HEAT CHANGES ACCOMPANYING ADSORPTION EQUILIBRIA

IN SOLUTION.

By

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Introduction.

Adsorption has for a long time been a well
recognized phenomenon and numerous investigations have
been made on the nature and magnitude of the energy
changes involved. Some of the measurements on the
adsorption of gases have shown these changes to be
enormous. Recently the heats of wetting or the heat
of adsorption of a liquid by a solid has received
considerable attention and the heat in many cases was
found to be fairly large. In solutions we find that
while much quantitative data concerning the degree of
adsorption is available, the energy changes connected
with the adsorption of electrolytes from solution have
been almost completely ignored.

In previous work here at Maryland it has been
found that phosphates in contact with various gels such
as might be expected to be present in most soils are
removed from solution to quite a marked degree. There
appeared to be evidence that not all this phosphate
was similarly held since some could be removed by wash-
ing while the rest was held there more firmly altho it

was still in a form that could be utilized by plants. If some of this phosphate was held in a manner different from the rest there should be a difference in the energy changes involved as the phosphate is taken up by the gel.

The present paper is the result of this belief and is an attempt to investigate and measure the energy changes that accompany the removal of phosphates from solution.

HISTORICAL REVIEW.

Introduction.

The study of heat effects in connection with colloid chemistry has been comparatively neglected. The earlier workers in the field of colloids, Graham, Linder and Picton attached much importance to the fact that there were no heat effects in the formation and coagulation of colloids, but wit the development of the science very little interest appears to have been manifested in this phase of the subject until quite recently.

The fact that energy changes are involved when certain different substances are brought into contact has been known for many years, but it assumes new importance with the development of colloidal chemistry

to a more advanced stage. The enormous increase in surface which occurs when a substance assumes the colloid state has rendered more noticeable this surface phenomenon. A review of the literature on this subject may be made most conveniently by dividing it into three parts; heats of wetting, heat of adsorption of gases and vapors, and heats of coagulation of colloids.

Heat of Wetting.

For over one hundred years it has been known that certain substances when brought into contact with a liquid with which they do not react or in which they are not soluble produce a rise in temperature. This was first announced by Pouillet[1] in 1822. Working first with metals, such as iron, bismuth, tin, antimony, later with a number of insoluble oxides of iron, tin, silicon, aluminum, and various organic substances he found rises in temperature from .2 to 5 degrees. The liquids used were water, alcohol, and oil of turpentine. He used a specially devised type of thermometer which permitted the reading of quite small temperature changes and found the lowest changes to occur with the metals and the greatest with organic substances which absorb large amounts of water. The heats of wetting of the same solids with different liquids were quite similar, altho the temperature rise in all cases was

least with the most viscous liquid.

These observations of Pouillet were confirmed by other investigators, but all these earlier observations were thermometric and not calorimetric and consequently are not of any value for comparison.

The idea that these thermal effects might be due to the compression of the liquid in the contact layers is also very old. In 1865 Junck[2] found that when sand is placed in water with a temperature above 4° C, there is a rise in temperature; if the temperature of the water is below 4° C there is a drop in temperature. This is in accordance with what would be expected if the temperature rise is due to compression of the liquid at the surface of the powder. These results are confirmed by Schwalbe[3], and these compression effects are discussed by Freudlich in his Kapillarchemie.

Meissner[4] in 1886 showed that certain powders when placed in water with a temperature below 4°C produce a rise in temperature. He rejected the hypothesis that heat effects are produced by surface pressures and adopted the ideas which had been previously suggested that just as some solids are dissolved by liquids, and then become liquid, so some liquids may be absorbed by powders and thereby become solids. The heat that is given out is equivalent to the latent heat which the liquid gives out

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on becoming a solid. It was later pointed out by various exponents of the compression theory that the results of Meissner were not directly antagonistic to the compression theory, for with an increase of pressure the point of maximum density of water is lowered and that at a pressure of only 200 atmospheres which is much lower than the supposed pressure, the point of maximum density of water is $0^{\circ}C$.

Williams[5] has carried on some extensive investigations on the properties of powders. He considers the Pouillet effect (i.e. the heat effect when a powdered or porous substance is placed in contact with a liquid in which it does not dissolve or react chemically) as corresponding to the heat of solution, since he finds that with silica and all other substances that the drier the substance the greater the heat effect. With silica there is no temperature change if the silica already contains an amount of water corresponding to a saturated vapor pressure. The liquid surfaces appear to unite with the vapor phase at a certain stage of adsorption, with the result that a greatly reduced surface is presented. This reduction in surface should be accompanied by an evolution of heat, and he finds that in some cases vapors show a maximum heat of adsorption on a powder shortly before arriving at the saturation point.

The main heat effects he considers as being
due to the compression of the liquid around the parti-
cles under the action of cohesive forces at the surface
of the powder. With an increase of the specific surface
the heat should increase in proportion since the
cohesive forces are constant as long as the radius of
the particle does not become less than the effective
range of molecular action.

Linebarger[6] has made numerous measurements on
the heat effects of different sized particles. The
nature of the work can perhaps be best shown by repro-
ducing one of his tables. The table shows the heat
effects when particles of silica having average dia-
meters of .0005 cm. and .001 cm. are wet by the liquids
indicated in the table.

TABLE I

The relation of the size of the particle to the heat of
wetting

Liquid	Heat per gram silica		Ratio
	Diam..0005	.001	
water	13.8	6.9	2
nitrobenzene	11.0	6.3	1.8
toluene	8.6	4.8	1.8
benzene	4.1	4.1	1.0
pyridine	12.2	5.0	2.4

The surfaces exposed are approximately 2:1 and the ratios of the heats of the two samples in all except one case are proportional to the areas.

In connection with the idea of compression of the liquid around the solid surface, Williams states that if the cohesion of the powder or solid instead of being greater is less than the cohesion of the liquid in which it is immersed, we should get not a compression of the liquid molecules around the powder but a distension and should therefore get an absorption of heat instead of an evolution. This distension he believes would occur at the interface liquid-vapor. For water the energy required to produce this extension of surface is about 110 ergs per sq. cm or .000003 calories. On measuring the heat effect on immersing one gram of charcoal in water he finds it to be 25 calories. The specific surface was estimated to be about 3,000,000 sq. cm. which would give a heat effect of .000008 calories per sq. cm. corresponding quite closely to the calculated value of the liquid-vapor interface.

Parks[7] measured the heat effects on immersing three different varieties of silica, namely precipitated silica, sand and glass. With water he finds that the heat evolved in each case is .00105 calories per sq. cm.

Using glass wool, he finds that the heat of wetting by mercury gives somewhat erratic results altho in general they are negative; the difficulty he ascribes to inability of getting the glass wool at the same temperature as the mercury and the formation of mercury globules thus changing the area exposed. On immersing the glass wool in the mercury and keeping it there until equilibrium had been established and then suddenly releasing it he finds that there is a slight rise in temperature, which would tend to support the ideas of Williams.

Patrick and Grimm[8] are not in accord with the idea that the heat of wetting of a liquid or the heat of adsorption of a gas is largely due to the compression of the adsorbed liquid. Their ideas of adsorption emphasize the attractive force between the molecules of the substance adsorbed rather than the attraction between the adsorbed material and the adsorbent. Their work was undertaken with the object of seeing whether the thermal changes could not be satisfactorily accounted for on the basis of the changes in the surface energies involved. One of the facts strongly relied on in the argument that this energy change, was due to compression, was that the heat of wetting by water was negative when measured between $0^{\circ}-4^{\circ}C$. They carried out some qualitative and fairly accurate quantitative

measurements and found the heat of wetting of silica
gel by water between these temperatures to be posi-
tive which they regard as strong evidence against the
idea of compression. They carried out measurements
on heats of wetting by five different liquids one
of which was water. Using the values obtained by
Harkins for the free surface energies of these liquids,
they were able to account quite closely for the heat
changes in terms of the changes in the surface ener-
gies. The surface presented by the silica gel was
regarded as a water interface and all calculations
made accordingly.

Gurvich[9] regards the heat of wetting as a
function of the attractive forces of the two substances.
He found that among organic compounds, hydrocarbons
have a greater heat of wetting and are more adsorbed
by charcoal while oxygen compounds are more adsorbed
and have a greater heat of wetting when in contact
with adsorbents containing oxygen. The former he
called "carbophil" and the latter "oxophil." He
finds that the amount of a substance adsorbed from
solution is inversely proportional to the heat of
wetting of the adsorbent by the solvent. The mole-
cules that have been adsorbed lower the attraction of the
adsorbent for molecules of the same compound, but in-

crease its attraction for other molecules, so that in
the adsorption of mixtures the adsorption is greater
than when each is adsorbed separately.

Koehler and Matthews[10] have recently measured
the heat of wetting of lead sulfate with the object of
establishing a relation between the heat of wetting
and the surface area. Different samples of lead sul-
fate were used and the surface areas determined by
the use of a radioactive isotope of lead, Thorium B,
as indicator. The areas in these samples varied from
5800 to 32,400 sq. cm. per gram of lead sulfate.
Using a maximum area of 529,000 sq. cm. in one deter-
mination they found that the heat effects if any,
were within the limits of experimental error, which
brings the heat of wetting of lead sulfate dried at
224° and a pressure of .005 bar to less than .09
calories per sq. cm. These measurements were carried
out in solutions saturated with lead sulfate so that
no heat changes would be caused by the solution of
lead sulfate.

In connection with the study of the soil,
the importance of colloids has been recognized for
sometime, but numerous difficulties have been encountered
in the study of soil colloids. No entirely satisfactory
method for their determination or estimation has been

TABLE 2.

Effect of ignition on the heat of wetting of soils

Rise of temperature caused by 50 gm. soil in 125 gm. water

| Soils used. | Heat of wetting | | | |
	Ignited at 110°C	Ignited at 230°C	Ignited at 485°	Ignited at 800°
	oC	°C	°C	°C
Penn silt loam	.90	.80	.60	0.0
Illinois clay loam	3.50	2.95	1.45	0.0
California clay	4.00	3.60	1.70	0.0
Peat	10.50	13.00	11.50	
Muck	8.6	11.50	10.00	0.0
Fullers earth	8.00			0.0
Ferric Hydroxide	3.75			0.0
Silica gel	9.60			0.0
Aluminum hydroxide	8.35			2.4

At 230°C the heat of wetting begins to drop
and at 485° the change is quite marked, while at 800° it
has dropped to zero. He also finds that other properties
which are regarded as being dependent on the colloid content
have changed accordingly. Aluminum hydroxide still shows
some heat of wetting which is probably due to hydration.
The rise in temperature of certain materials high in or-
ganic matter is probably due to partial cracking of the
organic particles or to a more thorough expulsion of

moisture. Soils when heated to 800° no matter how finely they are ground afterwards gave no heat of wetting. From this he suggests the possibility of evolving a method of determining or estimating the colloidal content or condition of soils and their degree of activation.

The investigation[12] of soil profiles shows that the heat of wetting is highest for the surface layer of the soil as would be expected since the colloidal content is highest in the surface layer.

Rosenbohm[13] has measured the heat of swelling of various colloidal substances and finds the total heat of swelling per gram of substance to be, gelatin 36.9, agar-agar 35.5, filter paper 9.6, pure cellulose 12.9, and cotton 20.8 calories. Using gelatin containing different amounts of water he calculated the heat effects produced in the various stages and finds that the heat change is large for the first 2%, and then drops. Up to about 20% the heat is proportional to the amount of water taken up, after which there is another drop. Gelatin on taking up 24% moisture produces a heat effect of 30 calories. From his work he concludes that the swelling of gelatin is divided into 2 phases, one where a small amount of water is taken up with a large evolution of heat, and the second where a large amount of water is taken up with no further evolution of heat.

HEATS OF ADSORPTION OF LIQUIDS AND GASES.

The first quantitative work on the adsorption of gases was done by Favre[14] who obtained values on a number of gases on charcoal in 1874, altho these effects had been mentioned previously by Mitscherlich[15]. Favre also determined the heat effects of hydrogen on platinum. Choppins[16] in 1883 measured the heat of adsorption of sulfur dioxide, ammonia, and carbon dioxide on charcoal and meerschaum. Quite recently we find that numerous investigations have been made on the adsorption of gases. Activity along these lines was greatly stimulated by the necessity of obtaining a thorough knowledge of the adsorption of gases by charcoal in connection with gas masks and by an increased use of charcoal and other adsorbents in industrial lines. Other investigations were undertaken in the hope of determining the nature of the changes occurring in certain catalytic processes with the hope of explaining the chemical changes involved.

Lamb and Coolidge[17] have measured the heats of adsorption of the vapors of some eleven organic liquids by charcoal of various types, and find the heats to be independent of the rate of adsorption and the previous history of the adsorbent. The heats of adsorption of these vapors are expressed by the formula, $h = mx^n$, where h represents the heat of adsorption per normal cc. of vapor, x the number of cc. adsorbed and m and n are

constants characteristic for each vapor. In their work
they find that the value for n is very close to unity,
showing that there is but slight decrease in the heat
with increasing amounts of adsorption. This decrease
or fatigue is less with liquids having relatively high
boiling points and high latent heats of vaporization.
The process of adsorption of a gas or vapor is regarded
as proceeding in two steps, first the compression of the
gas until liquefaction occurs, and second a further com-
pression due to the adhesive forces of the adsorbent.
From the fact that there is no change in the heat of
adsorption as adsorption proceeds, they assume that the
layers of the adsorbed material are many molecules thick,
which is also borne out by the amount adsorbed compared
with the probable area. They find that the net heats
of adsorption, that is, the total heat minus the latent
heat of vaporization is the same per cc. for each of
the liquids used, which includes ether, chloroform,
carbon disulfide, methyl alcohol, benzene and several
organic halides. These net heats are closely proportional
to the heats of compression at very high pressures, and
as the results show that equal volumes of the liquids are
attracted by the same force, they conclude that these
effects are really heats of compression of the order of
about 37,000 atmospheres.

The results of Lamb and Coolidge are supported by the investigations of Harkins and Ewing.[18] In their work on the adsorption of various liquids and gases by charcoal, they found that the volume of liquid adsorbed by an efficient charcoal depends on certain physical properties of the liquid, increasing as the compressibility of the liquid increases or the viscosity or surface tension decreases. These effects decrease as the adsorptive capacity drops, and entirely disappear as the charcoal becomes worthless as a gas adsorbent. They calculate that the internal pressure necessary to produce this change in volume must in some cases be as high as 20,000 atmospheres. They found that the heat of adsorption when a completely outgassed charcoal is immersed in water is 10.5 calories per gram of charcoal, and when merely dried at 150° , the heat is 7 calories, while if it contains just a thin film of water (.04 grams water per gram charcoal) the heat drops to 3.5 calories. From this it appears that the first tenth of the water entering the charcoal produces about half the heat of wetting, indicating that in accordance with Langmuir's theory the forces of adsorption and adhesion work only on an extremely thin layer of liquid.

The heat of adsorption of bone charcoal, not outgassed was 18.5 calories and of fuller's earth 32

calories, corresponding with the work of Gurvich who found the values of 18.5 and 30.2 calories respectively. These heat effects are regarded by Harkins and Ewing as the heat of spreading of a liquid on the surface of a solid rather than heat of adsorption. This heat effect is regarded as being due to the total energy changes in the film which includes both liquid and solid carbon of the interfaces.

In a later paper[20] Harkins and Ewing show that this high compression which occurs when vapors and liquids are adsorbed is probably much higher than was at first supposed, as this compression probably occurs only in the micropores, that is, in pores which are invisible when magnified 2000 times and are of about the order of .00001 cm. in diameter. These micropores are located in the walls of the larger pores giving them a comparatively open and spongy structure. While the hypothesis that the heat of wetting of the surface film or heat of adsorption is due to the compression of the surface layers is quite old, the authors claim that this is the first presentation of experimental data tending to support it.

Blench and Garner[21] found that when oxygen is adsorbed by charcoal the amount of temperature change depends on the temperature at which adsorption occurs.

They found that between 18 and 450 degrees the heat
of adsorption for the first small quantities of oxy-
gen varies from 60 to 220 calories per mole., but as
the surface becomes saturated the heat effects drop
rapidly. The differences in the heats of adsorption
at low and high temperatures is accounted for by the
fact that at low temperatures the oxygen is adsorbed
without chemical change while at higher temperatures
adsorption is attended by the formation of a compound
of carbon and oxygen on the surface.

While most of the measurements of heats of
adsorption have been made with charcoal as the adsor-
bent, some investigations have been made on the adsorp-
tion of gases by metals. Beebe and Taylor[22] measured
the heats of adsorption of hydrogen on nickel and cop-
per. They found the heat of adsorption of hydrogen
per mole on nickel was 13,000 to 21,000 calories.
Since the latent heat of vaporization of hydrogen is
only 450 calories at its boiling point, this is entirely
too large to be accounted for by condensation, since
the values are of entirely different order. In most
cases the heats appear largest for the first portions
adsorbed, but here it was found largest for the last
portion. With copper the heat of adsorption was 9540
calories.

HEATS OF COAGULATION.

Heats of coagulation received some attention in the earlier investigations of colloids, but little appears to have been done until quite recently. Most substances on dissolving unless accompanied by heats of hydration, ionization or hydrolysis have a negative heat of solution. The negative heat is regarded as due to the energy required to separate the molecules against the forces of cohesion within the crystal. In coagulation the opposite effect is produced and consequently we might expect it to be attended with an evolution of heat.

Doerinckel[23] precipitated a concentrated solution of a positively charged colloid by mixing it with a negative colloid. Using ferric oxide hydrosol and silver hydrosol he found that precipitation took place at practically all concentrations, contrary to the results of other investigators. This was probably due to the concentrated solution used. The heat varied with the concentrations used, for 10% silver being 8 calories, with a maximum of 45 calories for 60 to 70% silver. From 0 to 50% silver only traces of silver remained in suspension; using 85 to 90% silver only traces of ferric oxide remained in suspension. Using ammonium nitrate,

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the heat of coagulation of silver was 1-2 calories per unit weight of silver, while with aluminum sulfate, the heat effect was negative.

Doerinckel[24] also found that on using potassium oxalate and aluminum sulfate with hydrous ferric oxide that the heat of coagulation was dependent on the concentration of the ferric oxide. Using a sol with 10.8% ferric oxide and 2N potassium oxalate he attained the maximum heat effect of 164 calories and with a 5% solution 54 calories. He also noted the heat effects in relation to the amount of oxalate adsorbed and gives the following figures; 98 calories, .2064 g. $K_2C_2O_4$ adsorbed; 117 calories, .2600 g; 164 calories, .2618 g. He found that the heat effects rose as a linear function between 1.1% and 10.8% ferric oxide. His results with ferric oxide produced by different methods did not agree, probably due to a difference in the degree of purity. He also found that at a very high concentration of the colloid the heat effects were lower than with the more dilute, probably due to the inclusion of some of the unprecipitated colloid by the coagulant, so that reaction with the precipitating agent was too slow to produce a measurable change.

Kruyt and Spek[25] have measured the heats of coagulation of colloidal arsenious sulfide and colloidal

hydrous ferric oxide using electrolytes to precipitate
the colloids. With arsenious sulfide they found the
heat to be negative and with the hydrous ferric oxide
the heat was positive being two calories per gram.
They are of the opinion that the heat of coagulation
whether positive or negative may be due to the dilution
of the electrolyte used for coagulation; a decrease in
surface of the colloid involving a change in free energy;
the formation of new ions or molecules or changes in
the concentration of these, due to the adsorption of
one more than the other. In their measurement on the
heat of adsorption of crystal violet by charcoal they
found the heat to be three calories per gram of adsorb-
ing agent.

Probably the most important and thorough in-
vestigations have been carried on by Browne at Wiscon-
sin. Browne[26] has measured the heat of coagulation of
hydrous ferric oxide, prepared by different methods and
of various degrees of purity. Using .2M sodium sulfate
as the coagulant, he finds that the heat of coagulation
at the same degree of purity is the same for different
sols. The change in dispersity observed in coagulation
does not involve a measurable heat effect. "With ferric
oxide hydrosols the evidence seems conclusive that the
heat effects observed during coagulation with electro-

-21-

lytes is due to heat of dilution of electrolytes, interaction of electrolytes in the sol with coagulant and the heat effects accompanying ion adsorption during the process". Browne has also measured the heat of coagulation of sulfur sols and finds that it varies with the coagulant and the concentration of the coagulant. He finds the heat of coagulation per gram equivalent of sulfur using sodium chloride to be 16.5 calories, using potassium chloride 88.6 calories, magnesium chloride 20.5 calories, aluminum chloride 20.5 calories. He concluded that the heat effects are probably due to the action of the coagulant with the polythionic acids present in the sol. The sulfur in the coagulum appears to be in the same physical state as in the sol. This point is of unusual interest as in most cases coagulation is regarded as causing a decrease in surface, which is probably not the case with many colloids on precipitation.

EXPERIMENTAL

Materials Used.

The hydrous ferric oxide used in these investigations was prepared by dissolving 75 grams of ferric chloride in 5 liters of water, 5 cc. of concentrated hy-

drochloric acid were added to prevent appreciable hydrolysis
and the solution was heated to 60°C. A dilute solution of
ammonium hydroxide was then added to the solution until
it was distinctly alkaline. The gel was allowed to settle,
and was then washed by decantation, the supernatent water
being removed from the gel by suction, thus permitting
a more complete removal of the wash water. When the super-
natent liquid no longer showed the presence of chlorides
on the addition of silver nitrate the gel was washed
eight times with distilled water and then stoppered for
use.

The gel thus prepared was of a uniform consist-
ency, showing no lumps as is the case when the gel is
filtered and washed on a Buchner funnel with suction. It
was kept under water in a quite liquid condition so that
it could be readily pipetted with a ten cc. pipette.
This method of handling the gel was much more convenient
and satisfactory than the procedure in our previous work
where the gel was obtained in a form as dry as possible
with suction. The hydrogel in this form appeared to
undergo no changes on ageing. Gel when dried under suction
had always appeared to give off some of its water on
standing but this apparently remained unchanged.

The amount of ferric oxide present was determined
by the evaporation of a measured and weighed portion and

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drying at 105° C. This dried material was then ignited at red heat and weighed as ferric oxide. From these weights it was found that the material dried at 105°C corresponded to the formula $Fe_2O_3.H_2O$. The amount of iron was also determined by taking a known volume of the mixture, dissolving it in sulfuric acid, reducing the ferric sulfate with zinc in the Jones reductor and titrating with standard potassium permanganate. Different samples when determined in this manner gave very close results showing that this method of handling the gel was quite accurate. Different batches of gel of course varied somewhat in concentration, ranging from 1.92% to 2.69%. Even when filtered on a Buehner funnel under suction the moisture content is still about 92%.

The aluminum oxide hydrogel was prepared in a similar manner except that the nitrate was used as the starting point. The amount gel present was determined by drying at 105° C. On comparison with the weight after ignition it appeared to correspond quite closely to the formula $Al_2O_3.2H_2O$. The gel used here corresponded to 1.27% aluminum hydroxide. The aluminum hydroxide was found to undergo partial peptization as the washing process neared completion, some of the gel remaining in a suspended condition, settling somewhat after standing several

days, but leaving the supernatent liquid strongly
opalescent. On standing several weeks part of this
opalescent suspension settled out.

On treating the gel in suspension with bout
10% nitric acid, some passed into solution and some
precipitated, a part remaining in suspension. Even
on heating not all was dissolved. This has also been
reported quite recently by Willstatter[27] and his co-
workers who describe the alpha, beta and gamma alum-
inum hydroxides. The alpha form dissolves readily in
HCl and NaOH, the beta less readily and has colloidal
tendencies, while the gamma does not dissolve in
moderately concentrated HCl or NaOH.

The hydrous ferric and aluminum hydrogels were
dissolved in nitric acid and tested for chlorides with
silver nitrate, but in all cases only small amounts of
chlorides could be detected forming a slight cloudiness
in the solution. The amount of chloride was determined
by comparing the turbidity with a known sample and the
purity was found to be 5800. This is expressed in terms
of the ratio of the total iron content to the chlorine
present. With colloidal ferric oxide sol this ratio is
usually below 50.

In the washing of the hydrous ferric oxide

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until the wash water was free from chlorides, no peptizing effects were noticeable as the washing neared completion, altho in two cases, for some unknown reason the gel peptized shortly after the washing had started when the chloride content was still quite high. It was impossible to continue washing these gels and they were discarded.

The salts used in this work were those specially prepared for the National Research Council by the J.T.Baker Chemical Company, where these were available, and in other cases Baker's analyzed chemicals were used.

METHODS OF ANALYSIS.

The hydrogen ion concentration was determined with the Bailey electrode and the readings taken on a Leed's and Northrup student type potentiometer. The salt bridge contained a saturated solution of potassium chloride.

Phosphates were determined by precipitation with ammonium molybdate and titration with .2 normal alkali; potassium was determined by precipitation with platinic chloride; magnesium was precipitated, ignited and weighed as magnesium pyrophosphate; sulfates were determined by precipitation with barium chloride.

To galvanometer

To lighting circuit

water level

B.

A.
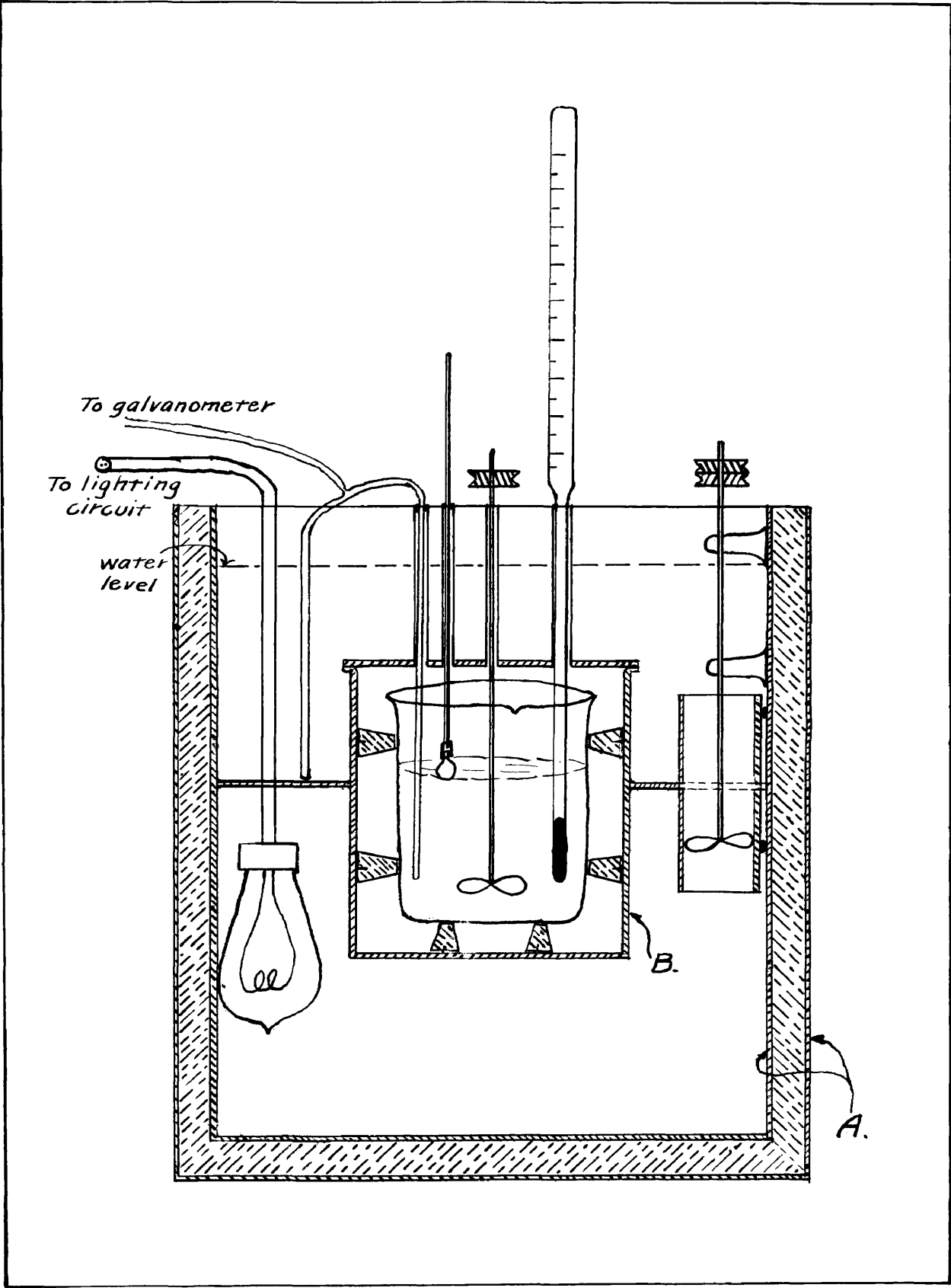
APPARATUS

The apparatus used to measure the temperature changes was essentially the type of adiabatic calorimeter described by Richards and Rowe,[28] and by Daniels.[29] It consists of an inner compartment submerged in water, with stirrers, Beckman thermometers and a thermocouple. A drawing of the apparatus is shown in figure 1.

The outside container A, consists of a double walled metal vessel, the walls of which are insulated with cork. On one side was attached a stirring devise, the stirrer of which was enclosed in a metal cylinder, the water being forced out at the bottom while at the same time water was sucked in at the top, thus insuring thorough circulation, and minimizing local heat effects. The water in the outer compartment was maintained at the same level, being about an inch below the top of the pipes leading to the inner compartment.

The inner compartment B, consists of a metal vessel with a polished inside surface to reflect the heat radiating from the reaction chamber. It is held in place by four arms soldered to it and extending out to the walls of the large container where they slide into slots, greatly simplifying the removal of the in-

ner compartment. The mixing chamber which must consist of some material not readily attacked by dilute acids or salts is a 600 cc. pyrex beaker. It is insulated from contact with the submerged metal container by corks there fourths of an inch in length placed at regular intervals along the sides and on the bottom of the container. The corks which are attached by small pegs extending inward from B, hold the beaker firmly in place. The top of the container B has a flange on which is placed a rubber washer. The lid is placed on this and is held on water tight by six small clamps.

In the lid are five circular openings, with pipes extending upward above the surface of the water. Thru the one in the center, a glass stirrer enters. The other four openings are arranged around it in a convenient manner, so that their projections downward will still fall inside the beaker. Thru one of the openings pass the wires leading to a heating coil, thru which a measured amount of current is passed from time to time to determine the heat constant of the calorimeter; thru the second passes a glass rod from which the solid salt, placed in a small glass bulb is suspended; in the third is placed one end of a thermocouple, and in the fourth the Beckman thermometer used in reading the temperature changes.

The thermocouple consists of twelve junctions of

copper and constantan wire connected in series and
then connected thru a two way switch to a high sen-
sitivity D'Arsonval galvanometer. The galvanometer
is placed on a platform attached to the basement wall
so as to be as free from vibration as possible. The
light is furnished by an encased electric light bulb,
and is reflected by the mirror of the galvanometer on a
scale about six feet away. The galvanometer is housed
in an enclosed wooden box so as to minimize temperature
effects. The end of the thermocouple dipping into the
calorimeter is encased in a piece of thin walled glass
tubing with a small amount of water in it to aid in
conducting the heat, and also that both ends of the
thermocouple may be in the same kind of environment.
A thermocouple of constantan and an alloy of iron and
nickel which was highly recommended was tried, but the
iron rusted and it gave consistent results for a short
time only. With a temperature difference of .01 degrees,
there was a deflection of 8 cm. on the scale so that it
admitted of quite close temperature regulation:

The temperature in the outer bath was controlled by
two carbon lamps which gave a temperature rise of about
.04 degrees per minute. In cases where the temperature
change was more rapid than this, the outer bath was brought
up to the approximate temperature by the addition of hot

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water.

The temperature changes were read on a 5 degree Beckman thermometer by means of a special telescope so that readings could be made to .001 degrees with estimations at times to .0005 degrees.

The calorimeter constant was determined by running in a current from a storage battery for a specified time and measuring the voltage and amperage and checking up on the amperage with a copper coulometer. The current was led in thru a heavy copper wire and then into a resistance coil underneath the water. The readings are given in Table 3.

TABLE 3.

Time in seconds	Voltage	Amperes	Temperature rise
600	.827	.700	.182
600	.863	1.056	.2865
600	.862	1.055	.2845
600	.865	1.062	.2875
600	.865	1.060	.2870

From these figures the heat constant of the calorimeter was calculated to be 5.7 calories per .1 degree rise in

temperature.

The amount of radiation occurring when the two baths are at different temperatures was next determined with the following results when the outer bath is higher than the inner.

TABLE 4.

Difference in Temp.	Radiation per min.	Difference in Temp.	Radiation per min.
.835	.0052	.353	.0024
.768	.005	.300	.002
.703	.0042	.246	.0016
.640	.004	.195	.0013
.578	.0037	.147	.001
.527	.0033	.104	.0008
.452	.0029	.047	.0006
.423	.0026	.016	.0002

PROCEDURE

In most cases the solutions used were tenth normal with respect to the phosphate group. Previous work had shown that from solutions of this concentration quite an appreciable amount of phosphate is re-

moved. The calculated amount of phosphate was weighed
out in a small glass bulb blown to such a thickness
that it would break when pushed against the bottom
of the beaker, but yet withstand a certain amount of
comparatively rough handling, which, if it survived,
insured its not having any small holes thru which water
might enter. If the amount of salt used is rather large,
there is a rapid and fairly large heat change attending
its solution, which introduces an error not present when
smaller amounts are used. The bulb was attached to a
glass rod and suspended thru the lid so that it was in
contact with the water, thereby bringing it to the
same temperature as the water in the beaker.

The required amount of water, 400 gms. and a
specified amount of gel were weighed out, brought to the
approximate desired temperature and placed in the cal-
orimeter. No effort was made to carry out the determi-
nations at an exactly specified temperature, but all
were made within a range of about 0.4 degrees, corres-
ponding to about 25° C.

The temperature of the outer bath was then
brought to the same temperature as the inner bath, and
the inside temperature was read accurately. Stirring
was continued and the outside temperature so regulated
that the inner bath remained constant. It was necessary

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to maintain the outside temperature slightly below the inner so as to allow for the heat of stirring. When the inner temperature had remained constant for a period of 20 to 30 minutes, the salt was released by pushing the glass bulb against the bottom of the beaker. There was an immediate change in temperature, either positive or negative depending on the nature of the salt, and the temperature of the outer bath was changed to correspond with it.

The heats of solution of the various salts were first determined with the results shown in Table 5.

TABLE 5.

Heats of Solutions of Salts		
Salt used	Weight	Temp. change
KH_2PO_4	1.8167	-.129,131
Na_2HPO_4	1.8939	-.1785,1775
" dried		-.183 .185 .183
K_3PO_4	1.4162	.082,.085,.084,.086
K_2HPO_4	2.3220	.090,.090,.090,.088,.085,.087
$CaH_4(PO_4)_2$	1.6932	.035,.032
$MgH_4(PO_4)_2$	1.5800	.077,.080,.080,.083
$MgSO_4$	4.9300	-.144,.147,.145
K_2SO_4(300 cc solution) -.247		

The weights of the different salts used are
the amounts required to make 400 cc. of .1N solutions,
except potassium tertiary phosphate where the amount
used corresponded to .05N. The heats of solution are
positive in some cases and negative in others.

In measuring the heat of reaction with the
gel, the procedure at first consisted in dissolving
the salt in water, with the gel suspended in a semi-
liquid condition in a small glass bulb. The gel used

in this manner contained about 92% moisture so that
a fairly large amount was required. It was rather
difficult to get the gel into the bulb in this
pasty condition and it was necessary to keep it sus-
pended a long time in the water to make sure that it
had attained a uniform temperature thruout. On re-
leasing the gel it required several minutes for it to
be spread uniformly thru the water, and at the same
time it changed the resistance offered to the stirer.
While the results obtained by this method checked very
closely with the one finally adopted, it was dis-
carded for the reasons just mentioned.

In Table 6 are the results obtained in mak-
ing a typical determination, showing the tempera-
ture changes when different amounts of gel react with
the same amount of potassium di-hydrogen phosphate,
and also the heat of solution. This shows clearly
the rate of temperature change in the various stages
of the reaction. The period required for solution
of the salt varies from 2 to 3 minutes depending on
the nature of the salt used.

TABLE 6.

Time	Temp. reading no gel	Temp. change	Temp. reading 1.5 gms, gel	Temp. change	Temp. reading 5.4 gms, gel	Temp change
Temperature Changes due to the Action of KH_2PO_4 with Different Quantities of Hydrous Ferric Oxide						
8.20	.521		.6265		.9315	
8.30	.521		.626		.932	
8.58	.521		.626		.932	
			Released salt			
8.59	.420	-.101	.570	-.056	.932	.000
9.00	.387	.134	.540	.086	.920	.012
9.01	.382	.138	.526	.100		
9.02	.381	.139	.523	.103	.909	.023
9.04	.381	.139	.523	.103	.9085	.024
9.10	.381	.139	.524	.102	.912	.020
9.15	.381	.139	.524	.102	.913	.019
9.25			.524	.102	.9165	.016
9.35			.524	.102	.917	.015
9.55					.917	.015

From the table it is seen that where one gram of gel is used, the total heat change is less than

where no gel is present, showing that the action of the hydrous ferric oxide with the salt produces a positive heat effect. The difference between the heat of solution and total heat effect is called the heat of reaction. In all cases the heat of reaction, or temperature change caused by the presence of the gel if anything, is found to be positive. The heat of reaction is fairly small with one gram of gel, but with 5.4 grams it is almost equal to the heat of solution.

The major portion of the heat appears to be over in a very short time proceeding almost as rapidly as the heat of solution. After this first rapid change the evolution of heat proceeds very slowly and after a period of about half an hour no further measurable change occurs; with smaller amounts of gel it is over in a much shorter time.

Experience had shown that the removal of phosphates proceeds quite slowly, when shaken at intervals requiring about two weeks, but that with continuous shaking equilibrium is attained in a much shorter time. When there was no further temperature change, the beaker was at once removed from the calorimeter and part of the contents filtered as quickly as possible in order that the change in concentration

occurring during the period of heat change might be
determined.

The temperature change and the total change
in concentration occurring when potassium di-hydrogen
phosphate is brought into contact with hydrous ferric
oxide are shown in Table 7. The unfiltered portion
was allowed to remain in contact with the gel until
no further change in concentration occurred and the
amount adsorbed or removed from solution was then
determined.

TABLE 7.

KH_2PO_4 with Hydrous Ferric Oxide

1.8167 g. with 400 cc. water. Gel used, 1 gram.

Time on gel	PH	K present	PO_4 present	K removed	PO_4 removed	Heat of re- action
no gel	4.56	.5082	1.2800			
no gel	4.56	.5035	1.2800			
30 min.	5.94	.4761	1.1200	.0321	.1600	.028
2 weeks	6.27	.4503	.9536	.0580	.3270	
20 min.	5.92	.4770	1.1200	.0310	.1600	.024
40 min.	5.95	.4750	1.1185	.0330	.1620	
2 weeks	6.27	.4450	.9536	.0630	.3270	
20 min.	5.87	.4800	1.1200	.0280	.1600	.024
2 weeks	6.22	.4500	.9606	.0580	.3194	

The results in the table show that there is considerable change in the hydrogen ion concentration during the first thirty minutes and other determinations carried on without the use of the calorimeter to avoid loss of time in removal and filtration show that about half of the change occurs during the period of temperature change. The other half is taken up very slowly, so that there is no further measurable heat change.

In Table 8 are shown the results with primary calcium and magnesium hydrogen phosphates in contact with hydrous ferric oxide.

TABLE 8.

$MgH_4(PO_4)_2$ on Hydrous Ferric Oxide 1.5800 g with 400 g. water. Gel used, 2 grams				
Time on gel	PO_4 present	PO_4 removed	Temp. change	Heat of reaction
no gel	1.1408		.080	
1 hour	.7584	.382	.140	.060
3 weeks	.7647	.540		
1 hour	.6004	.376	.138	.058
3 weeks	.5960	.544		
$CaH_4(PO_4)_2$				
no gel	1.2660		.032	
1 hour	.8797	.386	.088	.056

The heats of reaction of the magnesium and
calcium salts are approximately the same while the amounts
of phosphate removed are about the same in both cases.
The temperature rise with the magnesium and calcium
salts is over twice that produced by the potassium hy-
drogen phosphate as is also the amount of phosphate
removed from solution. This of course is accounted
for by the fact that in one case only a gram of gel
was used while two grams were used in the other. The
PH of the calcium phosphate changes from 3.43 to 4.91
and the change with the magnesium phosphate is about
the same.

In the work with potassium dihydrogen phos-
phate it was found that the change in hydrogen ion
concentration is considerable when it reacts with the
gel. With the calcium and magnesium salts the heat
effects per gram of gel were of about the same order
but increased with the amount of gel added. This
was contrary to expectations since the amount of gel
present at all times was more than sufficient to react
with the potassium acid phosphate if it was a straight
chemical reaction with the formation of the normal
phosphate. One gram of the gel is just sufficient
to react with two grams of the salt, assuming a neutral-
ization of the acid phosphate by the ferric oxide, but

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the heat with two grams of gel is twice as great as
with one gram showing that there is apparently an excess
of the acid salt and not of hydrous ferric oxide.

It was then decided to increase the concen-
tration of the hydrous ferric oxide to determine the
total heat effects that could be produced with a given
weight of the potassium acid phosphate, and varying
amounts of hydrous ferric oxide. The amounts used varied
from 1 gram to 5.4 grams. The heat effect together with
the change in phosphate and hydrogen ion concentration
are shown in Table 9.

TABLE 9

	KH$_2$PO$_4$ with varying amounts of Hydrous Ferric Oxide			
Amount of gel used	37 cc(1g.)	74 cc.(2 g.)	60 cc.	75 cc.
Total temp. change	.106	-.087	-102	-.085
Heat of reaction	.034	.053	.038	.055
Heat of reaction per gram gel	.034	.027	.025	.027
PO$_4$ removed during first 30 min.	.1620	.2470	.2190	.2500
PO$_4$ removed in 30 min. per gm. gel	.1620	.1235	.1300	.1240
Total PO$_4$ removed on standing	.223	.3885	.3320	.3885
Total PO$_4$ removed per gram gel	.2230	.1942	.2047	.1940
PH of solution on gel	6.07	6.43	6.35	6.44
PH of solution after 30 min. contact with gel	5.88	5.99	5.97	5.99

TABLE   9   (cont.)

	KH_2PO_4 with varying amounts of Hydrous Ferric Oxide			
Amount of gel used	100 cc.	125 cc.	200 cc.	210 cc.
Total temp. change	-.073	-.053	.010	-.0125
Heat of reaction	.067	.087	.150	.152
Heat of reaction per gram gel	.0248	.0256	.027	.027
PO_4 removed during first 30 min.	.3320	.4097	.6560	.6650
PO_4 removed in 30 min. per gm. gel	.1228	.1214	.1230	.1210
Total PO_4 removed on standing	.4660	.5480	.7930	——
Total PO_4 removed per gram gel	.1724	.1620	.1456	——
pH of solution on gel	6.64	6.76	7.18	7.24
pH of solution after 30 min. contact with gel.	6.34	6.44	6.84	6.85

The rise in temperature continues steadily
with a continued increase in the amount of gel added
and the rise for the last gram is the same as for each
of the others showing that the maximum heat effects
had not been attained, and that the potassium acid phos-
phate was still present in excess. The amount of phos-
phate removed during the period of temperature change
remains approximately the same per gram of gel except
that the change with the first gram is more than that
produced by each succeeding gram.

The hydrogen ion concentration changed consid-
erably with the first addition of the gel, but changes
more slowly on the addition of more gel. The total
amount of phosphate removed calculated on the basis of
one gram shows a drop as is to be expected from pre-
vious work which has shown that the total amount of
adsorption varies with the concentration.

On finding this continuous increase in the amount
of heat liberated, since the amount of gel used was now
rather large it was decided to use a smaller amount of
the potassium acid phosphate with the maximum amount
of gel used previously. Using 200 cc. (5.4 gms.) of
gel with the same amount of solution as previously but
with a concentration of .05N instead of .1N, the heat

of reaction produced a rise of .092 degrees. Using 150 ec. (4.05 gms) of gel the heat of reaction caused a rise of .0705 degrees. On calculation the second value is found to be three fourths that of the first, showing that the temperature rise still varies directly with the amount of gel present, but the value per gram has dropped to .017 degrees, showing that the concentration of the potassium dihydrogen phosphate is also a factor as well as the concentration of the gel.

After finding an appreciable heat change with acid salts having a fairly high hydrogen ion concentration, where one might expect to find a reaction between an acid and a basic material, it was decided to try the action of salts having a lower hydrogen ion concentration. Most of the work on phosphates had been carried out with acid salts, and it has been shown by Gordon and Starkey[31] that adsorption increases with a rise in the hydrogen ion concentration. In Table 10 are given the results obtained with secondary potassium phosphate, a salt having a PH of 7.58 in a tenth normal solution.

TABLE 10

K₂HPO₄ on Hydrous Ferric Oxide 2.3220 gms. in 400 gms. water. Conc. .1N gel used 1 gm.						
Time on gel	PH	K present	PO₄ present	PO₄ removed	Temp Change	Heat of Reaction
no gel	7.58	.9960	1.2970		.088	
60 min.	7.74	.9296	1.1768	.120	.1125	.020
3 weeks	7.93	.9296	1.1208	.177		
60 min.	7.79	.9030	1.1580	.139	.1135	.020
3 weeks	7.95	.9030	1.1212	.177		
60 min.	7.80	.9170	1.1740	.121	.114	.021
3 weeks	7.90	.9040	1.1356	.161		
3 weeks	7.92	.9050	1.1340	.161		

The amount of phosphate removed is slightly less than that removed by one gram of gel from the primary salt as is also the heat effect, but both are approximately the same as the effects produced per gram when larger amounts of the iron gel are added to the primary salt.

The action of hydrous ferric oxide with tertiary potassium phosphate, a strongly basic salt is shown in Table 11. It hydrolyzes to a considerable ex-

tent has the highest heat of solution of the phosphates used and a PH of 10.97 in a twentieth normal solution.

<div align="center">TABLE 11</div>

K_3PO_4 on Hydrous Ferric Oxide 1.4163 gms. in 400 gms. water. Cono. .05N.					
Time on gel	PH	K present	PO_4 present	PO_4 removed	Temp. change
no gel	10.97	.6580	.5190		.005
.5 gm gel	10.89	.6580	.5116	.0094	.004
60 min.					
3 weeks	10.77	.6580	.4969	.0280	
1 gm gel					
60 min.	10.88	.6580	.5000	.0290	.004
3 weeks	10.44	.6580	.4670	.0560	

It will be noticed that no potassium is adsorbed in this case and that the amount of phosphate removed is comparatively small. There is only a slight change in hydrogen ion concentration which shows a slight drop in alkalinity. There appears to be no measurable heat change altho there is a slight drop in temperature and the gel seems to have undergone more peptization than

in other cases where the same amount of gel was used. The concentration of the original solution was changed to .05 normal to avoid a certain amount of error attendant to large temperature changes on solution.

The oxides of iron and aluminum are both classed as soil colloids, and it has been shown by Flenner[32] that the behavior of aluminum oxide in the removal of phosphates from acid phosphate solutions is quite similar to that of hydrous ferric oxide. The action of primary, secondary, and tertiary potassium phosphates with hydrous aluminum oxide are shown in Table 12.

TABLE 12

Phosphates of Potassium with Hydrous Aluminum Oxide.

Salt	Time on gel	pH	PO_4 present	PO_4 removed	Temp. change	Heat of reaction
KH_2PO_4	no gel	4.56	1.2800		-.140	
	1 hour	6.12	1.0700	.2100	-.104	.036
	4 days	6.39	.9360	.3440		
	1 hour	6.09	1.0900	.1900		
	1 day	6.14	1.0500	.2300	-.101	.039
	2 weeks	6.37	.9340	.3460		
K_2HPO_4	no gel	7.58	1.2970		.088	
	1 hour	7.92	1.2050	.092		
	2 weeks	8.42	1.1440	.153	.112	.024
	1 hour	7.92	1.2000	.097	.111	.023
	2 gm gel					
	1 hour	8.54	1.1770	.120	.120	.032
	2 weeks	8.80	1.1210	.131		
K_3PO_4	no gel	10.97	.5200		.065	
	1 hour	10.70	.4680	.032		
	2 weeks	10.56	.4850	.035	.083	

The results obtained with hydrous aluminum oxide are quite similar to those obtained with hydrous ferric oxide. While the total amount of phosphate removed from the primary potassium phosphate solution by the two gels is about the same, the amount removed during the first hour is much greater in the case of the hydrous aluminum oxide than with hydrous ferric oxide, and the temperature change is approximately proportional to the amount removed. The change in the hydrogen ion concentration in both the first and final stages is greater with the alumina.

With the secondary potassium phosphate the heat effects with hydrous aluminum oxide are similar to those with the hydrous ferric oxide. The heats are of about the same order, and the change in hydrogen ion is somewhat greater.

With tertiary potassium phosphate the results are quite similar, no heat effects being shown in either case altho with the hydrous aluminum oxide the hydrogen ion concentration again changes most. The initial amount of phosphate removed is quite small, increasing somewhat on standing.

Aluminum hydroxide is more amphoteric than ferric hydroxide. The pH of water in contact with hydrous aluminum oxide after several weeks contact is 8.3, while that of hydrous ferric oxide is 7.5. This would seem to account for the greater initial activity of the aluminum oxide as compared with ferric oxide.

Sulfates also are adsorbed to some extent by the hydrous oxides of iron and aluminum as has been shown previously[33], altho the amount adsorbed is much less than with the acid phosphates. In using a neutral sulfate the probability of a chemical reaction between the solution and the oxide is practically eliminated. The amount of adsorption and the heat effects obtained with magnesium and potassium sulfates are shown in Table 13.

TABLE 13.

Sulfates on Hydrous Ferric Oxide				
Salt used	Sulfate adsorbed	Metal adsorbed	Temp. change	Heat of Reaction
K_2SO_4	.0059	.0043	-.247	0
$MgSO_4$	.0283	.0071	-.145	0
Sulfates on Hydrous Aluminum Oxide				
K_2SO_4	.0121	.0092	-.248	0
$MgSO_4$	.0659	.0146	-.146	0
$MgSO_4$			-.144	0

The temperature changes in all cases correspond very closely to the heat of solution, showing that there is no measurable heat of adsorption or heat of reaction. With the sulfates, the positive and negative ions are adsorbed or removed from solution in equivalent amounts, which is not the case with acid phosphates.

After allowing the solutions to attain maximum adsorption or equilibrium, some of the phosphate mixtures were taken and filtered and washed with cold water to remove the phosphate. This proved to be quite a long task as small amounts of phosphate kept on coming thru. When this amount remained constant for sometime it was thought probable that the appearance of this small amount of phosphate might be due to hydrolysis of ferric phosphate. The residue was then taken and dissolved in nitric acid, and analyzed for phosphate and iron. The results obtained on treating primary, secondary and tertiary potassium in this manner are shown in Table 14.

TABLE 14.

Salt used	Fe present	PO$_4$ present	Atomic Ratio Fe : PO$_4$
KH$_2$PO$_4$	.3190	.110	5:1
	.3864	.134	5:1
K$_2$HPO$_4$	.3190	.0493	1:090
	.2464	.0353	1:084
	.2268	.0316	1:083
K$_3$PO$_4$	.3976	.0335	1:.05
	.1568	.0158	1:.06

Analysis of Precipitate left after Washing free from Phosphates with cold water.

It is interesting to note that the atomic ratios of the phosphate held by iron are expressed approximately by the ratios 5:1 for the primary salt, 10:1 for the secondary and 20:1 for the tertiary salt, showing that the most phosphate is retained by the iron under acid conditions.

To show that water affects ferric phosphate a sample of the pure salt was prepared by mixing an equivalent amount of ferric chloride with di-sodium hydrogen phosphate and washing several times. When the wash water after standing on the ferric phosphate

give but a slight test for phosphates, the precipitate was taken and boiled with water when a very strong test for phosphates was found in the filtrate. This extraction was continued until no test for phosphates was given by the wash water. The precipitate which was almost white at first had changed to dirty yellowish color and was now quite brown, somewhat resembling ferric hydroxide, but lighter in color. This precipitate was then analyzed and found to correspond to the ratio of two Fe atoms to each PO_4 group, showing the formation of a basic ferric phosphate. The pH of the solution after boiling was 3.76 indicating that the ferric phosphate had been converted into the basic phosphate and phosphoric acid.

To get a clearer idea of the nature of the equilibrium between hydrous ferric oxide and phosphates, varying amounts of the gel and a dilute solution of phosphoric acid were mixed and allowed to stand for two weeks with occasional shaking. They were then made up to equal volumes and after setting several days the amount of phosphate left in solution was determined. The amount of hydrous ferric oxide varied from 10 cc. to 30 cc. and the phosphoric acid varied from 10 cc. to 50 cc. The ferric oxide was of such a concentration that/ the amount

of iron present in 37 cc. would correspond to 1 gram of
ferric hydroxide. The phosphoric acid used contained
.1068 grams PO_4 in 10 cc. or corresponded to a con-
centration of .306N. The results are shown in Table 15.

TABLE 15.

Phosphoric Acid on Hydrous Ferric Oxide.					
No. of sample	No. cc. gel used	No. cc. of acid used	Total PO_4 present	PO_4 left in solution	Final pH
0	0	10 + 50cc. water			2.04
1	10	10	.1068	.0186	2.81
2	20	10	.1068	.0035	5.34
3	10	20	.2136	.0978	2.13
4	10	30	.3204	.1986	1.87
5	20	30 plus H_2SO_4	.3204	.1530	1.74
6	10	50	.5340	.3882	1.60
7	10	20	.2136	.0940	2.08
8	20	30	.3204	.0936	2.12
9	30	10	.1068	.0025	6.80
10	20	10 heated	.1068	.0032	5.60

After equilibrium had been established between

the gel and acid, sufficient water was added to each
to make the total volume 60 cc. They were then allowed
to stand for a week with occasional shaking before analy-
sis. For comparison the hydrogen ion concentration of
10 cc. of acid made up to 60 cc. of solution is given as
number 0.

In no case was the phosphate removed completely
from solution. In number 2 the phosphate is removed
almost completely, but in number 9 where the same amount
of acid is used with 30 cc. of the gel, even though the
gel used is 50% greater the amount of phosphate removed
is but slightly more.

Number 7 is a duplicate of number 3, but differs
from 3 in that it was ground for several minutes in a
mortar after equilibrium had been established and then
allowed to stand to see whether any further reaction would
take place.

In number 5, 10 cc. of .136 N. sulfuric acid were
added. This amount would be sufficient to dissolve one
twelfth of the ferric oxide present. The amount of phos-
phate left in solution is much greater than in number 8,
which is similar except that no sulfuric acid has been
added. The amount of iron in solution is quite high and
the hydrogen ion concentration ranks second.

In number 10, we have a duplicate of number 2,

except that the mixture was heated to see whether all the phosphate could be removed from solution, but the amount in both cases is about the same.

By using a large excess of phosphoric acid with the hydrous ferric oxide it was found possible to convert it into a white granular precipitate by heating the mixture for about two days. This precipitate corresponded to the formula $FePO_4$.

In the ten solutions shown in the table, there were only those which did not give a white precipitate of ferric phosphate on neutralization, and also give a test for the ferric ion in solution. These three were 2,9, and 10 which were almost neutral.

To check the heat effects obtained when primary and secondary phosphates react with hydrous ferric and aluminum oxides, a small amount of potassium hydroxide, just sufficient to cause approximately the same change in hydrogen ion concentration as was caused by one gram of hydrous ferric oxide, was added to the water in the calorimeter and the heat of reaction of each of these salts was measured. The results obtained are shown in Table 16. The results with hydrous ferric and aluminum oxides are again shown for comparison.

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TABLE 16

Salt	Original pH	Basic material	Final pH	Heat of reaction
KH_2PO_4	4.56	4 cc. KOH .24N	5.86	.0325
	4.56	1 gm. $Fe(OH)_3$	5.88	.024
	4.56	1 gm. $Al(OH)_3$	6.12	.036
K_2HPO_4	7.58	4 cc. KOH .24N	7.92	.032
	7.58	1 gm. $Fe(OH)_3$	7.74	.020
	7.58	1 gm. $Al(OH)_3$	7.92	.024

The effect of basic materials with primary and secondary potassium phosphates.

The heat effects of ppotassium hydroxide with the primary and secondary salts are the same and of about the same order as those produced by one gram of hydrous ferric oxide. The potassium hydroxide present corresponds to .001 gram equivalent while the hydrous ferric oxide is present to the extent of about thirty times that amount, which tends to indicate that not all the molecules react or that they do not react to the full extent of their valences. That not all the molecules react is also borne out by the work of White[24] which shows that after equilibrium has been attained, more phosphate can be removed by grinding the gel,

thus exposing fresh surfaces, when further action takes place with a corresponding change in hydrogen ion concentration. The aluminum oxide which is present in larger equivalents than the iron, would naturally be expected to produce more heat than the iron oxide, and such is found to be the case.

In order to determine whether the phosphate removed from solution on standing was held in the same manner as that removed after the initial temperature change had taken place, several samples in which maximum adsorption had taken place on standing three weeks, were compared with one in which the gel was in contact only long enough for the salt to go into solution and then filtered. The amount of phosphate present in the solution wetting the paper and gel was determined by taking a similar portion on a weighed paper and heating to 105°C. From the moisture content the amount of adhering phosphate could be calculated by analysis of the corresponding filtrate.

The moist precipitates were then similarly washed with 20cc. portions of water and the phosphate washed out was determined. When the amount removed was practically the same on the different samples, the precipitates were placed into 500 cc. graduated flasks.

The flasks were made up to the mark with water and allowed to set three days with occasional shaking so as to attain equilibrium. The amount of phosphate present in solution was then determined. The result obtained are shown in Table 17.

TABLE 17.

The Effect of Washing on Hydrous Ferric Oxide in Contact with Primary Potassium Phosphate for different Periods of Time.

	Gel 1 3 weeks	Gel 2 3 weeks	Gel 3 3 weeks	Gel 4 20 min	Gel 5 20 min
Time o contact	3 weeks	3 weeks	3 weeks	20 min	20 min
Wt. of wet ppt.	13.500	13.495	13.590	13.150	13.150
Water in ppt.	12.63	-.-	13.15	11.80	
PO_4 in adhering solution	.0049	.0049	.0067	.0215	.0215
pH of filtrate	8.29	8.27	7.93	6.02	6.04
Total PO_4 in ppt.	.0653	.0653	.0715	.0901	.0901
PO_4 removed in 1st wash.	.0055	.0055	.0067	.0151	.0085
2nd washing	.0044	.0045	.0048	.0085	
3rd washing	.0028		.0035	.0058	
4th washing	.0021		.0029	.0588	
Total PO_4 removed	.0148		.0209	.0518	
PO_4 in ppt.	.0505		.0506	.0183	
Placed in 500cc flask.					
PO_4 in solution	.0119		.0119	.0123	
PO_4 in ppt.	.0386		.0386	.0460	
pH of sol.	7.05		6.92	6.74	

Gels 1 and 2 are duplicates as are also 4 and 5.
Numbers 1, 2 and 3 are from solutions which were only .05N
which accounts for the fact that 4 and 5 contain slightly
more phosphate. These were taken so that after washing
off the adhering solution the remaining phosphate would
be about the same in all cases. After this adhering
solution has been removed the phosphate seems to be re-
moved at the same rate from all of the gels, indicating
that the major portions are held in the same manner in
the sample which had been standing for some time as in
sample which had just been prepared.

While a small amount of the phosphate might
be held by physical adsorption this amount appears to
be quite small, and the heat effects if any would be
too small to be measurable with the amount of water
used. These heat effects would of necessity be quite
small and would probably be of the order of the heat
change produced when the liquid actually in contact
with the gel is brought to the same dilution as the
main body of the solution. Since the salt of course
remains in a wet condition this change would be small,
as the major portion of the removed phosphate appears
to be chemically held.

That heats of adsorption should be quite small
when adsorption takes place from solution is in accord-
ance with the results of Browne in his work on the heat

of coagulation previously cited, as in that case the adsorption of oppositely charged ions was necessary in order to produce coagulation of the colloid. In addition there was the possibility of a decrease in surface with a consequent release of energy, but the heat effects if any, were found to be quite small.

In the work with hydrous ferric oxide, there was usually peptization of the gel, indicating an increase of surface which should be accompanied by negative heat effects. This change however, took place very slowly, and at the end of an hour showed but slight peptization, altho at equilibrium it was very noticeable. The energy changes accompanying peptization would probably be quite small compared with the heat effects produced by the further action of the phosphate on the increased surface of the ferric hydroxide produced by peptization.

SUMMARY AND CONCLUSIONS.

The heats of solution of primary potassium, magnesium and calcium phosphates, secondary and tertiary potassium phosphates and magnesium and potassium sulfates were determined.

The heat changes occurring when hydrous ferric oxide is placed in contact with primary potassium phosphate

pH 4.56 or secondary potassium phosphate, pH 7.56 is positive. The heat change proceeds rapidly, taking place almost as rapidly as the salt passes into solution. Similar changes were found with primary calcium and magnesium phosphates.

With hydrous aluminum oxide the temperature changes were quite similar to those with hydrous ferric oxide, but were larger as is to be expected from the fact that its molecular weight is less and that it is more basic than hydrous ferric oxide.

With tertiary potassium phosphate which has a pH of 10.97, there is no appreciable temperature change with either the hydrous ferric or aluminum oxides.

Altho the hydrous ferric oxide is present in greater amount than is required to react with the phosphate, successive additions of the oxide produce a corresponding temperature change, showing that not all the ferric oxide has reacted with the phosphate.

In all cases where initial heat changes occur, it was found that during this period of heat change, a large amount of phosphate is removed from solution. After this period the removal of phosphates from solution proceeds more slowly. Most of the phosphate seems to be held quite similarly as is shown by washing with

water. From this it appears probable, that heat is evolved during the entire process of removal of the phosphate, but that after the surface of the particle becomes coated, the action is so slow that the heat change could not be measured.

The amount of heat was found to depend both on the concentration of the hydrous ferric oxide and on the concentration of the phosphates.

The equilibrium relations between phosphoric acid and ferric oxide gel were investigated, and it was found that a small amount of ferric phosphate tends to remain in solution, and that not all the phosphate is removed even when the ratio of the iron to the phosphate is quite large.

It was shown that ferric phosphate tends to pass over into the basic phosphate on washing with water, and that it is greatly accelerated by treatment with hot water, the phosphates no longer being removed when the atomic ratio of Fe to PO_4 is 2 to 1.

The amount of phosphate retained by the gel on washing is dependent on the amount originally taken up. This is in accordance with the preceding results. With tertiary phosphate where there is no heat change, the amount retained is slight.

The heat changes are of somewhat the same order

as those produced by the addition of an amount of potassium hydroxide producing a similar change in the hydrogen ion concentration.

The results with hydrous ferric oxide indicate that the heat effects are somewhat different for different batches of gel, and for the same gel the heat drops on long standing, indicating that the gel has undergone a change.

With potassium and magnesium sulfates, where the same equilibrium can be attained from either side, no measurable heat change was found.

The foregoing work proves that there are two types of so-called adsorption, one where there is a transfer of electrons, and another where there is no transfer of electrons. The former is no different than our ordinary chemical reaction and should not be confused with the latter which results from the magnetic effects of the ions and molecules.

It has been shown that in this latter type of adsorption there is no heat change, hence this investigation furnishes a criterion for differentiating between these two types of phenomena.

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