Bhatnagar, K. N. Mathur, and P. L. Kapur (8). They examined the adsorption from solution of iron, nickel, cobalt, and manganese salts by charcoal and by silica gel. They found that with silica gel the susceptibilities are not far from additive, but with charcoal the metal atoms lose their paramagnetism and become diamagnetic. The present investigation was carried out as a check on and an extension of this work.

EXPERIMENTAL

III. EXPERIMENTAL

The magnetic susceptibilities were determined by the Gouy method which involves measuring the apparent gain or loss in weight of the sample when it is placed in an inhomogeneous magnetic field. The amount of change in weight is measured by a balance from which the sample is suitably suspended. A diagram of the Gouy magnetic balance used is given in Figure 1.

The electromagnet used was constructed for this purpose in the machine shop of the Chemistry Department. The pole pieces, made of mild steel, are moveable along their common axis, so the gap between the pole pieces can be altered as circumstances require. The over-all features of magnet construction, together with relevant dimensions, are shown in Figure 2. Around each pole piece fits a brass spool upon which is wound No. 8 D. C. C. copper magnet wire. The wire is wound in double layers, alternating with one-eighth inch strips of insulation. There are 30 layers of wire per coil with 48 turns in each coil, giving a total of 1440 turns per coil. The total length of wire is about 7200 feet, and the resistance for both coils in series is about five ohms. The coils can be cooled by pumping oil through the windings. To facilitate oil circulation aluminum "spiders" are located at the sides of the coils, and these spiders are grooved in such a way that oil can move freely from one layer of wire to another.

In order to determine the field strength produced by various values of applied current between one and twenty amperes, measurements were
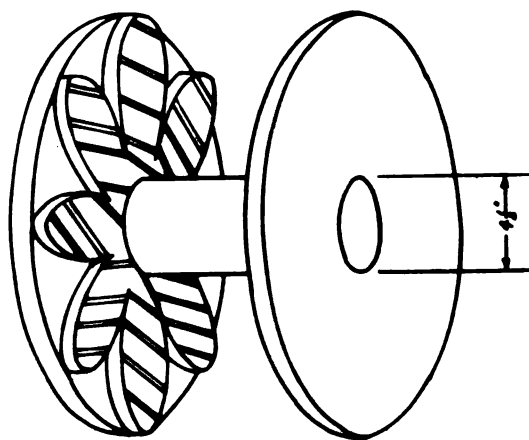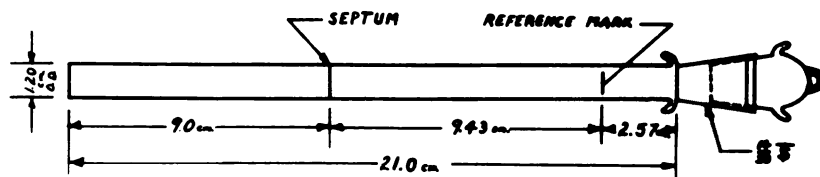
FIG.1   GOUY MAGNETIC BALANCE
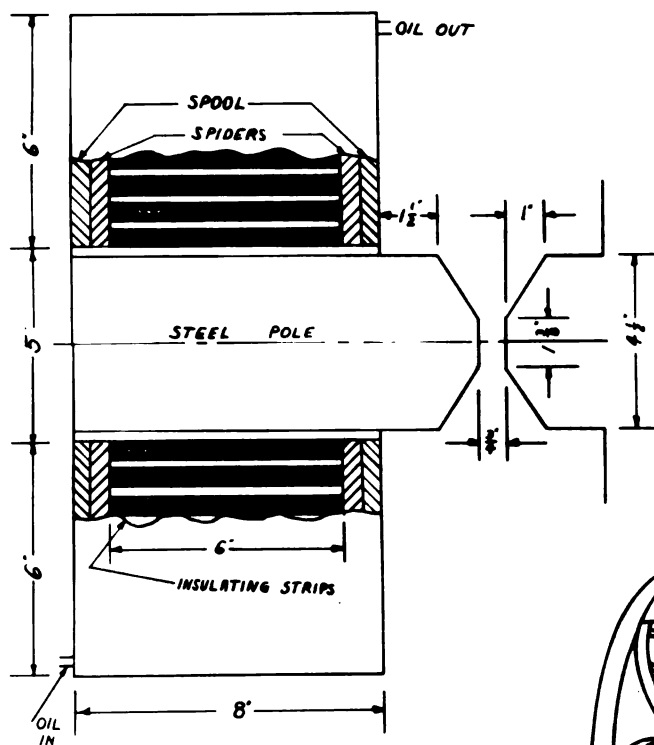
FIG. 2. MAGNET CONSTRUCTION

<u>a</u>. (Left) Coil and Pole

<u>b</u>. (Below) Spool and Spider

OIL OUT

SPOOL

SPIDERS

STEEL POLE

INSULATING STRIPS

OIL IN

FIG. 3. SUSCEPTIBILITY TUBE

SEPTUM

REFERENCE MARK

9.0 cm

9.43 cm

2.57 cm

21.0 cm

made of the amount of pull of the field on distilled water and on a standard $NiCl_2$ solution (29.20% $NiCl_2$ by weight, density 1.8356). The field strength H is obtained from the following relation:

$$\frac{1}{2}(K_1{}^* - K_2) \; H^2 A = g \Delta w$$

where

K_1 = volume susceptibility of the liquid

K_2 = volume susceptibility of air

A = area of the tube, parallel to the pole faces, from septum to reference mark; found to be 0.8224 cm^2.

g = gravitational constant

Δw = apparent change in weight of the sample when placed in the field.

The results obtained are presented in Table I, and the values for $NiCl_2$ are shown graphically in Figure 4.

The susceptibility tube was constructed of thin-walled glass, and was a double or compensated tube, with the halves separated by a septum. (See Figure 3.) This construction makes it possible to ignore the susceptibility of the tube; it was verified experimentally that the tube alone exerted no change in vertical force when the field was applied. The upper end of the tube consisted of a female ground-glass joint. The corresponding male joint, which closed off the tube, was provided with a loop which could be attached to the suspending chain. For each measurement the tube was filled to a specific reference mark near the neck; the distance from this mark to the pole faces was great enough so

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* K will be used in place of the customary Greek letter kappa to denote volume susceptibility, and X in place of chi to denote mass susceptibility.

FIG. 4.   FIELD STRENGTH VS.   CURRENT

A M P E R E S

O E R S T E D S

14,000

12,000

10,000

8000

6000

4000

2000

2   4   6   8   10   12   14   16   18   20
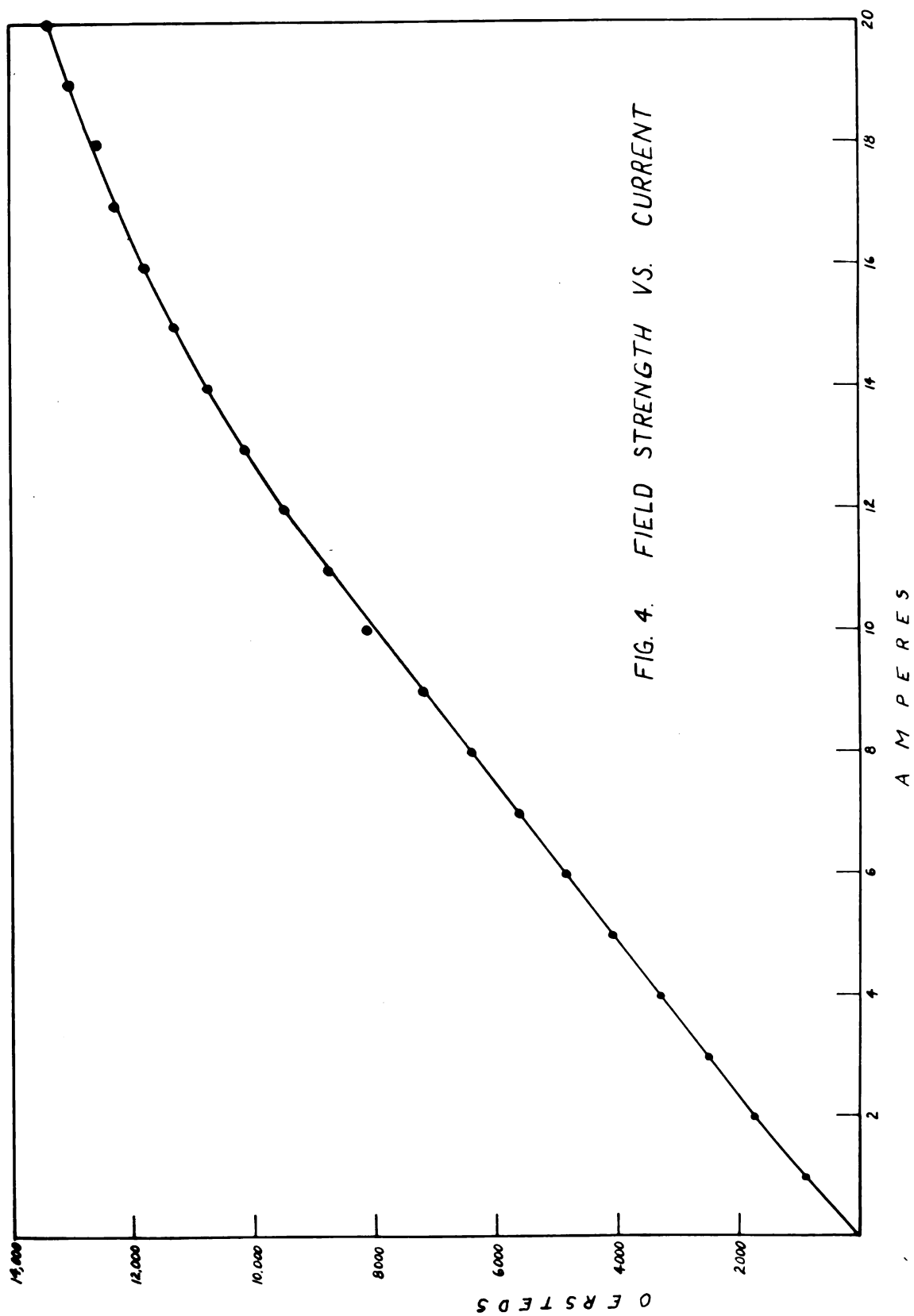
TABLE I

FIELD STRENGTH VERSUS APPLIED CURRENT

Current (amperes)	NiCl$_2$ Solution		Water	
	Δw (grams)	H (oersteds)	Δw (grams)	H (oersteds)
1	+0.00410	870	-0.00030	976
2	.01600	1,738	.00090	1,689
3	.03160	2,442	.00180	2,390
4	.0544	3,205	.00310	3,137
5	.0850	4,005	.00490	3,940
6	.1214	4,785	.00700	4,710
7	.1661	5,600	.00960	5,515
8	.2111	6,310	.01245	6,290
9	.269	7,125	.01590	7,100
10	.345	8,075	.02030	8,030
11	.400	8,695	.02330	8,600
12	.468	9,400	.02780	9,390
13	.535	10,050	.03130	9,960
14	.609	10,700	.03565	10,630
15	.671	11,240	.03930	11,150
16	.734	11,770	.04310	11,690
17	.793	12,220	.04680	12,170
18	.843	12,540	.04975	12,550
19	.897	13,000	.05270	12,900
20	.945	13,350	.05570	13,280

that the square of the field strength at the mark was negligible compared to the square of the field at the base. The volume of sample in the tube measured 7.65 cc.

The tube itself was suspended by a brass chain attached to the left pan of the balance. In order to prevent air currents from disturbing the system, the pole pieces, susceptibility tube and chain were enclosed in a compartment made from plywood and plexiglass and fitted with a suitable door. Inside the compartment and near the sample was hung a thermometer which permitted temperature measurements to $\pm$ 0.5 degrees.

The semi-micro balance used was capable of being read to the hundredth of a milligram, although, for the present work where the susceptibilities were rather large, it was found necessary to take readings only to the tenth of a milligram.

The source of power was a D.C. generator, operating normally at 110 volts. The current delivered by the generator could be varied by means of a series of resistances, and it was controlled to $\pm$ 0.1 ampere. With the large currents used, variations of this magnitude produced negligible field change.

Susceptibility determinations on each substance were made at 10, 12, 14, 16, 18, and 20 amperes, corresponding to a range in field strength from 8,000 to 13,500 oersteds. In most cases two measurements were made at each field strength, and the second measurement was made with the tube rotated through 90 or 180 degrees so that any inhomogeneity in the sample or in packing would show up. This proved, however, to be an unnecessary precaution. Taking measurements over a range of field

strengths like this was doubly advantageous: 1) from the series of values thus obtained, a good average could be taken for the susceptibility of the substance; and 2) this provides a convenient means of detecting ferromagnetic impurities.

Between each measurement the circuit was broken, and an attempt was made to eliminate any residual magnetism in the pole pieces. This was done in the following manner: the current was reduced to six amperes, and while the direction of the current was being repeatedly reversed by means of a reversing switch, the current itself was being progressively cut down to less than one ampere by a carbon-plate resistor connected in series with the circuit. In this way hysteresis was minimized and the residual field between the pole pieces was made negligible.

The charcoal used was Eimer and Amend C.P. Sugar Charcoal. Preliminary work showed the presence of small amounts of ferromagnetic impurity, and also of an impurity which could be oxidized with cerate solution. To remove these, the charcoal was finely ground and treated with concentrated sulfuric acid. Although the charcoal was subsequently washed repeatedly with distilled water, the last trace of acid could not be removed. This was not important in the susceptibility measurements, however, since sulfuric acid has the same diamagnetism as charcoal. The density of the charcoal, as packed in the susceptibility tube, was 0.829 ± 0.004 grams per cc.

The silica gel was obtained from Davisson Chemical Company. It contained just a small amount of ferromagnetic impurity. Density of the silica gel was 0.800 ± 0.006 grams per cc.

The adsorption experiments were carried out as follows. Ten milliliters of the standard salt solution was pipetted on to a weighed amount (about seven grams) of charcoal which had been previously heated at 110 degrees for two hours to drive off superficial water. The mixture was thoroughly agitated initially and at frequent intervals to insure intimate mixing. After half an hour or longer the mixture was filtered with a sintered glass filter, and the charcoal washed three or four times to remove the excess salt. The charcoal was then dried for two hours at 110 degrees, and after it had cooled in a desiccator its susceptibility was determined. The filtrate and washings were analyzed for salt not adsorbed. The difference between the salt content of the filtrate and the amount of salt contained in ten milliliters of stock solution was taken to be the amount adsorbed.

Anion analyses were also run on some of the samples, but neither anion, sulfate nor chloride, showed any tendency to be adsorbed. Further, pH measurements showed that the solutions became definitely more acidic after adsorption had taken place. At different times attempts were made to recover the adsorbed salt by prolonged washing with water, but in no case was more than a small fraction of the adsorbed salt recovered.

The various salt solutions were analyzed by the following methods:

1. $Fe_2(SO_4)_3$ was treated with concentrated HCl and reduced in a silver reductor. The ferrous salt obtained was titrated with ceric ammonium sulfate, using o-phenanthroline ferrous complex (ferroin) to indicate the endpoint.

2. $FeSO_4$ was titrated directly with cerate.

3. Nickel was determined gravimetrically as the dimethylglyoxime.

4. The cobalt salts were determined by potentiometric titration with ferricyanide in an ammonium citrate-ammonium hydroxide solution (9).

5. Manganese was determined potentiometrically with $KMnO_4$, using a neutral pyrophosphate solution (10).

RESULTS

IV. RESULTS

The vertical force acting on the sample suspended in an inhomogeneous magnetic field is given by:

$$F = \tfrac{1}{2} (K_1 - K_2) H^2 A \, ,$$

provided one end of the sample is in a negligible field.

K_1 and K_2 are the volume susceptibilities of the sample and the surrounding tube, respectively.

H is the maximum field strength to which the sample is subjected.

A is the cross-sectional area of the sample.

If the force is measured by a balance, we have

$$g \, \Delta w = \tfrac{1}{2} (K_1 - K_2) H^2 A$$

$$g = \text{gravitational constant}$$

$$\Delta w = \text{apparent change in weight of the sample when placed in the field.}$$

Rather than find the absolute value of the field strength H and the cross-sectional area A, it is more convenient to calibrate the instrument with a substance of known susceptibility. When this is done, the following relation is obtained:

$$\frac{K_1 - K_A}{K_2 - K_A} = \frac{\Delta w_1}{\Delta w_2}$$

or

$$K_2 = \frac{\Delta w_2}{\Delta w_1} (K_1 - K_A) - K_A$$

The subscripts 1, 2, and A refer, respectively, to the calibrating substance, the substance whose susceptibility is being measured, and air.

The volume susceptibility of air (K_A) is + 0.030 x 10^{-6}, but since, when the susceptibility of charcoal samples was being determined, not all the air was displaced, the value used for K_A was + 0.015 x 10^{-6}. This value was used since, in a displacement measurement with water, it was found that about one-half the charcoal volume was air. For silica gel the K_A correction was taken to be+0.020 x 10^{-6}.

One of the most suitable calibrating agents is a solution of $NiCl_2$. The gram susceptibility of $NiCl_2$ is established to be+34.2 x 10^{-6} (11), and this value is independent of concentration in the neighborhood of 30% $NiCl_2$ by weight. The solution used was found to contain 29.20% $NiCl_2$ by weight. As a check on the calibration, the measurements were repeated using conductivity water. From the calibration data of the $NiCl_2$ solution, the susceptibility value of water was calculated for the various field strengths measured. The results are given in Table II. It is seen that the average value calculated for the susceptibility of water, -0.718 x 10^{-6}, agrees satisfactorily with the accepted value, -0.720 x 10^{-6}.

TABLE II

CALIBRATION DATA AND GRAM SUSCEPTIBILITY OF WATER

Amperes	Field Strength	Δw ($NiCl_2$)	Δw (H_2O)	x_{H_2O} x 10^{+6}
10	8,075	+ 0.330 gm.	-0.0196 gm.	-0.724
12	9,400	.458	.0271	.722
14	10,700	.595	.0348	.712
16	11,770	.720	.0424	.717
18	12,540	.830	.0488	.715
20	13,350	.927	.0544	.715

Gram susceptibility values obtained for pure charcoal are given in Table III. The fact that the values obtained are independent of field strength shows that the charcoal is free from ferromagnetic impurities. From these measurements the gram susceptibility of pure charcoal is found to be -0.462 x 10^{-6}.

TABLE III

GRAM SUSCEPTIBILITY OF PURE CHARCOAL (x 10^{+6})

Sample Density Amperes	A 0.835	B 0.755	C 0.830	D 0.828
10	-0.455	-0.462	-0.453	-0.460
12	.461	.465	.472	.465
14	.460	.462	.468	.462
16	.464	.462	.471	.465
18	.463	.461	.463	.460
20	.465	.464	.465	.460
Average	-0.461	-0.463	-0.465	-0.462

These samples differ somewhat in their heat treatment prior to susceptibility determination:

A. Heated in air two hours at 110 degrees.

B. Heated in vacuum two hours at 250 degrees; measurements were made with the sample in a nitrogen atmosphere.

C. Heated in air two hours at 110 degrees.

D. Heated in air two hours at 150 degrees.

Gram susceptibility values obtained for silica gel are given in Table IV. All the samples were heated at 140 degrees. Samples A through D were heated in air for two hours, while E and F were heated

three and one-half hours in a CO_2 atmosphere. The latter samples are slightly more diamagnetic than the others, possibly due to adsorbed CO_2, whose gram susceptibility is -0.423×10^{-6}. The results indicate the presence of a trace of ferromagnetic impurity. The average obtained from these measurements for the gram susceptibility of silica gel is -0.317×10^{-6}.

TABLE IV

GRAM SUSCEPTIBILITY OF SILICA GEL ($\times 10^{+6}$)

Sample Density Amperes	A 0.803	B 0.808	C 0.795	D 0.790	E 0.805	F 0.815
10	-0.297	-0.308	-0.309	-0.302	-0.310	-0.311
12	.302	.309	.308	.306	.321	.314
14	.304	.312	.312	.306	.328	.324
16	.308	.313	.319	.310	.332	.330
18	.311	.319	.322	.315	.333	.334
20	.313	.318	.323	.319	.334	.335
Average	-0.306	-0.313	-0.316	-0.310	-0.326	-0.325

Using these susceptibility values for charcoal and silica gel, we can proceed to calculate the susceptibility of the absorbed salt. Using the additivity relationship:

$$X_{mixture} = X_{salt}P_{salt} + X_{adsorbent}P_{adsorbent}$$

where X = gram susceptibility

P = weight fraction

we obtain for the observed susceptibility of the adsorbed salt:

$$X_{salt} = \frac{X_{mixture} - X_{adsorbent}P_{adsorbent}}{P_{salt}}$$

The necessary data follow in Tables V and VI. In Table V are given gram susceptibility values found for mixtures of adsorbent and salt, at the various field strengths corresponding to the range in applied current from ten to twenty amperes. The average of these six values is that used in calculating the susceptibility of the adsorbed salt.

Table VI contains the susceptibility values found for the adsorbed salt as calculated from the equation given above. The susceptibilities are expressed in terms of the active paramagnetic constituent of the salt, and represent the gram atomic susceptibilities. Since the non-metallic part of the molecule makes no appreciable contribution to the susceptibility, these values are essentially the same as the gram molecular susceptibilities, except for $Fe_2(SO_4)_3$, where this corresponds to one-half the molecular susceptibility. Table VI also contains the susceptibility values which were found to exist in the pure solid. The value of $NiCl_2$ is taken from Selwood (11), and the others from the work of Herroun (12). A column is included giving the number of milligrams of paramagnetic constituent (e.g. Ni, or Fe (III)) adsorbed per gram of adsorbent. Also shown is the heat treatment given the mixtures before susceptibility measurements were made. For samples heated in vacuum these measurements were made in a nitrogen atmosphere; the others were exposed to air. The $FeSO_4$ adsorbed on silica gel was heated in a stream of CO_2 to prevent oxidation of the salt.

A convenient comparison of theoretical with observed susceptibilities is made by the use of "effective Bohr magneton numbers" instead of

TABLE V

GRAM SUSCEPTIBILITIES ($\times 10^6$) OF SALT-ADSORBENT MIXTURES AT VARIOUS VALUES OF APPLIED CURRENT (IN AMPERES)

Adsorbent	Samples		10	12	14	16	18	20	Av. X
Charcoal	NiCl$_2$	A	-0.040	-0.046	-0.046	-0.048	-0.051	-0.052	-0.047
"	"	B	.327	.338	.343	.349	.350	.352	.348
"	"	C	.058	.056	.059	.057	.057	.057	.057
"	"	D	.079	.080	.083	.083	.082	.082	.082
"	Fe$_2$(SO$_4$)$_3$	A	-0.034	-0.040	-0.040	-0.042	-0.042	-0.042	-0.040
"	"	B	.080	.084	.087	.088	.087	.088	.086
"	"	C	.378	.379	.380	.383	.383	.384	.381
"	"	D	.347	.356	.356	.357	.351	.351	.355
"	FeSO$_4$	A	-0.123	-0.120	-0.120	-0.120	-0.121	-0.121	-0.121
"	"	B	.108	.105	.110	.109	.114	.109	.109
"	CoCl$_2$	A	+0.097	+0.098	+0.093	+0.093	+0.092	+0.091	+0.094
"	"	B	.618	.626	.607	.606	.599	.597	.609
"	"	C	.319	.320	.318	.314	.310	.308	.315
"	CoSO$_4$	A	-0.123	-0.120	-0.123	-0.125	-0.125	-0.127	-0.124
"	"	B	.076	.076	.081	.083	.085	.083	.081
"	MnSO$_4$	A	+0.868	+0.865	+0.863	+0.869	+0.857	+0.869	+0.865
"	"	B	.766	.766	.760	.763	.760	.760	.763
Silica gel	NiCl$_2$	A	-0.224	-0.230	-0.236	-0.244	-0.249	-0.251	-0.239
"	"	B	.263	.266	.275	.272	.279	.282	.273
"	Fe$_2$(SO$_4$)$_3$	A	+0.094	+0.082	+0.077	+0.073	+0.070	+0.067	+0.077
"	"	B	.090	.078	.070	.065	.061	.059	.071
"	FeSO$_4$	A	-0.206	-0.212	-0.218	-0.212	-0.215	-0.218	-0.215
"	"	B	.139	.141	.149	.154	.157	.152	.150

TABLE VI

GRAM ATOMIC SUSCEPTIBILITIES OF PARAMAGNETIC IONS ADSORBED AND IN THE SOLID STATE

Adsorbent	Adsorbate		Mg. Ads.*	$X_{adsorbed}$	X_{solid}	Heat Treatment of Adsorbent
Charcoal	$NiCl_2$	A	4.63	0.00523	0.00443	1½ hours, 110° in air
"	"	B	1.88	.00372	"	2 hours, 250° in vacuum
"	"	C	6.15	.00404	"	2 hours, 110° in air
"	"	D	5.49	.00404	"	"
"	$Fe_2(SO_4)_3$	A	1.30	.0182	.01145	"
"	"	B	1.13	.0186	"	"
"	"	C	0.285	.0160	"	2 hours, 250° in vacuum
"	"	D	0.430	.0142	"	"
"	$FeSO_4$	A	1.56	.0140	.0101	2 hours, 110° in air
"	"	B	1.34	.0147	"	"
"	$CoCl_2$	A	3.40	.00960	.01170	"
"	"	B	5.84	.0108	"	"
"	"	C	4.61	.00990	"	"
"	$CoSO_4$	A	1.94	.01025	.00981	"
"	"	B	2.10	.0107	"	"
"	$MnSO_4$	A	4.57	.0159	.01409	"
"	"	B	4.49	.0150	"	"
Silica gel	$NiCl_2$	A	7.68	.00574	.00443	2 hours, 140° in air
"	"	B	6.71	.00359	"	"
"	$Fe_2(SO_4)_3$	A	2.69	.00810	.01145	"
"	"	B	2.46	.00870	"	"
"	$FeSO_4$	A	0.569	.01008	.01006	3½ hours, 140° in CO_2
"	"	B	0.85**	.01015	"	"

* Milligrams of the paramagnetic metallic constituent adsorbed per gram adsorbent.

** Ferric iron adsorption = 0.10 mg./gm.

susceptibilities. Assuming the validity of Curie's law at room temperature for these salts, the effective Bohr magneton numbers are defined by

$$\mu_{\text{eff}} = \sqrt{\frac{3kX_M T}{N\beta^2}} = 2.839 \sqrt{X_M T}$$

μ_{eff} = effective Bohr magneton number

k = Boltzmann's constant

X_M = molar susceptibility

T = absolute temperature

N = Avogadro's number

β = Bohr magneton, equal to 0.917×10^{-20} erg oersted^{-1}

The theoretical value can be calculated, assuming paramagnetism is due to spin only, from the equation

$$\mu_{\text{eff}} = \sqrt{n(n+2)}$$

where n = number of unpaired electrons

The effective Bohr magneton numbers observed for these adsorbed salts are given in Table VII together with the theoretical values and the experimental values of other observers (13). It is seen that the values obtained in the present investigation agree reasonably well with the theoretical, and in nearly every case fall in the range of values observed under other conditions. Exceptions to this are $FeSO_4$ adsorbed on charcoal and $Fe_2(SO_4)_3$ adsorbed both on charcoal and on silica gel. The value for ferrous iron is too high, really of the order of ferric iron. It is quite possible that the ferrous ion had

TABLE VII

EFFECTIVE BOHR MAGNETON NUMBERS

Adsorbent	Adsorbate		Temp. °K	$\mu_{eff} = \sqrt{n(n+2)}$	Other Observers	μ_{eff} Adsorbed
Charcoal	$NiCl_2$	A	298	2.83	2.9 – 3.4	3.53
"	"	B	298	"	"	2.99
"	"	C	300	"	"	3.12
"	"	D	300	"		3.12
"	$Fe_2(SO_4)_3$	A	301.5	5.92	5.4 – 6.0	6.65
"	"	B	301.5	"	"	6.78
"	"	C	302	"	"	6.24
"	"	D	302	"		5.87
"	$FeSO_4$	A	298	4.90	5.0 – 5.5	5.80
"	"	B	299	"	"	5.95
"	$CoCl_2$	A	303	3.87	4.4 – 5.2	4.85
"	"	B	301	"	"	5.13
"	"	C	301	"		4.90
"	$CoSO_4$	A	302	"	"	5.00
"	"	B	302			5.10
"	$MnSO_4$	A	302	5.92	5.2 – 5.56	6.22
"	"	B	302	"	"	6.04
Silica Gel	$NiCl_2$	A	298	2.83	2.9 – 3.4	3.71
"	"	B	298	"	"	2.94
"	$Fe_2(SO_4)_3$	A	298	5.92	5.4 – 6.0	4.42
"	"	B	298	"	"	4.57
"	$FeSO_4$	A	298	4.90	5.0 – 5.5	4.92
"	"	B	298	"	"	4.94

in fact been oxidised to the ferric, since no precaution was taken to protect the salt from air during drying of the sample and subsequent measurements. In contrast to this is the value of $FeSO_4$ on silica gel, where the agreement between the observed value for the ferrous ion with the theoretical is striking. In the latter case the ferrous ion was protected from air by heating under CO_2, and thus oxidation was prevented.

In the case of the ferric salt no explanation is immediately forthcoming. It may be interesting here to refer again to the work of Boutarie and Bethier (6), who also found with ferric salts deviation from magnetic additivity. When substances were adsorbed on ferric sols the susceptibility was lowered, but when the $Fe(OH)_3$ and $FeCl_3$ were adsorbed on bentonite the susceptibility was increased. Furthermore, Bhatnagar, Mathur, and Kapur found (6) that, although the other salts they adsorbed on silica gel obeyed the additivity rule, $FeCl_3$ was an exception, appearing to become more paramagnetic upon adsorption.

DISCUSSION

V. DISCUSSION

It is evident that the data presented show in adsorption both on charcoal and on silica gel that the paramagnetic ions do not lose their paramagnetism, but in the adsorbed state they have approximately the same magnetic moment they have in their salts. This is contrary to the findings of Bhatnagar, Mathur, and Kapur, whose observations showed that all these paramagnetic ions become diamagnetic when adsorbed on charcoal. Their charcoals, however, admittedly contained large amounts of paramagnetic impurities, which makes their work somewhat dubious.

It is not possible now to present with any certainty a mechanism for the adsorption, since little is known about the exact nature of the charcoal surface. It is of prime importance here to know what kind of surface oxides are likely to be present on charcoal, but that question is as yet unsettled. Besides, there is a great deal of disagreement even on fundamental aspects of the adsorption of electrolytes from aqueous solutions. A brief review is presented here of the pertinent work done on the subject.

Although the adsorption of electrolytes by charcoal has been the subject of a very large amount of work, progress in developing an unequivocal theory or mechanism for the adsorption has been hindered by an amusing lack of agreement in the data presented. The contradictory data seem due principally to two factors: 1) charcoal used in many experiments, especially in the earlier work, contained great amounts of

impurities; and 2) granted a pure charcoal, its adsorbing properties
depend very basically upon the method of activation. A few words about
the extreme importance of each of these factors may be in order.

Before the 1920's charcoals commonly contained five percent or
more ash, in spite of the fact that they were usually acid-treated.
This ash consisted largely of inorganic impurities which often reacted
chemically with the substances adsorbed, thus making the data meaning-
less. And the acid itself could not be completely washed out, even with
repeated extractions with water (14). Naturally the adsorbed acid neutra-
lized alkali in solution, and base adsorption was often erroneously
reported.

The effect of temperature of activation on the adsorptive properties
of charcoal has been studied extensively by A. King (15). Properties
which depend upon the temperature of activation in an oxygen atmosphere
are: acid adsorption, base adsorption, catalytic efficiency, extent
of hydrolytic adsorption, and the charge and pH of aqueous suspensions.
In addition to this, these properties change radically from one activat-
ing gas to another.

In general, it appears evident that adsorption of electrolytes from
aqueous solutions can be explained in two different ways. In the first
place, a sort of "chemical" interaction can occur between the adsorbed
electrolyte and some component of the adsorbent surface, whether that
be some surface oxide, chemisorbed water vapor, or the like. In the
second place, adsorption may be due to the attraction of electrostatic
charges on the surface of the adsorbent. A full explanation of adsorption

will probably have to take into account both of these, and possibly other, phenomena.

The existence of surface oxides on activated charcoal has been postulated to show that adsorption of electrolytes from solution is due to chemical interaction with an activated surface. Many investigators have interpreted their data as being evidence that such oxides are present. Miller proposed a mechanism of adsorption based on dissociation and displacement of H^+ and OH^- ions adsorbed by the charcoal (16). Schilow has proposed three specific surface oxides, each with different properties, which are formed at different oxygen pressures (17). They are:

A is stable at all temperatures and in oxygen up to a pressure of 2 mm., and with water gives the slightly basic group (-C-OH). **B** is formed from **A** at 2 mm. oxygen pressure and is stable up to very high pressures. With water it gives strongly basic hydroxides. **C** is formed from **B** by heating in oxygen at 300 to 700 degrees, and is strongly acidic in water. King found that charcoal exposed to oxygen, air, or

nitric oxide produced some oxalic acid on the carbon surface (18).
He concluded that for thoroughly dry charcoal the surface oxide is
probably $\begin{bmatrix} & \overset{O}{\underset{||}{C}} & & \overset{O}{\underset{||}{C}} & & \overset{O}{\underset{||}{C}} & \\ / & & \underset{C}{\diagdown} & / & & \underset{C}{\diagdown} & / & \diagdown \end{bmatrix}$, which is the same as Schilow's oxide B.
King also attributes the variation in adsorptive properties of the char-
coals with temperature of activation to different surface oxides which
are formed. At the activation temperature of 350 to 400 degrees an
acidic oxide is formed, and at 800 to 900 degrees a basic oxide (19).
A number of investigators have found surface oxides which can be dis-
tinguished magnetically (20). That oxides do exist on the surface of
charcoal seems evident from the fact that when oxygen is adsorbed on
charcoal it is not recoverable as O_2 but as CO_2 or CO, and that the
heat of adsorption of small amounts is much greater than that of larger
amounts. Ockrent, however, has disagreed with this, insisting that the
idea of surface oxides is fallacious, that the charcoals are composed
exclusively of water and carbon. His own experiments and examinations
of the data of others show that charcoal analyses often give O/H composi-
tion in the ratio 8/1, indicating that all the O is present as H_2O (21).

The other basic theory of electrolyte adsorption from solution is
the electrochemical theory, developed especially by A. Frumkin and his
co-workers (22). According to them, the adsorption of electrolytes is
determined by the potential at the charcoal-solution interface, which
in turn depends upon the presence of electrochemically active chemi-
sorbed gases on the surface. In effect, the charcoal acts as an oxygen
or a hydrogen electrode, depending upon which gas it is charged with.
If the charcoal is activated with oxygen at low temperatures, the

charcoal becomes positively charged in solution and attracts anions. If, on the other hand, it is treated with hydrogen, it is negative in aqueous solutions, discharging H^+ ions into solution and adsorbing cations. Adding a small amount of platinum to the charcoal usually enhances these activities. Their data indicate that, in the adsorption of both cations and anions, there exists a linear relation between the potential and adsorption, in complete agreement with this electrochemical theory.

Difficulty in evaluating data also arises from the fact that oxygen-activated charcoal seems capable of assuming either a positive or negative charge in aqueous suspension. For example, King found oxygen-activated charcoal always to be negative in water (23). Verstraete found that charcoal assumes a positive charge when activated at 950 degrees and negative when activated at 450 degrees (24). Frumkin's low-temperature oxygen-activated charcoals had a positive charge (22). Mukherjee and Roychoudhury said that activated charcoals generally have a negative charge, but become positive upon sustained washing with conductivity water (25). All this emphasizes again the importance of activation and impurities in the adsorption of electrolytes.

The two theories of adsorption mentioned above are certainly not mutually exclusive, but probably represent extreme or limiting conditions. That is, in some cases adsorption consists solely in a reaction between the dissolved electrolyte and the adsorbent, be it surface oxides, inorganic impurities, or the like. And on the other hand, sometimes adsorption occurs merely as the result of a surface charge on the adsorbent. Most commonly adsorption results from a combination of these two effects:

the ions are attracted and held fast by the oppositely-charged surface, and they also interact with the surface by virtue of what might be called a chemical affinity.

In the present investigation it was found that neither of the anions used, chloride and sulfate, was adsorbed, but that after adsorption had taken place the electrolyte solution became markedly more acidic. This corresponds to cationic adsorption with displacement of hydrogen ions and at least partial neutralization of the surface charges. Thus the cation is probably adsorbed by a sort of ion exchange process, in which it is electrostatically bound to the surface.

The results reported in this paper seem to support the idea that the adsorbed ions are bound to surface oxygen atoms rather than to the carbon of the charcoal. Binding between the metallic atoms used here and carbon atoms would almost certainly be of the covalent type. And when these paramagnetic atoms are bound to carbon atoms, in nearly every case the resulting substance is diamagnetic, or at least the paramagnetism is radically altered. On the other hand, the tendency for these atoms when linked to oxygen atoms is to form complexes which are essentially ionic, and the paramagnetism is thus unaffected. On this basis it is entirely to be expected that the paramagnetism of these salts should be the same on charcoal and on silica gel, since on silica gel the adsorbed salts are almost certainly bound to oxygen atoms.

Further evidence for a metal-to-oxygen linkage is the following. Most investigators find it impossible to remove the last traces of adsorbed oxygen from charcoal, but they find that practically no adsorption

occurs on charcoals which have their oxygen content reduced to a very minimum by outgassing several hours above 1000 degrees (26). Frumkin, however, seems to have gotten charcoal free from all gases and claims that such charcoal adsorbes neither acids nor alkalies (27). Therefore it appears that charcoal itself, that is, the pure carbon surface, is not able to adsorb electrolytes at all, but adsorption takes place through the medium of chemisorbed oxygen.

SUMMARY

VI. SUMMARY

A magnetochemical study has been made on the adsorption by charcoal and silica gel of some paramagnetic iron-group salts from aqueous solution. A known amount of salt was adsorbed, and the susceptibility determined by the Gouy method. The magnetic moment of the adsorbed salt was calculated, and, except for an anomaly in the case of $Fe_2(SO_4)_3$, it was found that the magnetic moment was not altered by adsorption, as previous workers have reported. This seems to point to an electrostatic type of force binding the adsorbed salt, and the paramagnetic ion is probably linked to surface oxygen atoms both in the case of silica gel and of charcoal.

A description is given of the electromagnet constructed for these magnetochemical measurements, and calibration data are included. The gram susceptibility of pure charcoal is found to be -0.462×10^{-6}, and of silica gel -0.317×10^{-6}. A review is given of work done on the adsorption by charcoal of electrolytes from aqueous solution.

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