A STUDY OF THE ADSORPTION OF SULPHURIC ACID BY LEATHER

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ABSTRACT

The adsorption of sulphuric acid from water solutions by a vegetable-tanned steer-hide leather is measured for concentrations ranging from 0 to 1.44 molal. Considering the adsorption as the sum of two effects (1) the effect of the chemical reaction of the sulphuric acid with the leather, and (2) the effect of the difference in concentration of sulphuric acid between the surface and the body of the solution, an expression is derived giving the quantity adsorbed as a function of the concentration.

CONTENTS

I. INTRODUCTION

In the course of a study of the effect of sulphuric acid on the life and properties of leather, it was found that a knowledge of the limiting combining ratios between sulphuric acid and the leathers employed would be of use in explaining the results obtained. No data could be found in the literature giving the quantity of acid adsorbed by any vegetable-tanned leather at concentrations great enough to give the equivalent weight of the leather.[1] This research was carried out in order to determine whether the results of an adsorption experiment would give a definite value for the equivalent weight of a leather.

The usual method of measuring adsorption, which consists in measuring the change in the concentration of a solution put in contact with the adsorbent, involves the determination of a small difference between two large quantities; that is, the total quantities of solute present in the solution before and after adding the adsorbent are determined, and the difference between these taken as the quantity adsorbed. As the equilibrium concentration is usually determined in a sample pipetted from the solution, the error is multiplied by the factor used to give the total quantity of solute in the solution.

A more direct method of measuring adsorption was used in this work. The quantity of solute in the part of the system immediately associated with the adsorbent was determined; the quantity of solute which would be present in that part of the system if there were no adsorption was calculated from the weight of solvent present there and the equilibrium concentration of the solution; and the difference between these quantities was taken as the amount adsorbed.

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[1] See J. A. Wilson and A. W. Bear, J. Ind. Eng. Chem., 18, p. 84; 1926.

II. EXPERIMENTAL PART

Commercial vegetable-tanned steer-hide leather was selected for these experiments. From each of two bends of the same tannage, a strip, approximately 12 inches in length and 4 inches in width, was cut lengthwise of the bend, beginning at a point approximately 36 inches from the root of the tail and 16 inches from the backbone. These pieces were analyzed for moisture and water-soluble matter by the official methods of the American Leather Chemists' Association, and for total sulphur by oxidizing a sample with nitric acid, and then determining total sulphate gravimetrically by the barium sulphate method. The results of these analyses are given in Table 1. The moisture is in per cent of the air-dry leather, the others in per cent of the dry leather.

TABLE 1.—*Results of analyses of the leather used*

	Moisture	Water-soluble matter	Total sulphur (as H_2SO_4)
	Per cent	*Per cent*	*Per cent*
Piece A	10.0	18.9	0.84
Piece B	10.0	17.2	.76

Twenty-four samples were cut from the two strips and used for determining the adsorption of sulphuric acid from solutions varying in concentration from 0 to about 12 per cent H_2SO_4. The solutions were prepared by pipetting from a gravimetrically analyzed solution of sulphuric acid.

A sample of leather weighing between 4 and 8 g was placed in a weighed beaker containing a known weight of sulphuric acid in about 300 ml of solution, and allowed to stand with occasional stirring at room temperature for 40 hours. At the end of this time the beaker, with the solution and leather, was weighed. As much of the solution as would easily drain was then poured off, and the beaker, with the leather and remaining solution, was weighed again. The total sulphur in the leather and the remaining solution was then determined as in the analysis of the leather, and calculated as H_2SO_4. The procedure was the same for each of the samples.

In order to determine the time required for such a system to come to equilibrium, a series of determinations of adsorption was made on a similar leather, at an acid concentration of about 0.3 m. The solutions were allowed to stand in contact with the leather samples for periods ranging from one-half hour to 200 hours. After two hours the system had reached equilibrium, as measured by these determinations. The values for X, the millimols of H_2SO_4 adsorbed per gram of leather, are given in Table 2.

TABLE 2.—*Variation of measured adsorption of H_2SO_4 on leather with time of standing*

Time in hours	X	Time in hours	X
	Millimols/g		*Millimols/g*
0.5	0.179	25	0.262
1	.206	50	.268
2	.258	100	.258
5	.277	200	.271
10	.267		

As the leather used in this experiment contained about 0.8 per cent total sulphur, calculated as H_2SO_4, it was necessary to subtract a blank from the determined value of the total sulphur remaining in the beaker, in order to obtain the weight of sulphuric acid derived from the solution. This blank was calculated from the weight of $BaSO_4$ obtained from the sample to which no acid was added, under the assumption that it was proportional to the weight of dry leather. The use of this assumption probably introduced a large error, as the calculated value of the blank might be in error by as much as 0.1 per cent of the weight of dry leather.

In order to find the weight of water remaining with the leather after the solution was poured off, it was necessary to know the weight of that part of the soluble matter in the leather which was poured off with the solution. To determine this, the solution poured off was evaporated to dryness with an excess of ammonium hydroxide, and the residue was weighed. This residue was made up of two parts: the dissolved solids from the leather, and the ammonium sulphate derived from the sulphuric acid present. The weight of H_2SO_4 in the solution poured off was $(A-B)$, where A stands for the weight of H_2SO_4 added to the leather, and B for the weight of H_2SO_4 remaining with the leather. The weight of $(NH_4)_2SO_4$ equivalent to this is $\frac{(NH_4)_2SO_4}{H_2SO_4} (A-B)$. Then S, the weight of dissolved solids, was found by subtracting this weight of $(NH_4)_2SO_4$ from the dry weight of the residue.

Some difficulty was experienced in drying the ammonium sulphate to constant weight. A series of determinations was made to determine the accuracy of the method, using 120° C. as the drying temperature. Samples containing from 0 to 2.5 g H_2SO_4 and from 0 to 0.26 g dissolved solids were dried, the weights being taken on three successive days. It was found that the ammonium sulphate lost about 3 mg per day after the water was driven off. The weights obtained on the second day, after which there was no rapid change, gave results none of which were in error more than 4 mg. Drying at 100° C. gave better results as the rate of loss of ammonium sulphate was lower, but with samples containing more than 3 g H_2SO_4 too much ammonium sulphate was lost before all the water was driven off.

The weight of leather remaining in the beaker after the solution is poured off is then $(L-S)$, where L is the weight of the sample of leather. If D is the weight of material in the beaker after the solution is poured off, $D-B-(L-S)$ is equal to the weight of water included in this material. The ratio of the weight of acid to the weight of water in the solution at equilibrium is found by dividing $(A-B)$, the weight of acid poured off, by $(C-D)-(A-B)-S$, the weight of water poured off, where C is the weight of the entire system at equilibrium. Then the weight of acid which would remain with the leather if there were no adsorption may be calculated by multiplying the ratio $\dfrac{A-B}{(C-D)-(A-B)-S}$ by $D-B-(L-S)$, for the reason that equal weights of acid would be associated with equal weights of water. Thus the weight of acid adsorbed is the difference

$$B - \frac{(D-B-L+S)\,(A-B)}{C-D-A+B-S}.$$

The weight of sulphuric acid adsorbed by the leather is defined as the difference between the weight of acid remaining with the leather and the calculated weight of acid which would remain if the leather had no effect on the solution. The calculation of this last weight is based on the known weight of water remaining with the leather, and the ratio between the weight of acid and the weight of water in the solution at the equilibrium concentration.

This definition does not take into account any distinction between chemical combination and strictly physical adsorption, but there is so much confusion in the literature concerning the use of this term that it will be used here in its most general sense.
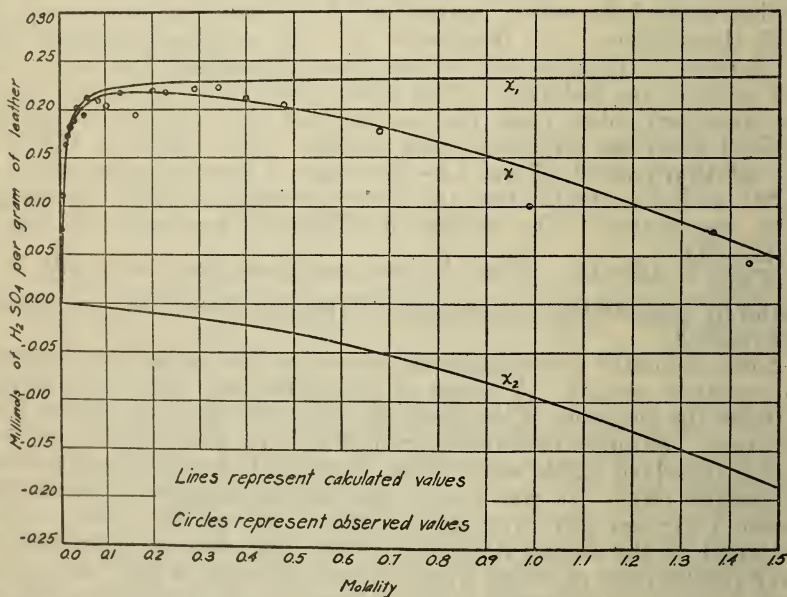

FIGURE 1.—*The adsorption of H_2SO_4 on leather (x) shown as the sum of two effects—x_1, chemical combination, and x_2 adsorption due to the surface tension effect*

The quantity which is desired is X, the number of millimols of acid adsorbed per unit weight of dry insoluble[2] leather. This is calculated from the formula

$$X = \frac{1,000}{98.1 \; L \; (1-P)} \left[B - \frac{(D+S-B-L)\,(A-B)}{(C-D-S-A+B)} \right]$$

in which P is the fraction of the leather dissolved by the procedure of analysis for water-soluble matter.

The experimental results for X are given in the following table and graph. (Fig. 1.) The accompanying calculated values will be discussed later in connection with the development of the theory.

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[2] "Insoluble leather" will be used to denote that part of the leather which is not dissolved by the procedure of analysis for water-soluble matter.

TABLE 3.—*Observed* (X) *and calculated* (X_c) *values of the millimols of H_2SO_4 adsorbed per gram of dry insoluble leather*

Molality	X	X_c	Molality	X	X_c
0. 0022	0. 07	0. 06	0. 167	0. 19	0. 22
. 0047	. 11	. 10	. 20	. 22	. 22
. 0112	. 16	. 14	. 23	. 22	. 22
. 0177	. 17	. 17	. 29	. 22	. 21
. 024	. 18	. 18	. 34	. 22	. 21
. 032	. 19	. 19	. 40	. 21	. 21
. 040	. 20	. 20	. 48	. 20	. 20
. 053	. 19	. 20	. 68	. 18	. 18
. 061	. 21	. 21	. 99	. 10	. 14
. 083	. 21	. 21	1. 37	. 07	. 07
. 101	. 20	. 22	1. 44	. 04	. 06
. 115	. 22	. 22			

Some idea may be obtained of the probable error of a single observation at the concentration 0.3 m by using the values in Table 2, excluding the first two. The figure obtained is 0.005, which indicates that the values for X are significant to only two decimal places, as the limiting error is probably about 0.02.

III. DISCUSSION OF RESULTS

As the concentration of sulphuric acid is increased from zero the quantity, X, increases rapidly to a value of about 0.2 at a concentration of 0.05 molal. Further increase of concentration causes less increase in X, a maximum value being reached at a concentration of about 0.2 molal. With still further increase of concentration, X decreases, at first slowly and then more rapidly.

A consideration of the factors influencing equilibrium in the system offers three possible explanations for the adsorption.

1. The adsorption of ions on the surface of the leather, forming a Helmholtz "double layer."

2. The adsorption of acid due to change in surface tension with change in concentration of acid.

3. Chemical combination of the acid with the leather.

Because of the necessity for uniformity of electrical potential throughout a solution at equilibrium (except where molecular magnitudes are considered) the first and third explanations become the same in effect, so consideration may be limited to the second and third.

J. Willard Gibbs [3] derived an expression for adsorption due to change of surface tension with change of concentration, which, for constant temperature and pressure, may be put in the form

$$u = -\frac{a}{RT}\frac{d\gamma}{da} \tag{1}$$

where a is the activity of the solute, γ is the surface tension of the solution, and u is the number of mols adsorbed per unit surface.

From the measurements of J. Livingston R. Morgan and Clarke E. Davis [4] the following data for the surface tension of sulphuric acid solutions at 25° C. are obtained.

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[3] Trans. Conn. Acad., **3**, p. 439; 1876.   [4] J. Am. Chem. Soc., **38**, p. 559; 1916.

Molality_____	0. 00	0. 50	1. 00	2. 00	3. 00
$\gamma \left(\dfrac{\text{dynes}}{\text{cm}} \right)$	71. 86	71. 90	72. 02	72. 54	73. 26

If it is assumed that the surface tension at a leather-solution inter-face varies with the concentration in the same way that it does at an air-solution interface, it is seen from Gibbs' formula that adsorption due to the surface-tension effect is negative throughout the range of concentration covered in this investigation as $\dfrac{d\gamma}{da}$ is positive. The positive adsorption found must then be explained by the chemical combination of acid with the leather.

In order to express the quantity of chemically combined acid as a convenient function of the equilibrium concentration, some assumption must be made as to the reaction involved. If it is assumed that the quantity of normal sulphate formed is negligible, no further assumption need be made as to the mechanism of the adsorption.

The product of the activity of sulphuric acid and that of the reactive groups in the adsorbent is proportional to the activity of the reaction product, the constant of proportionality being the dissociation constant, K, of the compound. Let W be the weight of adsorbent containing reactive groups sufficient to fix one mol of acid, X_1, the millimols of acid fixed per gram of adsorbent, and a the activity of H_2SO_4 in the solution. Then

$$a \left(\frac{1}{W} - \frac{X_1}{1{,}000} \right) = a\, K \left(\frac{X_1}{1{,}000} \right) \tag{2}$$

where α is a factor representing the ratio of the molecular activity coefficient of the reaction product to that of the reactive group. This gives

$$X_1 = \frac{1{,}000a}{W\,(a + \alpha\, K)} \tag{3}$$

As no data are available giving even the order of magnitude of the quantity α in this equation, no use can be made of the equation unless α is assumed to be a constant or some simple function of X_1 and a. In order to put the equation in a usable form, a simple approximation will be used—it will be assumed that $\dfrac{\alpha}{\beta}$ is constant, where $\beta = \dfrac{a}{m}$ at the equilibrium concentration, m. Writing k for $\dfrac{\alpha}{\beta} K$, this gives

$$X_1 = \frac{1{,}000\, m}{W\,(m + k)} \tag{4}$$

This expression takes the form of Langmuir's adsorption isotherm, as was pointed out by D. I. Hitchcock.[5]

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[1] J. Am. Chem. Soc., 48, p. 2870; 1926.

It should be noted here that if water is considered to be eliminated between the protein and the acid by the reaction, that the measured values of the total adsorption are slightly in error, due to the resulting increase in the weight of water remaining with the leather. This correction is equal to

$$\frac{H_2O}{1,000} \left(\frac{X_1}{C-D-A+B-S} \right)$$

and thus for these measurements would amount to about 0.4 per cent of the combined acid. This figure could have very little significance in this work, so no further consideration will be given to its possible effect.

In case the adsorbent is a gel such that the solution is diffused through it, the value of the adsorption obtained is lower than the quantity which has been removed from the solution by reacting with the adsorbent or by increasing the concentration at its surface. This is due to the fact, as Wilson [6] has pointed out, that the concentration of free acid is less in the gel than in the surrounding solution, as a result of the ionization of the salt formed. The system is a special type involving the Donnan membrane equilibrium. The effect is the same whether or not water is eliminated by the reaction, as 1 mol of hydrogen ion is removed from solution for each mol of acid reacting in either case.

A precise expression for this effect can not be formulated in terms of measured quantities, because the activities of the substances in the gel are not known, and apparently can not be measured by methods known at present. It may be of interest to derive an expression under the assumptions used in developing the Procter-Wilson theory of swelling,[7] these assumptions being that the electrolytes involved are completely ionized and that all activities are equal to concentrations. Let m' be the molality of free acid in the gel, and Y be the grams of water swelling 1 g of the adsorbent. Then, as the product $[H^+]$ $[HSO^-_4]$ is the same in the gel and in the free solution

$$m^2 = m' \left(m' + \frac{X_1}{Y} \right) \tag{5}$$

$\frac{X_1}{Y}$ being the molality of HSO^-_4 ion derived from the protein salt. As the measurement of adsorption is based on the total sulphate present, X_3, the apparent adsorption due to the membrane equilibrium effect, will be determined by the difference in concentration of free acid multiplied by the weight of water swelling 1 g of adsorpent, or

$$X_3 = Y \ (m' - m) = -mY - \frac{X_1}{2} + \sqrt{\left(\frac{X_1}{2}\right)^2 + m^2 Y^2} \tag{6}$$

The weight of water taken up by a piece of leather in an acid solution is known to be small in comparison with that taken up by collagen, this lack of swelling being a criterion of the completion of tanning. There seems to be no way, however, to measure just how much water is intimately associated with the leather, as this measurement

[6] J. A. Wilson, The Chemistry of Leather Manufacture, 1, p. 142.
[7] J. Am. Chem. Soc., 40, p 886; 1918.

requires a distinction between solution swelling the leather, and solution which is present between the fibrils of the leather. The same difficulty is found in the case of collagen, but as the magnitude of the swelling is so much greater, the error introduced by the mechanically included solution is not so serious.

In view of the fact that the swelling of leather is small, the effect of swelling on the measurements of adsorption will be neglected in this work.

The approximate expression for the combined acid, then, is in the form $X_1 = \dfrac{1,000\,m}{W(m+k)}$. This represents the experimental data fairly well up to a concentration of about 0.4 molal, but it will not explain any decrease in adsorption with increasing concentration.

It becomes necessary, then, to combine the chemical reaction and surface-tension effects in order to derive a satisfactory expression from the explanations considered.

Let X_2 = the number of millimols of H_2SO_4 adsorbed by the surface tension effect per unit weight of leather.

Let σ = the specific surface area of the leather.

Then $\dfrac{X_2}{1,000} = \sigma\mu$, and, substituting the value of μ given in equation (1)

$$X_2 = -\frac{1,000\,\sigma}{RT}\,a\,\frac{d\gamma}{da} \tag{7}$$

A curve giving values of $a\dfrac{d\gamma}{da}$ for values of m up to 2.2 was obtained by measuring graphically the slope at various points of the curve $\gamma = f\,(\log a)$. The values of γ at 25° C. were taken from the abovementioned data of Morgan and Davis,[8] and the values of a from the table of activity coefficients for sulphuric acid at 25° C. given by Lewis and Randall.[9]

The expression which will be used to calculate the equivalent weight of the leather is

$$X = X_1 + X_2 = \frac{1,000\,m}{W(m+k)} - \frac{1,000\,\sigma}{RT}\,a\,\frac{d\gamma}{da} \tag{8}$$

As the surface tension data used are expressed in dynes per centimeter, corresponding to ergs per square centimeter, the constant R is expressed as ergs divided by temperature, or 8.32×10^7 ergs/deg. The thermodynamic temperature was approximately 298°.

Approximate values of the constants of the equation were obtained from three experimental values, and these were corrected by successive approximations. The constants were found to have the following values:

$$W = 4.29 \times 10^3; \quad k = 0.0065; \quad \sigma = 1.79 \times 10^7$$

The values of these constants would be expected to vary with the type of leather and with the acid used. W and σ would depend on the nature of the tanning material and on the degree of tannage,[10] and k would depend also on the particular acid used.

The values of X calculated by inserting these constants in the above equation are tabulated with the experimental results.

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[8] See note 4, p. 1113.
[9] Lewis and Randall, Thermodynamics, first ed., p. 357.
[10] See footnote 1, p. 1109.

The agreement between the observed and calculated values is consistent with the conclusion that the theory under which the calculations were made represents approximately the actual mechanism of the adsorption. This does not imply that the theory is proved, but merely that it may be used as a working basis.

Returning to the consideration of the approximate expression for the apparent adsorption due to the ionization of the protein salt formed, it may be seen that the assumptions under which it was derived limit its application to systems containing a highly ionized monobasic acid and an adsorbent which is much swollen by water. The system collagen-hydrochloric acid-water fulfills these conditions, and the expression may be tested out by its application to this system.

Kubelka and Wagner [11] measured the adsorption of hydrochloric acid on collagen, and the amount of solution swelling the collagen at concentrations up to about 1 molar. They used air-dry hide
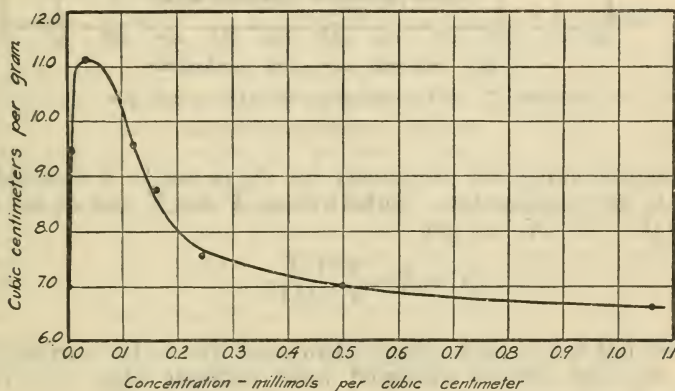

FIGURE 2.—*The swelling of hide powder in HCl solutions*

From data of Kubelka and Wagner.

powder containing 12.6 per cent moisture; all concentrations were expressed as millimols per cubic centimeter of solution, which corresponds closely to molarity.

The notation used by Kubelka and Wagner has been changed to make it consistent with that used above.

The data which will be used are the following: C_0, the initial concentration of the solution into which the hide powder was introduced; h, the air-dry weight of the hide powder; C_1, the concentration of the solution in equilibrium with the hide powder; and V', the volume of solution taken up by 1 g. of air-dry hide powder from 100 cc of a solution of given initial concentration. The adsorption in millimols per gram of dry hide powder was calculated from the formula

$$X = \frac{100(C_0 - C_1)}{h(1 - 0.126)} - \frac{0.126\ C_1}{1 - 0.126},$$

the last term being introduced as a correction for the water in the hide powder. A curve (fig. 2) representing the volume of solution

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[11] Kolloid-Zeit., **46**, p. 107; 1928.

taken up by 1 g of hide powder at given equilibrium concentrations was obtained by successively approximating the quantity of acid adsorbed from the solution by the hide powder present. The desired values of V were read from this curve.
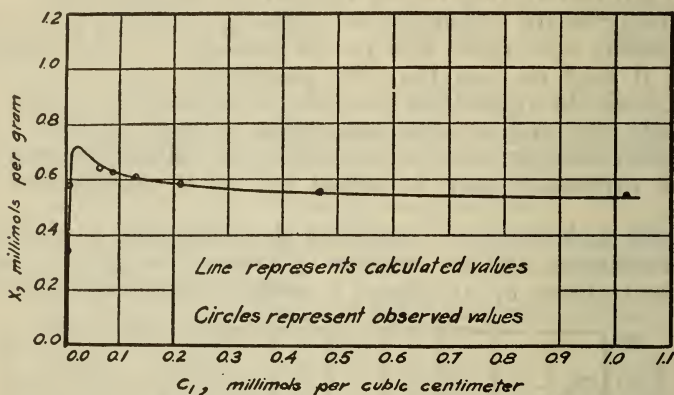

FIGURE 3.—*The adsorption of HCl on collagen*

From data of Kubelka and Wagner.

The expression given previously for X_3 is not in a desirable form for use in this connection. Substituting V for Y and C_1 for m, and putting $X = X_1 + X_3$, we get

$$X_1 = X + \frac{C_1 V X}{X + C_1 V}. \tag{9}$$

This does not take into account adsorption due to the surface tension effect, but the results obtained later indicate that this may be neglected in this case.
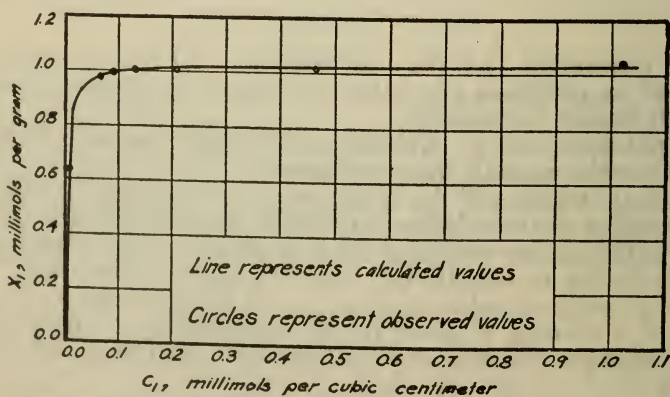

FIGURE 4.—*Showing the quantity of HCl combined with collagen*

From data of Kubelka and Wagner.

The values of X and X_1 obtained in this way are shown in Figures 3 and 4 plotted as ordinates against corresponding values of C_1 as abscissas. In Figure 4 is given a curve showing values of X_1 calcu-

lated from the formula $X_1 = \dfrac{1,000\,C_1}{969(C_1+0.0032)}$. (See equation (4).)
The agreement between the corrected observed values and the calculated values may be seen to be very close. It may be noted that this gives 9.7×10^2 as a provisional value for the equivalent weight of collagen.

The constants in the expression for X_1 may be used to calculate values of X from the formula

$$X = X_1 + X_3 = \frac{1,000\,C_1}{(2)(969)(C_1+0.0032)} - C_1 V$$

$$+ \sqrt{\left[\frac{1,000\,C_1}{(2)(969)(C_1+0.0032)}\right]^2 + (C_1 V)^2}. \qquad (10)$$

The smooth curve through the points representing X on the graph of Figure 3 was obtained from this formula.

The results obtained by the application of the above-derived formulas should be compared with the best calculated values obtained by a continuation of the reasoning used by Kubelka and Wagner in their discussion of their experimental results. This comparison may be made by deriving an expression for X in terms of C_1, following their method of calculating corrected values of the adsorption, and testing the agreement of values given by this expression with their results.

First they calculate values of X without correcting for the water introduced into the system with the hide powder. Then they correct these values on the basis of two assumptions—that the swelling per gram of a quantity of air-dry hide powder introduced into a given volume of HCl solution of a given concentration is independent of the quantity of hide powder inserted; and that the material which swells the hide powder is simply water and not acid solution. Thus they have $X = \dfrac{100\,(C_0 - C_1)}{h}$, and $X' = X + C_1 V'$, where X' is the corrected adsorption per gram of air-dry hide powder, and V' is the volume of solution taken up by 1 g of air-dry hide powder when put in a solution of the same initial concentration as that used for the determination in question. They then plot these corrected values of adsorption against corresponding corrected concentrations. These corrected concentrations are given by $C' = \dfrac{C_1(100 - hV')}{100}$.

TABLE 4.—*Adsorption results for hydrochloric acid on hide powder as corrected by Kubelka and Wagner*

C'	X'	C'	X'
0.0027	0.656	0.1197	2.213
.0249	1.308	.2784	3.897
.0404	1.493	.6310	7.441
.0642	1.762		

Putting $X' = b(C')^n$, the Freundlich absorption isotherm, we may find the most probable values of the constants for the given data by applying the method of least squares to the equation

$$\log_{10} X' = \log_{10} b + n \log_{10} C'.$$

The constants were found to have the values $b = 6.651$ and $n = 0.42546$. Then

$$X = X' - C_1 \ V' = 6.651 \left[\frac{C_1(100 - hV')}{100} \right]^{0.42546} - C_1 V'. \qquad (11)$$

The values of X given by Kubelka and Wagner are plotted in Figure 5 as ordinates against corresponding values of C_1 as abscissas. The curve in Figure 5 represents X as a function of C_1 as calculated from the above expression.
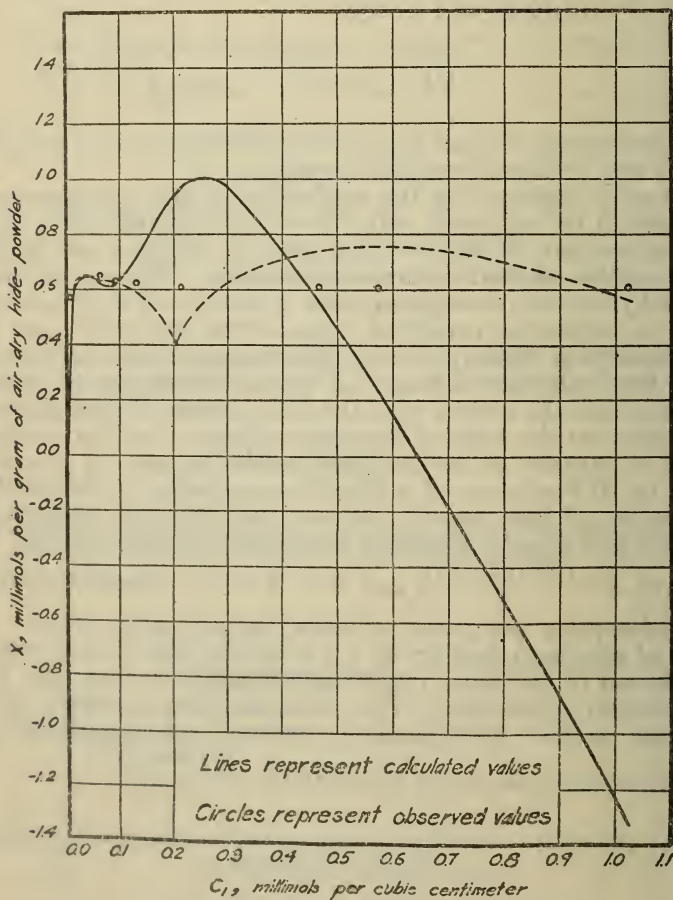

FIGURE 5.—*The adsorption of HCl on collagen*

Data of Kubelka and Wagner.

The authors point out that instead of falling on a straight line, the logarithmic plot of their corrected results forms two straight lines, no explanation of this discontinuity of slope being given. Calculations were made to determine how well this broken line respresents the data, the procedure being the same as for the single line, except that two formulas were used, the point of division being at $C' = 0.1071$. The resulting curve is shown as a dotted line in Figure 5.

The agreement between the observed values of X and X_1 and those calculated from the expression derived from theoretical considerations verifies the prediction made by Wilson and Wilson[12] that theoretical treatment would give a more satisfactory expression for adsorption of hydrochloric acid on proteins than the empirical "adsorption isotherm" due to Freundlich.

The results obtained indicate that for the purpose of work on adsorption, leather may be considered as a solid presenting a definite surface to a liquid, and that collagen in equilibrium with acid solutions may be considered as a gel which is completely permeable by the solution. The expressions which have been developed giving the adsorption as a function of the equilibrium concentration may then be used to determine constants giving provisional values for the equivalent weight of the leather or the collagen. These provisional values may have to be changed to be consistent with new data, but they may be used as working values at present.

IV. CONCLUSION

1. The results obtained substantiate the theory that sulphuric acid reacts with the proteins of leather.

2. The equivalent weight, as a base, of the commercial vegetable tanned steer-hide leather used in this study was 4.3×10^3. This refers to the reaction of this particular leather with sulphuric acid.

3. The Gibbs adsorption equation has been applied with reasonable accuracy to the adsorption on this leather of sulphuric acid from water solutions.

4. The specific surface of the leather was of the order of magnitude of 10^7 square centimeters per gram.

Washington, April 13, 1930.

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[12] See footnote 7, p. 1115.