ON THE ADSORPTION OF WATER VAPOR AND OF
CERTAIN SALTS IN AQUEOUS SOLUTION
BY QUARTZ¹

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Adsorption may be defined as the action by which the concentration or density of a gas, liquid or dissolved substance at a surface is changed with respect to that of the surrounding medium. This term was first applied to this class of phenomena by duBois-Reymond, and seems preferable to "absorption,"—a term which is also used to designate the solution of a gas in a liquid.

Gibbs² and J. J. Thomson³ have investigated theoretically the adsorption of a dissolved substance by considering the change in the surface tension of the liquid-solid surface as the concentration of the solution increases. They have shown that if the surface tension of the film increases as the concentration increases, a part of the dissolved salt will pass out of the film, so that there will be less salt in a unit volume of the surface film than in a unit volume of the liquid in bulk; while if the surface tension is diminished by the addition of salt, the salt will move into the film, and the surface film will contain more salt per unit volume than the rest of the liquid. The latter condition is thus essential for positive adsorption of the solute.

Thomson refers, in support of these deductions, to the experiments of Röntgen and Schneider,⁴ who found, "that for most solutions, the product of the height to which the solution rises in a capillary tube into the density of the solution is greater for a solution of a salt than for pure water, and that for dilute solutions of most (though not all) substances this product increases with the strength of the solution. It follows from this fact that the tension of the surface of contact of the solution with air in-

¹ Published by permission of the Secretary of Agriculture.

² Trans. Conn. Acad., Vols 2 and 3.

³ Applications of Dynamics to Physics and Chemistry, 1888, p. 190.

⁴ Wied. Ann., 29, 165 (1886).

creases with the strength of the solution, while the tension of the surface of contact of the solution with glass or any other solid body diminishes as the solution gets stronger."¹

I am unable to see that Prof. Thomson's conclusion, that "The tension of the surface of contact of the solution with glass, or any other solid body diminishes as the solution gets stronger" necessarily follows from the experiments of Röntgen and Schneider. Their measurements were made by means of a capillary tube, the walls of which were wetted with the solution above the meniscus. The measurements consequently do not involve the tension of the liquid-solid surface, and no conclusion regarding the tension of this interface can therefore be drawn from their results.

These interesting theoretical deductions regarding adsorption cannot therefore be experimentally verified for solid surfaces until we possess a method for measuring the tension of the liquid-solid interface. Zawidski² has, however, tested these conclusions for the liquid-gas surfaces of two different systems. Saponine was added to aqueous solutions of hydrochloric and acetic acids, and bubbles of air were then slowly drawn through the solutions. The foam was collected and analyzed, and was found to be more concentrated than the original solutions. This is wholly in accord with the theory, since hydrochloric and acetic acids both decrease the surface-tension of water. Similar results have been obtained by Miss Benson,³ using aqueous amyl alcohol.

This suggests that the decrease in the surface-tension of the liquid-gas interface of a solution which generally occurs when a liquid surface is allowed to stand for a time and which is usually ascribed to the presence of impurities on the surface may be due, in part at least, to changes in the concentration of the surface-layer, which would always take place in such a direction as to lower the surface-tension.

The investigation described in the following pages may be

¹ Thomson, *Dynamics*, p. 190.

² *Zeit. phys. Chem.*, **35**, 77 (1900).

³ *Jour. Phys. Chem.*, **7**, 532 (1903).

divided into two portions: Part I deals with the adsorption of substances in aqueous solution by quartz, under conditions such that changes in the concentration of the liquid-gas interface are eliminated; Part II deals with the adsorption of water-vapor by quartz at different vapor pressures.

Part I. The Adsorption of Dissolved Substances by Quartz

Review of Earlier Work

A general historical account of investigations on the adsorption of dissolved substances up to the year 1890 may be found in Ostwald's *Lehrbuch der allgemeinen Chemie, Vol. I.*¹ These investigations nearly all deal with adsorption by wood or bone charcoal, substances which, while showing marked adsorption effects, are poorly suited for quantitative investigations, owing to the great difficulty in obtaining uniform samples. The foreign substances contained in the charcoal also make chemical reaction possible with the substance under investigation. In fact, Graham,² whose experiments are among the most extensive of those employing animal charcoal, satisfied himself that chemical action did take place, and was inclined to consider the effect as being largely due to chemical action when this substance is employed.

Van Bemmelen³ appears to have been the first to investigate the adsorption of salt and acid solutions in a quantitative way. He worked with sulphuric, nitric and hydrochloric acids, and their three potassium salts. He used amorphous silica as the adsorbing substance, prepared by precipitation from soluble silicates by hydrochloric acid. Ten grams of silica, dried at 100° C, were used in each case. The silica was kept in contact with 100 cc of the solution for twenty-four hours, the mixture being frequently shaken. The results are given in the following table. The first column expresses the number of milligram-equivalents (gram-molecules ÷ 1000) of salt in 100

¹ For a bibliography of the adsorption of gases, see Mülforth: *Drude's Ann.*, 3, 328 (1900).

² *Pogg. Ann.*, 19, 139 (1830).

³ *Jour. prakt. Chem.*, 23, 324 (1881).

cc of solution. The remaining columns give the number of milligram-equivalents of the various substances removed from solution by the silica.

Concen.	K ₂ SO ₄	KNO ₃	KCl	H ₂ SO ₄	HNO ₃	HCl
20	1.0	0.9	0.85	1.1	0.86	0.81
50	2.5	2.14	2.16	2.17	2.17	2.27
100	4.56	—	—	4.0	4.0	4.2

It will be noted from an inspection of the above figures that the quantity of acid or salt removed by the silica is approximately proportional to the concentration of the solution, although in the case of the most concentrated solutions, the amounts removed are somewhat less than would be required by such a relation.

Van Bemmelen, in discussing these results, calls attention to an apparent relation between the amount of salt removed and the amount of water which the silica would give up if dried at 100° C. He found the latter amount to be about 55 percent, which for 10 grams of silica would be 5.5 cc. From an inspection of the table, it will be seen that the amount of salt taken up corresponds to a bodily removal of from 4 to 4.5 cc of the solution. This led Van Bemmelen to suggest that when the silica was put into a solution, the water it contained was replaced by an equal volume of the solution.

Schmidt¹ has investigated quantitatively the amount of adsorption in the following systems: Iodine, from alcohol and benzol solutions, by blood and bone charcoal; acetic, oxalic and succinic acids in aqueous solutions by blood and bone charcoal; picric acid by cellulose; eosine and malachite green by silk. He found in every case that the ratio of the amount of material adsorbed to the concentration decreased as the concentration increased, the adsorption in most cases being relatively much greater for the more dilute solutions.

Schmidt also investigated the adsorption of potassium chloride by precipitated silica, and obtained results agreeing with

¹ Zeit. phys. Chem., 15, 56 (1894).

those of van Bemmelen; that is, the amount of adsorption was very nearly proportional to the concentration, the ratio increasing slightly as the concentration diminishes. He consequently concludes that dissolved substances are taken up by precipitated silica mainly in the form of a solid solution rather than through adsorption processes.

Van Bemmelen¹ shows that in colloids, there is no way by which we can distinguish between absorption and adsorption. He also states² that the phenomenon of physical adhesion must in some cases be considered as a kind of loose chemical combination.

The adsorption of very dilute acid and alkaline solutions by platinum black has been investigated by Kellner,³ by means of the electrical conductivity method. His results show that the amount of adsorption is relatively greater as the concentration diminishes.

Object of the Investigation

The object of this part of the investigation was to determine the amount of adsorption on quartz surfaces of known area from dilute aqueous solutions of various salts. Quartz is one of the chief constituents of the soil, and a knowledge of its action as an adsorbing agent is of fundamental importance in the study of the retention of soluble substances by soils. Furthermore, quartz is one of the most nearly insoluble substances known, which makes it of special value in adsorption investigations. Finally, it is possible to calculate roughly the surface area exposed in a sample of powdered quartz by separating the particles into groups according to size, and determining the percentage of particles in each group and their mean diameter.

Preparation of the Quartz

The quartz used was obtained from a vein in Lancaster County, Pennsylvania, where the material is crushed to fine powder in large quantities for the purpose of manufacturing

¹ Zeit. anorg Chem., 23, 321 (1900).

² Loc. cit., p. 380.

³ Wied. Ann., 57, 79 (1896).

porcelain. Upon examination, the material was found to contain a small amount of chlorides, carbonates and bicarbonates, so that a thorough washing was necessary before the material could be used. The washing was carried out in the following manner: About 150 grams of material were placed in a bottle containing distilled water acidulated with hydrochloric acid, and shaken for several hours in a mechanical shaker. These bottles were then placed in a centrifugal apparatus and rotated until practically all the suspended particles were thrown down when the supernatant liquid was decanted. Fresh distilled water was then added and the operation repeated until the specific electrical resistance of the decanted water was from 100,000 to 200,000 ohms. The quartz was then removed from the bottles, dried thoroughly at 110° C, and after thorough mixing was ready for use. A microscopic examination of the quartz showed the grains to be sharp and angular, free from seams and fissures, and practically free from occlusions.

Measurement of the Surface Area of the Powdered Quartz

The calculation of the surface area necessitates the separation of the soil grains into groups according to size, and the subsequent determination of the relative percentages by weight of the various groups, and the mean diameter of the particles constituting each group. The different groups were separated by means of their different rates of subsidence in water, the process being accelerated with the aid of a centrifugal apparatus.¹

The composition of the material employed in the following experiments as determined by several analyses, is given below:

Diameter mm.	Percentage
0.25-0.1	2
0.1- 0.05	12
0.05-0.005	85
0.005	1

In calculating the surface area, the particles were considered cubical in form, and the mean diameter of any group was assumed to represent the longest diagonals of the cubical particles

¹ Bull. 24, Bureau of Soils, U. S. Dept. Agr., 1904.

constituting that group. On this basis of calculation, the powdered quartz used was found to have a surface area of about 1000 sq. cm. per gram.

*Method Employed in Measuring Adsorption
in Aqueous Solutions*

The method employed in measuring the adsorption consisted in preparing a series of solutions of each substance under investigation and determining by titration the concentration of each solution before and after adsorption. One hundred and fifty cc of solution were used for each 100 grams of quartz. The solution and powdered quartz were always shaken together for at least thirty hours in a rotating shaker, which insured constant and thorough contact between solution and solid. The glass bottles employed in this work were all treated with sodium hydroxide solutions previous to their use in the adsorption experiments, in order to minimize the action of the alkaline solutions upon the glass. The systems were subject to the fluctuations of the temperature of the room, which averaged about 22° C.

Explanation of Tables

In the following tables, the first column, in the case of each solution, gives the concentration of the solution after adsorption in gram-molecules per liter. In the case of the carbonates the molecular weight was divided by two. The second column gives the total adsorption of salt in gram-molecules by 100 grams of quartz (100,000 sq. cm. of surface) for that particular concentration. Several titrations of each solution were made, hydrochloric acid being used as the titrating reagent. Methyl orange was used as indicator in all titrations of the carbonate and hydroxide solutions. The color change was determined by comparison with an equal amount of indicator diluted to the same volume in beakers of the same size and form.

In addition to the determinations given in the accompanying tables, the adsorption of sodium, ammonium, and magnesium chlorides was investigated. These salts failed to show any meas-

TABLE I
Adsorption of Hydroxides by Quartz

Sodium hydroxide		Potassium hydroxide		Ammonium hydroxide	
Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mols.
0.0007	0.42×10^{-4}	0.0009	0.33×10^{-4}	0.0008	0.55×10^{-4}
0.0026	0.79	0.0021	0.91	0.0032	0.74
0.0078	1.48	0.0063	1.63	0.0102	1.04
0.028	3.45	0.0235	3.3	0.0344	2.94
0.0866	8.10	—	—	0.1052	7.68

TABLE II.
Adsorption of Carbonates by Quartz

Sodium carbonate		Potassium carbonate		Ammonium carbonate	
Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mol.
0.0004	0.06×10^{-4}	0.0029	0.45×10^{-4}	0.0022	0.09×10^{-4}
0.0012	0.18	0.0093	0.76	0.0065	0.45
0.0032	0.97	0.0302	1.65	0.0208	0.45
0.0106	1.13	0.0910	2.4	0.063	1.8
0.0356	1.65	—	—	—	—
0.108	1.95	—	—	—	—

urable adsorption either by titration or conductivity methods.¹ The same result was obtained in the case of sodium nitrate and sodium sulphate, even when an amount of solution was used only sufficient to saturate the quartz, which, for the same amount of adsorption, would produce a relative change in the concentration of the solution about five times as great as in the preceding experiments. These statements must not, of course, be interpreted to mean that there is no adsorption of these neutral salts. The measurements serve simply as a basis for assigning a superior limit to the magnitude of the effect—an effect which may or may not exist. The conductivity method

¹ An exception occurred in one series of experiments with sodium chloride, when a slight adsorption was observed, but subsequent experiments failed to show any definite effect.

is by no means ideal for such measurements, since there is always the possibility of some substance going into solution, which serves to mask the effect sought. This was avoided as far as possible by washing the powdered quartz thoroughly. The resultant change in the conductivity of the neutral solutions by the addition of the quartz amounted to less than one part in two hundred. This serves to show that there is a radical difference between neutral and alkaline salts in their adsorption by quartz, which is in general agreement with the experiments on the adsorption of these salts by other substances.

Returning now to the adsorption of the carbonates and hydroxides, an examination of Tables I and II shows that while there are many irregularities, the amount of adsorption is dependent upon the acid radical, the adsorption of the hydroxides being more marked than that of the carbonates. On the other hand, the results obtained for potassium, sodium and ammonium hydroxide are quite similar, and the same relation is to be observed in the corresponding carbonate series. In other words, in this series of salts, the influence of the basic element is small compared with that of the acid radical.

These conclusions lead to the idea that possibly the adsorption observed may be largely due to the presence of the hydroxyl ion. Shields¹ has investigated the hydrolysis of a tenth-normal solution of sodium carbonate, and finds it to be about 3 percent at 25° C. On the above supposition, therefore, the adsorption of a tenth-normal sodium carbonate solution and a three-hundredth-normal sodium hydroxide solution should be the same. Reference to the data shows that the adsorption of tenth-normal solution of sodium carbonate is about four times greater than could be explained on this basis. This hypothesis cannot, therefore, explain the marked adsorption of the carbonates, although hydrolysis undoubtedly has some influence on the amount of adsorption.

While precautions were taken to reduce to a minimum the action of the alkaline solutions upon the glass bottles used in

¹ Zeit. phys. Chem., 12, 167 (1893).

the experiments, the results obtained are liable to some uncertainty in this respect. To investigate this point, experiments were made upon the adsorption of potassium hydroxide by quartz contained in a platinum bottle. Quartz sand was chosen for this purpose in order that the material might be more readily washed. Eighty grams of quartz sand were used, to which 20 cc of approximately tenth-normal potassium hydroxide solutions were added. This amount of the solution was just about sufficient to fill the interstitial space in the amount of quartz sand used. When the system had attained equilibrium, a portion of the solution was removed from the quartz sand by means of a centrifugal machine, care being taken to avoid evaporation during this process. Weighed portions of the solution thus removed were titrated, and the concentration compared with that of the original solution. Three experiments were made with the same sample of quartz, which was washed after each experiment until conductivity measurements showed that no soluble material was being removed. The results are given in the following table, being determined from a mean of at least two titrations of the hydroxide solution in each case. The amount of the salt adsorbed is expressed both in terms of the total adsorption and as a percentage of the total amount of the salt originally present in the 20 cc of solution used:

TABLE III
Adsorption of Potassium Hydroxide by Quartz Sand

Experiment No.	Time Days	Adsorption Percent	Total adsorption Gm. mols.
1	25	1.22	2.44×10^{-5}
2	18	1.24	2.48
3	35	0.98	1.96

The quartz sand used in the experiments in Table III was made up of grains of the following sizes:

Limits mm.	Percent
1-0.5	4.7
0.5-0.25	36.9
0.25-0.1	57.7
0.1-0.05	0.7

This gives a calculated surface area, in accordance with the method already described, of about 175 sq. cm. per gram.

The 80 grams of quartz sand employed would then present a surface area of 14000 sq. cm. This surface adsorbed from a tenth-normal potassium hydroxide solution 2.3×10^{-5} gram-equivalents, the mean of the three determinations given in Table III. This corresponds to 1.66×10^{-9} gm. mols. per sq. cm., or 1.66×10^{-5} gm. mols. per sq. meter, which is equivalent to about 0.6 mg. of potassium hydroxide per square meter of surface.

There is, however, another point which must be considered in this connection. The alkaline solution thrown out of the quartz sand by the centrifugal machine was found to be very slightly turbid. This turbidity indicates that some chemical action had taken place between the quartz and the hydroxide solution. This could not be detected in the former experiments on account of the fine state of division of the powdered quartz. The carbonate and hydroxide systems investigated cannot then be considered free from chemical action.

The apparent adsorption per square meter is considerably higher for the experiments with powdered quartz in glass bottles than for quartz sand in the platinum bottle, and I consider the latter value more reliable, since the surface could be calculated more accurately, and chemical action between the hydroxide solution and the glass was avoided.

From a consideration of the results given above, we are led to the conclusion, that so far as quartz is concerned, the phenomenon of adsorption is of minor importance in the retention of soluble substances in the soil. The apparent adsorption of potassium hydroxide by fine quartz sand amounted to but little more than one per cent of the salt present in an amount of the solution sufficient to fill the interstitial space of the sand. With the neutral salts, no appreciable adsorption could be observed, even when the powdered quartz was used, which presented as great a superficial area as is found in many soils. The marked retention of dissolved salts which has often been observed in connection with soils appears, therefore, to be due to causes other than

direct adsorption on the surfaces of the crystalline quartz particles. In some instances the retention of a dissolved substance by a soil has been shown quite conclusively to be due to chemical fixation or substitution; in other cases, it appears to be associated with colloidal substances in the soil. We have only to refer to van Bemmelen's experiments with colloidal silica to note the marked retention of salts by this class of substances.

Part II. The Adsorption of Water Vapor by Quartz

The adsorption of water vapor by glass surfaces of known area has been investigated by Bunsen,¹ Warburg and Ihmori,² Ihmori,³ and Parks.⁴

Warburg and Ihmori divide the water film condensed on the surface of a solid into two portions, which they call "temporary" and "permanent." The "temporary" portion is that which disappears when the vapor-pressure is reduced to zero. Obviously this is only a relative classification, the temporary portion depending upon the temperature of the system.

Bunsen investigated the "permanent" water film absorbed on a glass surface at a temperature ranging from 20° to 500° C. He passed a stream of dry air slowly over glass fibers, which were kept at constant temperature, and collected the water-vapor which was given off in phosphorus pentoxide tubes, which were weighed before and after each experiment. The temperature was then raised and the process repeated. Bunsen found that water-vapor was given off from glass up to the highest temperature investigated, namely, 500° C. The total amount liberated from 2.11 sq. meters of glass surface, which had previously been thoroughly dried at 20° C. was 22.3 mg.

Warburg and Ihmori suggest two possible causes for the formation of films of water on glass: First, that the vapor pressure of a very thin film of water is lower than the vapor pressure of a thick film; second, that substances of a hygroscopic charac-

¹ Wied. Ann., 20, 545 (1883); 24, 321 (1885).

² Ibid., 27, 481 (1886).

³ Ibid., 31, 1006 (1887).

⁴ Phil. Mag. [6], 5, 517 (1903).

ter, such as free alkalis, are present in the glass in small amounts and exert an attraction for water. They consider that the first assumption is not valid since Sir William Thomson¹ has shown that the surface tension of a very thin film must decrease as the thickness is diminished, and consequently the vapor pressure must increase as the thickness decreases.

Granting that a *free* film can theoretically be made so thin as to decrease the surface tension, and consequently increase the vapor pressure, it does not appear to me that Warburg and Ihmori are justified in applying these conclusions to a film held upon the surface of a solid. As the film on the surface of a solid diminishes in thickness, the tension of the liquid-air interface must *increase* as the surface comes within the radius of attraction of the molecules of the solid. Such a film would therefore have a lower vapor pressure than a free liquid film. Condensation would consequently take place until the vapor pressure of the film is equal to that of the surrounding vapor. The matter may be put more simply by saying that the molecules of the vapor are attracted more strongly by the molecules forming the surface of the solid than by a free liquid surface. Condensation consequently occurs until the surface of the adsorbed film is sufficiently removed from the action of the molecules of the solid to have the same vapor pressure as the free liquid surface. We thus see that contrary to Warburg and Ihmori's conclusions, the condensation of films of water upon solid surfaces may be rationally attributed to an attraction between the solid and the vapor.

Warburg and Ihmori investigated the temporary film on glass surfaces of various kinds at ordinary temperatures by the method of direct weighing. Thin bulbs of glass were suspended from the arm of a delicate balance of great sensibility enclosed in an exhausted receiver, which could be connected at will with a water chamber or with a phosphorus pentoxide drying tube. They found that measurable amounts of water vapor were condensed upon the surface of freshly blown glass bulbs and of

¹ Nature, March 1870; Natural Philosophy, 1, Part 2, Appendix F., p. 499.

bulbs which had not been thoroughly washed. After washing or boiling these glass surfaces and then thoroughly drying, no adsorption of water vapor could be detected. These results supported their second assumption that the formation of the water films was due to the combination of water with some of the constituents of glass, which were set free when a fresh glass surface was exposed, and which were subsequently removed by washing or long boiling in water.

The adsorption of water vapor by a number of substances, including quartz, was later made by Ihmori, with an improved balance, by the same method. He found no measurable adsorption on washed quartz crystals, although unwashed crystals showed a slight effect.

Dobeneck¹ has made an extensive investigation of the adsorption of water vapor, ammonia and carbon dioxide by various soil constituents including quartz. In his experiments with water vapor, saturated air was passed over the powdered material contained in a U-tube, the whole apparatus being kept at a constant temperature by a thermostat. The results he obtained for the adsorption of water vapor by quartz are much higher than those given in the following experiments, due, I believe, to the capillary condensation which is unavoidable when working at or near the dew-point with a powdered material that is not continually stirred. This phenomenon is entirely distinct from that of adsorption, since it is dependent only upon the form of the liquid surface and should consequently not be confused with adsorption measurements.

An interesting question is raised in this connection, namely, the extent to which adsorption is dependent upon the form of the solid surface. An approximate idea of the magnitude of the effect may be obtained by considering the somewhat analogous case of the capillary surface. A capillary tube 0.001 mm. in diameter would support a capillary column approximately 33 meters in height at ordinary temperatures. The weight of a column of water vapor at this height and 1 sq. cm. in cross section

¹ *Forschungen auf dem Gebiete der Agrikulturphysik*, 15, 163 (1892).

at 30° C is about 0.1 gm. The vapor pressure at the top of the column is then about 0.07 mm. or 0.2 percent less than at the bottom. Consequently, we may say that in the case of a thin film on the surface of a spherical solid particle 0.001 mm. in diameter, the vapor pressure would be approximately 0.2 percent greater than for a film of equal thickness, held upon a plane surface of the same solid. The influence of the geometrical form of the solid is therefore so small that it falls well within the limit of error in adsorption investigations.

Object of the Investigation

Warburg and Ihmori, as we have already seen, concluded that the formation of water films on the surface of solids was due to the presence of substances capable of forming solutions with the water vapor. Unquestionably such substances do play an important part in the formation of water films on solid surfaces. However, it is evident that the failure of Warburg and Ihmori to obtain a measurable film in the case of surfaces which had been thoroughly washed, may have been due to lack of sufficient sensibility in their balance rather than to the actual non-existence of the film.

The theory of Gibbs regarding the adsorption of dissolved salts should apply equally well to the formation of films of gases or vapors on the surface of a solid. In the case of any solid which is wetted by water, we know that the surface tension of the solid-gas surface must exceed that of the solid-liquid surface, since the first surface contracts at the expense of the second. Such a solid, if exposed to the vapor of water will, therefore, condense upon its surface a film of the vapor, since by this action the surface energy of the system will be diminished. An aqueous film should thus be found upon the surface of any solid which can be wetted by water, without regard to the presence of soluble substances.

It was determined to test this hypothesis in connection with a carefully washed surface which is wetted by water, and under conditions such as to avoid condensation in capillary spaces. Quartz appeared particularly well suited to an investigation of

this kind. Its very slight solubility (if it is at all soluble) in water at ordinary temperatures reduces to a minimum the possibility of the existence of substances on the surface of the quartz grains capable of forming a solution with water. The results of the following investigation show that washed quartz has both a temporary and permanent adsorption film.

Description of Apparatus

The apparatus used in the following investigation consisted of pairs of cylindrical glass bulbs, connected in the manner shown in the accompanying figure (Fig. 1) and supported on the periphery of a rotating drum which was immersed in a thermostat at 30° C. In one of the bulbs of each pair a weighed

Fig. 1

amount of powdered quartz was placed after having been thoroughly washed and dried, while in the other bulb was placed an aqueous solution of sulphuric acid, the concentration depending upon the vapor pressure at which the adsorption determinations were to be made. The bulb containing the quartz was provided with a smaller auxiliary bulb to catch any of the quartz that might work out of the larger bulb during the course of the experiment. The two bulbs were connected by heavy black rubber tubing, which fitted snugly over the tubulures. The metal drum supporting the cylindrical bulbs was placed with its axis horizontal in a thermostat, and was driven by a helical spring-brass belt from the shaft of the stirrer. The bulbs containing the quartz and the acid solutions thus

slowly rotated about a horizontal axis parallel to, but not coincident with, their common axis. As a result of this rotation, the powdered quartz was continuously stirred, while the walls of the bulb containing the acid were kept wetted with the solution. This stirring is of the utmost importance, as otherwise condensation will occur in the minute capillary spaces formed by the contact of the quartz particles.

The concentration of the sulphuric acid solution used in the adsorption experiments, together with the corresponding vapor pressure at 30° C is given in the following table:

TABLE IV
Vapor Pressures of Solutions used in Adsorption Experiments

	Percent H ₂ SO ₄	Sp. gr. ¹ 15°/4° C.	Vapor pressure ² 30° C.
H ₂ SO ₄ + H ₂ O	84.58	1.780	0.225
H ₂ SO ₄ + 5H ₂ O	52.13	1.420	10.684
H ₂ SO ₄ + 9H ₂ O	37.69	1.287	19.594
H ₂ SO ₄ + 17H ₂ O	24.26	1.176	26.117
H ₂ SO ₄ + 296H ₂ O	2.67	1.016 ³	31.35 ⁴
H ₂ O	0.		31.510 ⁵

Experimental Results

In investigating the adsorption of water vapor on quartz, two methods were employed. In the first method, the adsorbed water was removed from the surface of the quartz by exposing the latter to phosphorus pentoxide at room temperature. This removes the "temporary" film. In the second method, the quartz, with its adhering film of water, was weighed, then dried at 110° C, and weighed again. The loss in weight gives the

¹ Lunge and Isler: Zeit. angew. Chem., 1890, 129; Landolt and Börnstein: "Tabellen," 2 Auf., p. 196.

² Regnault: Ann. Chim. Phys. (3), 15, p. 179, 1845. Landolt and Börnstein: "Tabellen," 2 Auf., p. 65.

³ Determined for the writer by Miss J. R. Pearce.

⁴ Interpolated from Regnault's measurements of the vapor pressure of sulphuric acid solutions, and of pure water.

⁵ Regnault: see Landolt and Börnstein, "Tabellen," 2 Auf., p. 53.

"temporary" portion plus that part of the "permanent" film which is released by raising the temperature to 110°C .

First Method

The powdered quartz, after having been thoroughly dried, was exposed to water vapor at constant temperature for a time sufficient to bring the system into equilibrium, which was determined by preliminary experiments. The bulbs containing the quartz were then detached from the bulbs containing the sulphuric acid solution, and attached to small glass weighing tubes which contained phosphorus pentoxide supported on glass wool. These systems were rotated as before on a drum, so as to expose all portions of the quartz to the drying reagent. Successive weighings of the pentoxide tubes were made until no further change in weight was observed. The gain in the weight of the pentoxide tube represented the amount of water vapor removed from the bulb containing the quartz. This amount of water vapor was not, however, all obtained from the surface of the quartz particles, a part coming from the water existing in the vapor phase, and from the surface of the glass bulb. To obtain this correction, the quartz was removed from the bulbs, which were once more attached to the corresponding acid bulbs and rotated in the thermostat until equilibrium had been established, when they were again attached to fresh phosphorus pentoxide tubes, and the gain in weight of the latter noted. The total weight recorded in the first experiment less the gain in weight from the empty bulbs gave the weight of water vapor adsorbed upon the surface of the quartz. Care must be observed in such experiments regarding the use of rubber in the form of tubing or stoppers, as it is capable of giving up or absorbing a very appreciable amount of moisture.

The results of duplicate experiments carried on in this manner are given in the following table. The first column gives the vapor pressure at 30°C of the solution employed. The second column gives the total adsorption in milligrams observed in the first experiment. The third column shows the adsorption of the empty bulbs as observed in the second part of

the experiment. The fourth column is obtained by subtracting the results in column three from those in column two, and represents the amount of water vapor adsorbed on the surface of quartz particles. Fifty grams of quartz were used in each of these experiments, having a superficial area calculated from mechanical analyses of 400 square centimeters per gram.

TABLE V
Adsorption of Water Vapor by Powdered Quartz

Vapor pressure mm.	Total ad- sorption mg.	Adsorption by bulb mg.	Adsorption by quartz mg.
26.1	10.4	1.0	9.4
	9.7	1.0	8.7
19.6	6.2	1.8	4.4
	5.3	0.5	4.8
0.2	0.5	0.1	0.4
	0.3	0.1	0.2
	0.9	0.0	0.9

Second Method

In this series of experiments, the quartz was first dried to constant weight at 110° C, and the adsorption was determined from the subsequent gain in weight when exposed to water vapor. The bulbs containing the quartz were closed with well-ground glass stoppers immediately after being taken from the oven, and were cooled in phosphorus pentoxide desiccators. The weighings were made with a counterpoise bulb of the same form, and made of the same glass as those containing the quartz. The bulbs in every case were left upon the balance until successive weighings showed that no further change in weight had occurred. It was not possible to obtain as close weighings as in the former experiments where the smaller phosphorus pentoxide tubes were used on account of the greater amount of surface exposed.

After obtaining the dry weight, the bulbs containing the dry quartz were attached by means of heavy black rubber tubing to the bulbs containing the acid solutions, as before, and placed

in the thermostat. The following table shows the gain in weight due to the adsorption of water vapor. The experiments were made in duplicate. The first column gives the number of the bulb; the second, the time in days in which the systems were in the thermostat; the third, the weight of the bulbs containing the quartz; the fourth, the gain in weight; that is, the amount of water vapor adsorbed. Experiments were made with solutions of three concentrations, as indicated in the titles of the tables. Twenty-five grams of quartz were used in each of the experiments, having a calculated surface area of 400 sq. cm. per gram.

TABLE VI
Adsorption of Water Vapor by Powdered Quartz from Sulphuric Acid Solution ($H_2SO_4 + 5H_2O$) at 30° C.

Tube No.	Time Days	Weight gms.	Adsorption mg.
20	0	23.4298	0.0
23	0	23.2442	0.0
20	5	23.4333	3.5
23	5	23.2464	2.2
20	12	23.4331	3.3
23	12	23.2464	2.2
20	19	23.4333	3.5
23	19	23.2465	2.3

It will be noted in Table VI that determinations with tube No. 20 were invariably higher than with tube No. 23. This is probably due to the presence of a film of foreign material left on the surface of the bulb after having been used in an experiment with an adobe clay. This film resisted washing with water and scouring with sand, but was found at the end of the experiment to have been removed by the continuous scouring action of the sharp quartz particles.

It will be seen from the results given in Table VIII that the time necessary to establish equilibrium in this case was much greater than in former experiments. This is probably due in part to the fact that capillary condensation occurred to

TABLE VII

Adsorption of Water Vapor by Powdered Quartz from Sulphuric Acid Solutions ($H_2SO_4 + 9H_2O$) at $30^\circ C$.

Tube No.	Time Days	Weight gms.	Adsorption mg.
17	0	24.9770	0.0
18	0	24.6982	0.0
17	5	24.9812	4.2
18	5	24.7033	5.1
17	12	24.9827	5.7
18	12	24.7042	6.0
17	19	24.9829	5.9
18	19	24.7038	5.6

TABLE VIII

Adsorption of Water Vapor by Powdered Quartz from an Aqueous Sulphuric Acid Solution ($H_2SO_4 + 196 H_2O$) at $30^\circ C$.

Tube No.	Time Days	Weight gms.	Adsorption mg.
25	0	23.5638	0.0
17	0	24.9771	0.0
25	3	23.5774	13.6
17	3	24.9915	14.4
25	7	23.5844	20.6
17	7	24.9965	19.4
25	12	23.5853	21.5
17	12	24.9993	22.2
25	19	23.5883	24.5
17	19	25.0006	23.5
25	26	23.5910	27.2
17	26	25.0047	27.6
25	33	23.5912	27.4
17	33	25.0030	25.9

some extent. The quartz showed a tendency in the latter part of the experiment to stick to the walls of the tube, which would

make capillary condensation possible. This action finally became so pronounced that it was necessary to arrange a mechanical hammer in such a manner as to subject the tube to a continuous series of sharp blows, which dislodged the quartz grains from the inner surface of the tubes. This device prevented the particles from maintaining fixed positions with reference to each other, thus preventing capillary action, and it will be noted that neither tube gained in weight after the hammer was attached; in fact, tube No. 17 diminished somewhat in weight.

Thus we have, in the case of quartz, an adsorption of water vapor which increases as the vapor pressure approaches the dew-point, similar to the observations of Warburg and Ihmori for glass and other substances. Furthermore, quartz possesses also the so-called "permanent" film, as shown by the increased amount of water vapor liberated when the quartz is dried at 110° instead of at 30° C. This quartz had been thoroughly washed with distilled water, and I am, therefore, inclined to the opinion that the formation of the water film in this case is due not to the presence of soluble material on the surface of the quartz particles, but to the attraction of the quartz itself for the water vapor, in accordance with the theory of Gibbs.

The thickness of the "temporary" film in a five-sixths saturated atmosphere, as calculated from the preceding experiments is 4.5×10^{-7} cm, assuming the density of the adsorbed film to be uniform and equal to unity. The maximum thickness calculated from the results obtained by the second method which includes a portion of the "permanent" film is 2.66×10^{-6} cm in an atmosphere within one percent of saturation. This latter value is of the same order as that recently found by Parks, for the thickness of the adsorbed film on glass wool in a saturated atmosphere at 15° C, namely 13.3×10^{-6} .

Summary

An examination of the results given in the preceding pages leads to the following conclusions:

1. Quartz finely divided shows an adsorption action, but the effect is much less than in the case of amorphous silica.

2. The amount of adsorption in the case of solutions of carbonates and hydroxides is not directly proportional to the concentration, but relatively greater in very dilute solutions, the ratio of the amount of salt adsorbed to the concentration of the solution decreasing as the concentration increases.

3. The adsorption of the various salts investigated appears to be a function of the acid radical rather than the basic element. The adsorption of the hydroxide series is more marked than that of the carbonates. On the other hand, the potassium, sodium and ammonium hydroxide curves are similar in form, and the same relation is to be observed in the corresponding carbonate series. The numerical values are somewhat in doubt, owing to the apparent chemical action of the alkaline solutions on the quartz.

4. The apparent adsorption of potassium hydroxide by quartz when in equilibrium with a tenth-normal solution is 1.66×10^{-5} gm. mols. per sq. meter, which is equivalent to about 0.6 mg. of potassium hydroxide per square meter of surface.

5. The adsorption of potassium hydroxide by a fine quartz sand from a tenth-normal solution amounts to only 1 percent of the salt contained in a volume of solution sufficient to saturate the sand. The retention of dissolved salts by soils appears therefore to be mainly due to causes other than direct adsorption on the surfaces of the crystalline quartz particles.

6. No positive evidence of the adsorption of chlorides, nitrates or sulphates could be obtained by the method employed.

7. Quartz, like glass, is capable of condensing a water film upon its surface from an unsaturated atmosphere. A part only of this film is liberated when the vapor pressure is reduced to zero at 30° C.

8. The weight of the water film condensed on the surface of quartz at 30° C. in an atmosphere within one percent of saturation is 26.6 mg. per square meter determined by drying at 110° C. This corresponds to a calculated thickness of the water film of 2.66×10^{-6} cm., assuming the density of the film to be uniform and equal to unity.

9. The results obtained with washed quartz do not support

the conclusion of Warburg and Ihmori, working with glass surfaces, that adsorption is due to the presence of soluble substances on the surface of the solid. The condensation of water vapor on the quartz appears to be due to the attraction of the solid for the molecules of the vapor, in accordance with the theory of Gibbs as applied to the adsorption of dissolved substances.

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