ON ADSORPTION AND PERCOLATION

A Thesis

by

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Historical

Within recent years the problem of adsorption has become a well-tilled and hence fruitful corner of the wide field of Physical Chemistry. Much of the ground, however, is still unhusbanded, for adsorption still offers work, and a great deal of it, to the scientist of exploring tendencies. The uprooter of weeds, too, has a task ahead of him, for many of the observations in the field of adsorption, as in every other new field, need careful criticism.

It is perhaps wise to insist at the outset of this paper, that the point of attack in this field should not be a priori reasoning as to the possible causes underlying adsorption, but an accurate description of the phenomenon and its characteristics, a study of the quantitative relation involved, finally leading to quantitative deductions from these relations. The plan of procedure accordingly was, first, a thorough understanding of Freundlich's adsorption isotherm, and second the application of this quantitative relationship to the process of percolation.

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Early observations upon the phenomenon of adsorption were not such as to differentiate between adsorption proper, i.e. surface condensation and absorption, i.e. penetration into the interior of the adsorbent. The earlier literature therefore speaks of "absorption", meaning thereby primarily adsorption, and hence I shall retain its nomenclature.

Priestley and Scheele[1] were aware of the "absorptive" power of charcoal for different gases. Guyton de Morveau[1] in 1782 remarked on the removal by charcoal of gases contained in a jar, and Lowitz[1] recognized the deodorizing and decolorizing effect of charcoal.

The first attempts of a quantitative nature on "absorption" were those of Count Morozzo[1], and particularly of Th. de Saussure[1]. J. Hunter in 1863 began a series of experiments on "absorption" in which he pointed out some of the general characteristics of the phenomenon, such as the variations in "absorption" with the type of charcoal employed[1], the effect of temperature and pressure upon "absorption"[2], the speedier termination of "absorption" with vapors than with permanent gases[1], and the state of the "absorbed" gas in the pores of the "absorbent"[2]. L. Joulin[3] in 1880 pointed out the apparent instantaneousness of the process of "absorption", indicating that the time needed for completed "absorption" was too small to admit of measurement. Again, he pointed out that this time varied from gas to gas.

M. Lachaud , in his investigations came to such conclusions as the following:

(1) The amount of "absorbed" material depends upon the nature of the absorbent and on the temperature.

(2) The greater the degree of dispersion of the charcoal, the more quickly did "absorption" occur.

(3) Equilibrium was more rapidly reached with concentrated than with dilute solutions.

(4) With mixed solutions preferential "absorption" manifested itself.

The use of charcoal as a decolorizing agent in sugar refining processes added to the store of knowledge concerning "absorption". "Was this decolorizing power manifested by charcoal a result of its surface, or a result of the impurities it contained?", such was the question asked by investigators in this field. Scheibler[5] showed that the removal of lime and of colored compounds from sugar solutions was not bound up with the oxygen or carbon dioxide present in the charcoal. But, since animal charcoal on the one hand was so valuable as a decolorizing agent, and wood charcoal, on the other hand, so useless, investigators sought for the explanation in differences in the chemical nature of these two forms. Wallace[6], hence, associates the decolorization capacity of charcoal with its nitrogen content. F. Meyer[7], by preparing a cheap substitute for animal charcoal from clay, seemed to invalidate this contention. He and F. Jicinsky[8] emphasized the fact that surface attraction was the dominating factor in the decolorizing process.

The field of "absorption", a fruitful field for experimentation and theorizing, was rapidly growing in popularity with investigators. Such work as that of Van Bemmelen, Walker and Appleyard, G. C. Schmidt, and others, in the last decade of the nineteenth century, attests to the truth of the foregoing statement. The standpoint from which these investigators proceeded was: "Absorption" was to be considered as a special case of Henry's Law of Distribution.

Henry's Law may be stated as follows: "When a gas dissolves in a liquid the concentration of the dissolved gas is directly proportional to that in the free space above the liquid". In other words, if c_2 represents the concentration of the gas in the liquid, c_1 its concentration in the free space above the liquid, the following equation holds:-

$$\frac{c_2}{c_1} = k.$$

Nernst extended this law to the distribution of a solute between two immiscible solvents. If however, the solute suffered polymerization in one of these solvents, i.e., the following equation held good, $A_n \rightleftharpoons nA$, where A_n represented the solute in its polymerized form, then the expression

$$\frac{c_2^n}{c_1} = k$$

would represent the facts. Here c_2^n was the concentration of the solute in the non-associating solvent, while c_1 was the concentration in the associating solvent. It was this potentiated form of the original distribution law that the phenomenon of "absorption" was thought to follow.

Van Bemmelen[9], in an endeavor to explain the "absorption" of water by gelatinous hydrates, emphasized many of the now well-established phenomena characteristic of absorption.

He summarized his observations somewhat as follows:-

(1) The "absorption" of water by gelatinous hydrates was distinct from a chemical compound formation.

(2) The "absorptive" power weakens as "absorption" continues.

(3) The "absorptive" power of colloids differs with their mode of formation.

(4) "Absorption" decreases with rising temperature.

(5) "Absorption" from dilute solutions is relatively greater than it is from concentrated solutions.

(6) The final state of equilibrium reached expresses the relation between the quantity of material "absorbed", and the final concentration of the solution.

(7) Selective "absorption" is possible, in that one material may displace another from the "absorbent".

G. C. Schmidt[10] (1894) was one of the first to adopt the distinction between adsorption and absorption, a distinction which had been introduced by E. du Bois Reymond. His paper, "On Adsorption", was again an attempt to extend Henry's Distribution law to adsorption in solution, but his efforts showed him that Henry's Law was not obeyed unless c_2 was raised to some power. He did not indicate that this power could and did deviate in some cases from an integral quantity. He further emphasized that adsorption occurred between the adsorbent and the undissociated molecules of the solute, and hence introduced a correction for dissociation in his expression.

Walker and Appleyard[11], in an investigation, "The Absorption of Dilute Acids by Silk", pointed out the distinction between "absorption" and chemical compound formation, the reality of the equilibrium obtained in that it could be equally well reached from both sides, the exponential form of the distribution law, and the greater degree of "absorption" of aromatic acids as compared with aliphatic.

The exponential form of the distribution law was again emphasized by Biltz[12] in some experiments carried out on the nature of agglutination. Biltz showed that the value of n in the equation: $\frac{c_2^n}{c_1} = k$, was greater than one.

Freundlich[13] in 1906 in his monumental and exhaustive work, "Adsorption in Solutions", fully developed the exponential form of the adsorption isotherm. This he expressed by the following formula:-

$$\frac{x}{m} = \beta c^{1/p}$$

where x = no. of grams of adsorbed material,
m = no. of grams of adsorbent,
c = concentration of the solution when equilibrium has been reached,

and β and $1/p$ are constants depending upon the temperature and nature of the participating substances.

Theoretical

A. Adsorption from Solution

1. Characteristics of adsorption from solution

What then is adsorption, and what are its distinguishing characteristics? How truly does the adsorption isotherm fit the facts? These are the questions that naturally arise.

Adsorption may be defined as the change in concentration occurring at the surface of two phases of a heterogeneous system. This change in concentration may occur at a solid-gas interface, a liquid-gas interface, and a solid-liquid interface. It is with the third of these possibilities, i.e., adsorption from solution by a solid, that we are here concerned.

What are some of the characteristics of this adsorption from solution?

That adsorption was a true equilibrium, i.e., an equilibrium which could be reached from either side was emphasized by the work of Walker and Appleyard[11] on the dyeing of silk by picric acid. This view was corroborated by Freundlich[13] on the adsorption of organic acids by charcoal. The irreversibility of the process, met with in many dyeing procedures, may be explained by assuming a chemical reaction to follow the preliminary adsorption.

Again, adsorption is relatively greater in dilute than in concentrated solutions. The exponential form of of the adsorption isotherm was recognized by early workers in the field, and fully formulated by Freundlich.[13]

2. Relation of adsorbent to degree of adsorption

What relation does the adsorbent bear to the degree of adsorption? What does the nature of the adsorbent have to do with adsorption, and what its degree of dispersion with the final equilibrium attained?

Early investigators in this field were aware of the dependency of adsorption upon the variety of charcoal used.[14] Workers in the sugar refining industry asked the question as to whether decolorization was due to mere surface or to some foreign element in the charcoal.[15] Within more recent years this question again begs for answer[16]. Various possible impurities have been held responsible for the removal of coloring matter from solutions, e.g., the oxygen content of charcoal, the $=N-C-N=$ grouping, or the nitrogen content.[17, 18, 19]

Freundlich's view as expressed in his paper in 1906[13] was that adsorption on the whole was independent of the nature of the adsorbent, but dependent upon its physical condition,i.e., its extent of surface. In support of this he compares his work on the adsorption of picric acid by charcoal with the adsorption of picric acid by silk ,done by Walker and Appleyard. The ratio of the adsorption in water to the adsorption in alcohol when silk was used as adsorbent, and the same ratio when charcoal was used, compare with one another very favorably as the equations below indicate.

$$\left(\frac{\lambda\ \text{water}}{\lambda\ \text{alcohol}}\right)_{\text{silk}} = 1.742 \text{ (Walker and Appleyard)}$$

$$\left(\frac{\lambda\ \text{water}}{\lambda\ \text{alcohol}}\right)_{\text{charcoal}} = 1.750 \quad \text{(Freundlich)}$$

Davis[20], who worked upon the adsorption of iodine by three varieties of charcoal, i.e., sugar, animal and coconut, comes to the conclusion that adsorption is not independent of the nature of the adsorbing surface for identical surface area, but is specific - depending both on the nature of the solvent and on that of the adsorbent.

In a later paper of Freundlich's (in conjunction with A. Poser)[21], this same problem is again attacked. The adsorbents used were positive aluminium oxide, negative bole (clay), and neutral charcoal. Two different kinds of adsorption were distinguished, (a) adsorption due to surface, dependant merely upon the extent of surface of the adsorbent, and (b) adsorption due to electro-chemical forces, influenced by the nature of the charge of the adsorbent.

Kolthoff[22] in a recent paper on the estimation of the adsorbing power of various forms of charcoal, groups them according to this adsorption capacity as follows: Merck's blood charcoal > vegetable carbon = medicinal carbon > bactanate > norite. This arrangement, however, is frequently violated.

Within more recent years, to the question of the influence of extent of surface upon adsorption, has been added the question of the influence of the structure of that surface upon adsorption. One not only asks "Is the surface of the adsorbent large?,"[7] but "What is the condition of that surface?" Bancroft says,[23] "Since adsorption is specific, we must distinguish two factors, the nature (by that he means the extent of surface exposed) and the structure of the surface. If a given surface will not take up a dissolved or dispersed substance, we can get results by impregnating with a third substance which is adsorbed strongly by the surface and adsorbs the dissolved or dispersed substance."

"On this hypothesis it is easy to see why people working with different charcoals may get apparently contradictory results. There has been no way of making quantitative comparisons between structures,and consequently this factor has only been recognized to a minor extent. People have realized that the porosity of the charcoal was important; but they have not asked themselves what was the proper size or shape of pores to give the best results."

Thus the problem rests. Is one's explanation of the mechanism of adsorption a chemical one, naturally one would emphasize the fact that adsorption is dependant upon the nature of the adsorbent. Is one a member of the opposing camp, one would attribute differences in the adsorbing power of materials to differences in their area of surface, and the structure of this surface.

To return to the second question proposed above, i.e., how does the degree of dispersion of the adsorbent influence the equilibrium finally obtained. If adsorption is a matter of surface condensation, the degree of dispersion of the adsorbent should be a matter of prime importance. Little work, however, has been done upon this point, for few investigators have taken into consideration the size of the particles of the adsorbent. K. Estrup and E. B. Andersen[24] have pointed out that with larger size crystals of adsorbent, less potassium permanganate is removed from solution. C. Kühn[25], who worked on the adsorption of brilliant green by silicates, called attention to the fact that β increased with greater dispersion of the adsorbent. Freundlich[26] made an interesting observation in this connection. He precipitated mercuric sulphide sol. with new fuchsin. These precipitated flakes grew coarser with time, and the dye was returned to the solution, thus showing that less material was adsorbed the greater the size of the particles of adsorbent.

3. Factors influencing rate of attainment of equilibrium

The instantaneousness of the process of adsorption has been a point generally conceded by investigators. It is, however, doubtful whether adsorption occurs as rapidly as one would be led to believe by an examination of the literature upon this point.

The velocity of the attainment of equilibrium is influenced by a variety of factors. These factors are:

(1) Temperature. Equilibrium is reached more rapidly at higher than at lower temperatures. An observation made by Schmidt[27] upon the effect of heating and subsequent cooling on the adsorption of acetic acid by

sugar charcoal is of interest here. With heating and subsequent cooling equilibrium was reached after three hours, but without this previous heating only after ninety-six hours.

(2) Concentration of the solution. Equilibrium is more rapidly attained the more concentrated the solution.

Lachaud[4] in 1897 was aware of this fact. Ostwald also emphasized it. Freundlich[13], however, declared that the rate of attainment of equilibrium was independent of the concentration, and that equilibrium could be reached with the same speed from the side of greater dilution, as from the side of greater concentration. Schmidt[27] pointed out this relation between speed of attainment of equilibrium and the original concentration of solution. He stated that this rate was a function of the difference between the original concentration and the final concentration, and varied directly with the difference. Georgievics[25] also emphasized this relationship.

(3) Stirring. As is to be expected, stirring influences the speed of attainment of equilibrium. R. Marc[29], in a paper dealing with the adsorption of starch by barium and strontium carbonate, declares that the rate of adsorption is almost directly proportional to the rate of stirring; a conclusion which was confirmed by O. Arendt.[30]

(4) Character of adsorbent.

The type of adsorbent employed is also a factor in the rate of attainment of equilibrium. The more complex the internal structure of the adsorbent, the less readily will equilibrium be reached.

G. C. Schmidt's[27] observations upon this point were such as to force him to conclude that the speed of the attainment of equilibrium was dependant upon the variety of charcoal, upon the character of its surface and form, and upon the number of canals present. He attributes the greater speed of adsorption in purified samples of charcoal to the removal of fine particles of dust, thus giving ready access to the hollow spaces present in the charcoal.

(5) Vacuum.

Since a solution could only enter into the canals of an adsorbent of a fine porous structure by first forcing out the air present in those canals, one would expect adsorption to reach a state of equilibrium much more rapidly were the gases adhering to the adsorbent first removed by the use of a vacuum pump. This possibility suggested itself to Davis [20]. Iodine in an organic solvent with coconut charcoal as the adsorbent were the materials used. After a period of 24 hours the following results were obtained:

Normality of original solution = N/10

With use of vacuum

$m = 2; \ \frac{x}{m} = 0.006; \ a - x = 0.90$

Without use of vacuum

$m = 2; \ \frac{x}{m} = 0.006; \ a - x = 0.90.$

From these observations, Davis concluded that a vacuum had nothing to do with hastening the establishment of equilibrium. The experiment, however, can be very readily criticized in that a 24 hour period was the time selected and any differences observable with the lapse of shorter periods of time would have disappeared after so long an interval. On the other hand, the present writer believes that a vacuum has a potent influence upon hastening the establishment of equilibrium. The differences, however, are manifest in short periods of time, i.e., 2, 5 and 30 minutes, and are no longer noticeable after a 24 hour period. For confirmation of this statement, see Appendix ~~data~~, page 61 .

4. Kinetics of Adsorption

The conception that the rate of adsorption is too great as to admit of measurement, a very general conception, though erroneous, has probably been responsible for the little work done upon the important question of the kinetics of adsorption.

Early investigators in the field of the kinetics of adsorption from solution have been E. J. Mills, G. Thompson, and J. Takamine, [31,32] who worked on the adsorption of rosanilin hydrochloride and acetate, sulphuric acid, hydrochloric acid and sodium hydroxide by silk, wool and cotton fibers. They expressed the relationship between time and amount unadsorbed by the following formulas:-

$$y = A.\alpha^t$$

and

$$y = A.\alpha^t \pm B\beta^t$$

where y = the concentration of the dye-bath at the time t.

A, and A $\pm$ B = the concentration of the original solution

t = time

$\alpha + \beta$ = constants dependant upon the adsorbent and the dye-bath respectively.

Dietl[33] criticizes the formula in that it gives no place for the equilibrium concentration, and hence may be said to be faulty in that it neglects the reversibility of the process of adsorption.

Lagergren[34] stands next in line as an investigator of the problem of the kinetics of adsorption. He proposes that the course of adsorption may be expressed by the formula for a mono-molecular reaction.

$$\frac{dx}{dt} = k(x_\infty - x)$$

where x = the amount adsorbed in time t.

x_∞ = the amount adsorbed in time ∞.

This integrated resolves itself into the expression:

$$k = \frac{1}{t}\log_e \frac{x_\infty}{x_\infty - x}$$

Freundlich[35], recalculating Lagergren's data on the adsorption of succinic acid from aqueous solution by animal charcoal of medium adsorptive power, cites the following table:-

Normality of succinic acid = 0.5693

t in minutes	x $\left(\frac{\text{in milliequivalents}}{\text{gram charcoal}}\right)$	k
5	0.183	0.034
10	0.325	0.033
30	0.752	0.034
60	1.06	0.041
		Mean 0.036

$x_{\infty} = 1.16$

With oxalic acid k is equally large, having a value of 0.038.

The agreement is good in the little data given by him. The formula, however, does not rest upon sound theoretical footing. Schmidt[27] pointed out that the equation refers to a reaction of the first order, an irreversible reaction, and therefore does not consider adsorption as a reversible process. Hence an equation that takes into account forward and reverse reactions must be an equation possessing greater theoretical justification. Schmidt's criticism, however, upon closer investigation, is foundationless.

Mellor[36] has pointed out the formal resemblance between the equation for a forward reaction of the first order and the equation for a reversible reaction, unimolecular in both directions. In other words, the equations:

$$\frac{dx}{dt} = k(a - x) \qquad \text{and} \qquad \frac{dx}{dt} = k_1(a - x) = k_2(x)$$

reduce to much the same form.

The following deduction, which shows the relation between the Lagergren equation:-

$$\frac{dx}{dt} = k(x_{\infty} - x) \qquad (1)$$

and the equation:-

$$\frac{dx}{dt} = k_1(a - x) - k_2(x) \qquad (2)$$

where $x =$ the amount adsorbed in time t

$a - x =$ the amount left in time t

is due to E. F. Farnau.

If the symbol y be used to designate the difference between the amount adsorbed at infinite time and that adsorbed at time t, i.e.,

$$y = x_{\infty} - x$$

and $a - x = a - x_{\infty} + y$

then

$$-\frac{dy}{dt} = k_1(a - x_{\infty} + y) - k_2(x_{\infty} - y)$$

Changing signs

$$\frac{dy}{dt} = k_1(x_{\infty} - a - y) + K_2(x_{\infty} - y)$$

Expanding

$$\frac{dy}{dt} = k_1x_{\infty} - k_1a + k_2x_{\infty} - k_1y - k_2y$$

$$= \left[k_1(x_{\infty} - a) + k_2x\right] - (k_1 + k_2)y$$

$$= A - By$$

where $A = k_1(x_{\infty} - a) + k_2x$

$B = k_1 + k_2$

Integrating the expression -

$$\frac{dy}{dt} = A - By \qquad (3)$$

leads to the following:

$$\int_{y=x_\infty}^{y=x_\infty - x} \frac{dy}{A-By} = \int_{t=0}^{t=t} dt$$

$$\frac{1}{B}\log\left(\frac{A}{B} - y\right)\Bigg|_{y=x_\infty}^{y=x_\infty - x} = t$$

$$\frac{1}{B}\log\frac{\frac{A}{B} - x_\infty - x}{\frac{A}{B} - x_\infty} = t$$

Substituting values for A and B, leads to:-

$$\frac{1}{k_1+k_2}\log\frac{k_1(x_\infty - a) + k_2x_\infty - (k_1+k_2)x_\infty + (k_1+k_2)x}{k_1(x_\infty - a) + k_2x_\infty - (k_1+k_2)x_\infty} = t$$

Simplifying gives:-

$$\frac{1}{k_1+k_2}\log\frac{-k_1a + k_1x + k_2x}{-k_1a} = t$$

$$-\frac{1}{k_1+k_2}\log\frac{k_1a}{k_1a - (k_1+k_2)x} = t$$

$$-\frac{1}{k_1+k_2}\log\frac{\frac{k_1a}{k_1+k_2}}{\frac{k_1a}{k_1+k_2} - x} = t \qquad (4)$$

At equilibrium where $\frac{dx}{dt} = 0$, and $x = x_\infty$

$$k_1a = k_1x_\infty + k_2x_\infty$$

Hence $x_\infty = \frac{k_1a}{k_1+k_2}$

Substituting this value for x in equation (4) gives:-

$$-\frac{1}{k_1+k_2}\log\frac{x_\infty}{x_\infty - x} = t \qquad (5)$$

Comparing equation (5) with the integrated form of the Lagergren equation, which is

$$\frac{1}{k} \log \frac{x_\infty}{x_\infty - x} = t \qquad (6)$$

shows that they are identical, except insofar as

$$\frac{1}{k} = - \frac{1}{k_1 + k_2}$$

It may therefore be seen that Schmidt's criticism which is that Lagergren's equation does not refer to a forward and reverse order, is without point.

P. D. Zacharias[37] modified Lagergren's equation, giving it the form of a bimolecular reaction. His equation is:-

$$\frac{dx}{dt} = k(a - x)(d - x)$$

where $d = x$

a = the original concentration of the solution.

Körner applied this successfully to the adsorption of dyes by fibers. The equation however is meaningless in that it does not apply over the whole course of adsorption, but reduces to an absurdity when $t = 0$.

Further experimentation on this subject was carried out by G. C. Schmidt[27], A. Rakowski[38], T. Oryng[39] and L. Gurwitsch[40]. These investigators either remain silent when it comes to an equation expressing the course of adsorption, or state that the velocity constant, as calculated from the equation of Lagergren, falls off with time. (G. C. Schmidt and T. Oryng)

The study of the kinetics of the adsorption of gases by porous solids has also occupied the attention of research workers. Giessen's[41] results on the adsorption of gases by wood charcoal have been recalculated by Freundlich, and found to follow Lagergren's formula if certain assumptions were made. McBain[42] regards the speed of adsorption as regulated by diffusion. Bergter[43] found the following equation:

$$M = M_o(1 - e^{-at})$$

the equation for mono-molecular reactions, to express the adsorption of air by charcoal at low pressures. At higher pressures the equation did not hold, nor did it for the adsorption of nitrogen. Complicated empirical formulas had to be used by him in these cases.

Dietl[33], whose investigations on the kinetics of adsorption are such as to demand one's admiration, recalculates much of the data of other investigators on the basis of Lagergren's formula, and corroborates the observations made by Schmidt and Oryng on the decrease with time of the value for the velocity constant. The following are tables copies from his paper. (The constants are calculated according to Briggsian logarithms.)

Adsorption of S by caoutchouc

t in minutes	k (Lagergren)
10	0.0210
20	0.0248
30	0.0175
40	0.0131
50	0.0154

Adsorption of petroleum residues by floridin[40]

t in minutes	Floridin (coarse) k	Floridin (fine) k
1	0.196	0.359
3	0.105	0.149
5	0.0850	0.116
10	0.0534	0.078
30	0.0304	0.0512
60	0.0220	0.0302
120	0.0144	0.0173
240	0.00834	0.00993
720	0.0037	0.0037
1440	--	θθ

Adsorption of Acetic Acid by Sugar Charcoal[45]

Normality of acid - 1.017

Temperature = 28°C.

t in hours	k (Lagergren)	k (Dietl) $\eta = 0.56$
3	0.1	0.136
6	0.092	0.180
18	0.04	0.0998
45	0.024	0.0993

The k, calculated according to Dietl's formula, an explanation of which I shall give in detail later, shows considerably better agreement.

How interpret this fall in the value of k with time? Dietl[33] offers two possible explanations:-

(1) The adsorbed material influences the rate of adsorption, thus causing a decrease in k.

(2) As the concentration of the solution drops off, the rate of adsorption does also, thus explaining the fall in the value of k.

If the former is true, then x, the amount adsorbed, should be inversely proportional to the rate of adsorption, or

$$\frac{dx}{dt} = k\,\frac{a-x}{n}$$

where a = amount originally present in the solution. This integrated gives:-

$$k = \frac{a}{t}\log\frac{a}{a-x} - \frac{x}{t}$$

Velocity constants calculated according to the above formula give more consistent values for k, but are as yet far from satisfactory.[33]

Dietl[33] then turns to the equation for negative autocatalysis, as giving a means whereby the rate of adsorption may be calculated. He justifies his acceptance of this equation somewhat as follows. In the case of negative autocatalysis some material is formed which hinders the rate of the reaction, thus causing the velocity constant, if calculated according to the equation for a monomolecular reaction, to fall off with time. In the same way the velocity constant, if calculated according to the Lagergren formula, shows a decrease with time. The equation for negative autocatalysis is:-

$$\frac{dx}{dt} = (k_1 - k_2x)(a - x)$$

If for $\frac{k_2}{k_1}$ one substitutes the symbol η, the expression upon integration gives:-

$$k_1(1 - \eta a) = \frac{1}{t}\log_e \frac{a(1 - \eta x)}{a - x}$$

The quantity y was determined by choosing the same a and intervals of time that stood to each as 1:2, and thus, through substitution, k could be derived. When the quantity $\frac{k_2}{k_1} = 0$, the above expression goes over into the simple well known form, i.e.,

$$k_1 = \frac{1}{t}\log_e \frac{a}{a-x}$$

The following tables are copied from Dietl's paper.

Table XXV

Adsorption of Oxalic Acid by Wool

$\eta = 1.95$ k = Lagergren's constant k_1 = Dietl's constant

t in minutes	k	k_1
2	0.417	0.647
5	0.301	0.653
10	0.258	0.639

Table XXXIII

Adsorption of acetic acid by wool

$\eta = 25$

t in minutes	k	k_1
1	0.619	0.781
2	0.551	0.782
5	0.384	0.682
10		

The agreement is undoubtedly better than the agreement obtained with Lagergren's formula. But a more careful glance at all of the tables cited by the author indicates that the k, obtained by him to some extent decreases with time. The frequent omission of k, when the time interval grows at all large looks a bit suspicious, too. The formula denotes progress, no doubt, over that proposed by Lagergren, in that it gives more consistent values for the velocity constant. It does not, however, apply within the limits t = 0 and t = infinity, unless one accepts the deduction that $\frac{1}{x_\infty} = \eta = \frac{k_2}{k_1}$. This deduction must follow from the differential equation when applied to equilibrium. If $\frac{dx}{dt} = 0 = (k_1 - k_2x_\infty)(a - x_\infty)$, where x_∞ = the amount adsorbed when t = infinity, either $a = x_\infty$, which is contrary to all present conceptions of adsorption, or

$$\frac{k_1}{k_2} = x_\infty .$$

It is doubtful whether Dietl applies this deduction from his equation to his conception of x_{∞}.

The problem of the kinetics of adsorption has been attacked by another worker in the field, namely R. Marc[29] of Jena. Much of his work has been done on the relation between rate of adsorption and rate of stirring, investigations which led him to conclude that the rate of adsorption increases with intensity of stirring. The adsorption-time curves indicate that the course of adsorption does not follow the law of direct proportionality. These curves first rise abruptly, make a sharp turn and then continue to rise very slowly until the equilibrium concentration is reached. A study of them leads to the conclusion that an equation which places the rate of adsorption at any time t as proportional to the unadsorbed mass present at that time t, or to this quantity raised to the second or third power, that such an equation will not accord with the facts. A closer observation of these curves shows that they can be expressed by a formula which assumes the rate of adsorption as infinitely great, or nearly infinitely great at the beginning, which means that the clean surface of the adsorbent exercises an almost infinitely great attraction over the material to be adsorbed. This attraction falls off rapidly with increasing contamination of the surface. The relation between the attraction exercised by the adsorbent and the adsorbed mass can be expressed by the following equation:-

$$A = C.x^{-n}$$

where A = the attraction

c = a constant

x = the adsorbed mass

n = a number greater than 1.

This attraction works against the kinetic energy of motion of the adsorbed molecules in the surface, which inhibition of the attraction may be expressed by a constant C. On the other hand, the osmotic pressure of the molecules in the solution is to be added to this attraction. Whence follows:-

$$\frac{dx}{dt} = c.x^{-n} - C + k(a - x)$$

where a = the original concentration.

After making certain assumptions the author gives the integrated form of the above equation, which is:-

$$\frac{x^{n+1}}{t} (2x_e^{n} + k'x^{n}) = K''$$

where x_e = the equilibrium concentration of adsorbed material,

K'' = the velocity constant.

Marc's work was done on the adsorption of starch by strontium carbonate. Various tables give values for his K'', which show relatively good agreement. The equation, however, may be criticized in that it becomes meaningless when t = infinity.

Investigations of the present writer thoroughly justify Dietl's criticism of Lagergren's formula. The following tables will show how rapidly the velocity constant, as calculated by the Lagergren formula, decreases with time.

Adsorption of acetic acid by charcoal

Table I

Normality of acid = .1058

x_{∞} = .016125

t in minutes	gms. adsorbed per gm. charcoal	k
2	.0238	.1069
5	.0308	.0608
30	.0452	.0127
1440	.0573	.009
∞	.0613	

Table II

Normality of acid = .9895

x_{∞} = .12625

t in minutes	gms. adsorbed per gm. charcoal	k
2	.0677	.1669
5	.0747	.0738
30	.1057	.0359
1440	.1217	.0010
∞	.1263	

Table III

Normality of acid = 1.5535

$x_{\infty} = .12850$

t in minutes	gms. adsorbed per gm. charcoal	K_n
2	.0713	.1758
5	.0870	.0982
30	.1050	.0212
1440	.1220	.0009
∞	.1285	

An equation, which from theoretical considerations, seemed to be based on sounder footing, was accordingly developed.

Let M = the initial concentration of the acetic acid in the water.

m = the concentration of acetic acid at the time t.

n = the concentration in the charcoal at the time t.

Then $M = m + n$

and

$$\frac{dm}{dt} = K_1 m \quad \text{(velocity of adsorption)}$$

$$\frac{dn}{dt} = K_2 n^2 \quad \text{(velocity of desorption)}$$

The resultant velocity will therefore be given by the following expression:-

$$\frac{dm}{dt} = K_1 m - K_2 (M - m)^2.$$

The differential equation upon integration leads to the following:-

$$\log \left[1 + \frac{-2\ A\ (M - m)}{K/2.M + K/2.m + AM - Am} \right] = 2K_2At.$$

where $A = \sqrt{KM + K^2/4}$

and K = the equilibrium constant.

An approximation gives the equation below:-

$$\frac{-2A\ (M - m)}{K/2.M + K/2.m + AM - Am} = 2K_2At.$$

This, upon simplification, goes over into the final expression

$$\frac{1}{\frac{1}{2}\cdot\frac{M+m}{M-m} - \sqrt{\frac{M}{K} + \frac{1}{4}}} = -KK_2t.$$

The equation has merits in that it possesses meaning over the whole range, i.e., when time = 0, and when time = ∞ . This is true of both the differential form, and the approximate integrated form.

The equation, however, does not accord with the facts. How far $-KK_2$ deviates from a constant may be seen from the following table.

time in minutes	N/10 acetic acid $-KK_2$	1 N acetic acid $-KK_2$	1 1/2 N acetic acid $-KK_2$	5 N acetic acid $-KK_2$
2	.1452	.03699	.02352	.00894
5	.0828	.01646	.01198	.00385
30	.0250	.00405	.00249	.00120
1440	.0009	.0001	.00006	

A decrease in the value of $-KK_2$ with time and with increasing normality is to be noticed.

It was found necessary, therefore, to resort to an equation which would more closely approximate the facts. The following was used:-

$$K' = \frac{M_1{}^{.8}}{t^{1/8}} \cdot \frac{M - m}{(M-m)^2 - Km}$$

where M = the initial concentration of acetic acid in the water,

m = the comcentration of acetic acid in the water at time t,

K = equilibrium constant,

M_1 = 1000 M.

No claim is made as to the theoretical justification of the equation, for it has none. But this may be said in its favor; (1) it applies at the two limits, i.e., at zero and infinite time, (2) it takes into consideration the reversibility of the process of adsorption, including as it does the equilibrium constant, and (3) it fits the data given.

The following tables will give the value of the constant as it applies over the entire range of time and normality.

$M_1 = 6.352$ $\qquad K = .5073$ $\qquad K'' = \frac{K'}{1000^{.8}}$

t in min.	M	m	log K'	K"
2	.006352	.004926	.3612	.009145
5	.006352	.004503	.4644	.011600
30	.006352	.003643	.4619	.0115300
1440	.006352	.002917	.6166	.016460

$M_1 = 59.4$ K = .5073

t in min.	M	m	log K'	K"
2	.0594	.05534	.5428	.013900
5	.0594	.05492	.5384	.01375
30	.0594	.05304	.6091	.01618
1440	.0594	.05210	.4651	.01161

$M_1 = 93.24$ K = .5073

t in min.	M	m	log K'	K"
2	.09324	.08908	.5022	.01267
5	.09324	.08802	.5563	.01433
30	.09324	.08682	.5553	.01430
1440	.09324	.08584	.4111	.01026

$M_1 = 309.6$ K = .5073

t in min.	M	m	log K'	K"
2	309.6	.3042	.4996	.01258
5	309.6	.3038	.4809	.01205
30	309.6	.2990	.4365	.01087
1440	309.6	--	--	--

Average value of K" = .01250 ± .00164

5. Relation between surface tension and adsorption

The definition of adsorption as it stands today includes nothing which can lead one to infer anything as to the underlying cause of adsorption. But since there is a faculty in the human mind which is never content with a mere collection of facts and their classification, but seeks further in that it attempts to explain these facts, much theorizing has arisen as to the cause of adsorption. One of these theories points to surface tension as the dominant factor in explaining the "why" of adsorption phenomena.

It is well established that some substances in solution decrease the surface tension of the solvent, others increase it. J. Willard Gibbs[46], working from the principle that the surface energy of a solution will always tend to reach a minimum, deduced the following laws:-

1. If a solute decreases the surface tension of a solvent it will tend to accumulate in the surface of the liquid; and
2. If a solute increases the surface tension of a solvent it will tend to accumulate in the body of the liquid.

These two laws, as Gibbs made clear, applied to the liquid-gas interface. Freundlich[13] carries over this conception to the liquid-solid interface and then deduces that those substances that cause a decrease in surface tension will be positively adsorbed because of their accumulation at the surface. Further, since small amounts of a substance can cause a marked decrease of surface tension, but not a marked increase, negative adsorption occurs rarely, and if at all only to a small extent. He also states that in a solvent with a large surface tension, those substances will be the more strongly adsorbed the smaller their surface tensions, and that strong adsorption occurs only in solvents with high surface tensions.

Whereas the deductions made by Freundlich generally express the truth, the logic which is based on the possible analogy as to the conditions of surface tension occurring, at a liquid-gas interface, and a liquid-solid interface can hardly be called sound. As Bancroft says,[47] "It is very difficult to prove or disprove Freundlich's conclusions experimentally; but it is a great pity to have people believe, as many now do, that the generalization is based on sound thermodynamics".

6. Negative Adsorption

A phase of adsorption that has excited to experimentation and controversial papers has been the phenomenon of negative adsorption. Negative adsorption from solution means adsorption of solvent in preference to adsorption of solute, hence at equilibrium a more concentrated solution than at the beginning of the process. In every case of positive adsorption, undoubtedly adsorption of solvent as well as of solute occurs, but the comparative amount of solvent thus removed is negligible. Cases of negative adsorption are met with relatively rarely. Freundlich[13] denied the possibility of the phenomenon, basing this denial upon the fact that small amounts of a dissolved substance can cause a marked decrease but not a marked increase in surface tension, and only those substances that decrease surface tension are adsorbed to an appreciable extent. Negative adsorption could also not be observed by Kellner[48] or Van Bemmelen[9].

Lagergren[34,48], working with solutions of sodium chloride, potassium chloride, ammonium chloride, magnesium chloride, potassium bromide and ammonium bromide, and such adsorbents as charcoal, kaolin, and glass powder, claims to have observed negative adsorption. These experiments were repeated by E. Hägglund[48], who discredited Lagergren's results, again denying the possibility of negative adsorption. K. Estrup[49], who has done some work on negative adsorption isotherms, states that a negative ion in acid solutions suffers positive adsorption, but as the acid concentration decreases the adsorption becomes less, finally becoming negative in an alkaline solution. A. Pickle[50] showed that alkali halides showed negative adsorption towards finely divided birch charcoal. Osaka[51] affirms to the reality of negative adsorption. Sodium nitrate, potassium bromide, potassium iodide and potassium nitrate are adsorbed positively by blood charcoal while sodium chloride, sodium sulphate and potassium sulphate are apparently adsorbed negatively. Again with high concentrations of potassium chloride positive adsorption occurs, with low the reverse is true. "Mathieu[52] observed negative adsorption with a number of dilute solutions when adsorbed by porous plates, membranes, or capillaries. With normal solutions the concentrations in the capillary tubes were often only one-tenth that. The difference in concentration increases with decreasing radius of the capillary tubes and Mathieu considers it quite possible that with very fine tubes water alone would be adsorbed, a conclusion which, as Mathieu himself points out, is of distinct importance for the theory of semi-permeable membranes".

In the light of the observations reported by believers in the reality of negative adsorption, one is forced to accept Freundlich's conclusions with more than one grain of salt.

7. Limits of adsorption isotherm

The question arises as to the limits of the adsorption isotherm. Can it be applied to widely varying concentrations, or is it true only within a narrow range?

Freundlich[13] is aware of the inapplicability of the isotherm to concentrations exceeding certain values. This limiting value he regards as the concentration of a normal solution. With increasing strength of solution the deviations become more and more marked.

Georgievics[53] and A. M. Williams[54] point out that as the concentration drops off the adsorption isotherm approaches more and more closely to Henry's distribution formula. At extreme dilutions Henry's law is true of both the adsorption of gases, and the adsorption of solutes from solution. Georgievics shows that x in Boedecker's formula, $\frac{\sqrt[x]{\text{conc.}_{\text{in solution}}}}{\text{conc.}_{\text{in fiber}}} = K$, approaches unity with dilution of solution, while A. M. Williams indicates that $\frac{1}{p}$, whose limiting value is usually considered $\frac{1}{2}$, in very dilute solutions becomes unity.

The work of G. C. Schmidt[27] indicates that the adsorption isotherm does not apply within wide limits. It is on this ground that Schmidt criticizes Freundlich's adsorption isotherm, and recommends his own. His study of the system charcoal, acetic acid and water leads him to state that the concentration of the acetic acid may vary 1000 fold and that of the charcoal 8 fold if his formula be used, but that with Freundlich's formula far greater restrictions must be placed upon the variations in concentration. Bancroft concludes that whereas other adsorption formulas have been proposed, yet "no formula is strictly accurate and the simplest one (i.e, the one proposed by Freundlich) seems the best for the time being".[55]

8. The constants β and p in the adsorption isotherm.

What significance may be attached to the constants β and p appearing in the adsorption isotherm, and within what limits do they vary?

Freundlich[13] states that β and p depend upon the temperature and the nature of the dissolved substance. $\frac{1}{n}$, which is $1 - \frac{1}{p}$, varies only within very narrow limits at a given temperature, such limits as 0.5 and 0.8. It is independent of the nature of the solvent, dissolved material and adsorbent. A contradiction to this last statement is to be found in a later article of his on the adsorption of dyes by charcoal and fibers.[56] Here $\frac{1}{n}$ has an average value of .84, hence depends somewhat upon the nature of the materials used. β and p vary slightly with the temperature. Freundlich gives the following data on an acetic acid solution in water and charcoal.

$t = 0°$ $\alpha = 3.148$ $\frac{1}{n} = 0.550$

$t = 50.2°$ $\alpha = 2.851$ $\frac{1}{n} = 0.394$

$t = 93.8°$ $\alpha = 2.938$ $\frac{1}{n} = 0.185$

where $\alpha = \beta$ and $\frac{x}{m}$ and c are expressed in millimols per gram of charcoal and per c.c. of solution respectively, and $\frac{1}{n} = 1 - \frac{1}{p}$.

Davis[20] makes more clear the meanings to be attached to the constants, $\frac{1}{p}$ and β . If the logarithm of the concentration in the charcoal is plotted against that of the concentration in the solution, p indicates the slope of the straight line. β , on the other hand, is equal to the number of grams of material adsorbed per gram charcoal that would be in equilibrium with a solution containing one gram of that same material per 100 c.c. of solution.

McBain[57] states that p lies between 2 and 4. Ostwald gives p , or what is equivalent to it, a wider range of values. In the equation $p = kb^m$, where p is the concentration in the unadsorbed phase, b that in the adsorbed phase, m is always greater than one, and in some cases approaches 10 or 12.

Georgievics[53], who uses the Boedecker distribution formula $\frac{\sqrt[x]{c_{solution}}}{c_{fibers}} = k$, shows that x varies from 6.95 to 1.48.

A. M. Williams[54], who uses the following expression for Freundlich's adsorption isotherm, $a = a_o c^{1/n}$, where a = concentration of adsorbed material, c = the concentration of unadsorbed material, states that $\frac{1}{n}$ is only a mean value for the gradient of the so-called straight line obtained by plotting log c against log a. This gradient increases as c diminishes, and as its limiting value reaches 1, not 1/2 as other investigators have inferred.

Bancroft[58] in his Applied Colloidal Chemistry gives a very complete list of the values assumed by p in the adsorption formula. The exponent may vary anywhere from 1 to 10, and does not always assume integral values, e.g., Walker[11] and Appleyard found it to be 2.7 for the adsorption of picric acid by silk from a water solution, Wagner[59] found it to be 4.5 for the adsorption of lactose by charcoal from a water solution and so on.

9. Relation of solvent and solute to degree of adsorption

What relation does the nature of the solvent and of the solute bear to adsorption? In what solvents does one find strong adsorption, and what solutes will be strongly adsorbed? These questions have as yet not been satisfactorily answered, but quite a good bit of data on the subject is to be found in the literature.

Freundlich[13] found that the adsorption isotherm was not true of strongly dissociated substances. Substances adsorbed from water solution were placed into three groups:

(a) Those showing weak adsorption. In this group were placed inorganic salts and acids, and substances containing many hydroxyl groups.

(b) Those showing medium adsorption. Here are to be found the aliphatic acids, and aromatic acids possessing sulphonic acid groups.

(c) Those showing strong adsorption. This group includes the aromatic acids, chlorine, bromine, phenylthiourea. Midway between (a) and (b) the organic salts may be found. Freundlich also found that adsorption was weak in organic solvents.

Some attempts have been made to relate the strength of an acid to its degree of adsorption. Walker and Appleyard's[11] excursion into this field did not meet with much success. No regularities between the degree of dissociation of an acid and its degree of adsorption were to be observed. The regularities were only apparent within a group, such, for example, as the group of fatty acids, or of aromatic acids. Georgievics[60], on the other hand, seems to have found a very plausible relationship between the x in the Boedecker formula and the dissociation constant of the acid. The following table gives his data:-

Acid	x values
Nitric acid	6.95
Hydrobromic acid	6.35
Hydrochloric acid	5.25
Sulphuric acid	4.37
Oxalic acid	3.00
Malonic acid	2.46
Salicylic acid	2.15
Phosphoric acid	2.00
Formic acid	1.89
Succinic acid	1.82
Benzoic acid	1.78
Adipic acid	1.79
Acetic acid	1.63
Propionic acid	1.59
Butyric acid	1.48

10. Choice of adsorbent, solvent and solute

With the foregoing discussion as to the characteristics of adsorption from solution, one can deduce some general rules as to how one shall be guided in one's choice of adsorbent, solute and solvent.

An adsorbent should live up to the following specifications:-

(1) It should have a large surface.

(2) It should be insoluble in the solution.

(3) It should not react chemically with either solvent or solute.

(4) It should have no catalytic effect upon the components of the solution.

Freundlich[13] found, for instance, that the adsorption of acetic acid from an alcohol solution could not be determined because of the catalytic action of the charcoal, which esterified the acid. Again he found it impossible to work with a solution of chlorine in water, for the charcoal apparently catalyzed the reaction,

$$2Cl_2 + 2H_2O \longrightarrow 4\ HCl + O_2.$$

As regards the choice of solvent and solute, this should be conditioned by the stability of the solution, and the weak dissociation of the solute in the solvent.

11. <u>Special Studies on the system charcoal, acetic acid and water</u>

Since the work included in this paper was almost entirely restricted to a study of the system charcoal, acetic acid and water, a review of the work of other investigators on the same system will be of value here. The plan of attack will be a comparison along three lines; (1) the preparation of adsorbent, (2) the procedure followed and (3) the results obtained.

Freundlich's[13] adsorbent was a sample of Merck's blood charcoal purified with acid. To insure greater purity of adsorbent, he proceeded as follows: the charcoal was boiled for 24 hours with concentrated hydrochloric acid, then heated with fresh volumes of water until an acid reaction was no longer noticed, a procedure which took several weeks. Drying in a drying oven followed, then the passage of nitrogen, freed from water and oxygen, over the charcoal, for a period of 48 hours. Both the purified and non-purified charcoal was used. The latter showed a decrease in adsorption capacity, probably due to the removal of the finer particles of charcoal. No attempt at sifting to insure greater uniformity in adsorbent was made.

Schmidt's[27] methods for the preparation of adsorbent involved similar principles. He used cane sugar charcoal and animal charcoal (Merck's purissimum). The two varieties of charcoal were treated as follows: They were digested with concentrated nitric acid for three days, then with concentrated hydrochloric for two more days. The acid was decanted and the charcoal washed for a period of four months with freshly distilled water. It was then dried at 200° and kept in glass bottles. Schmidt concluded that to obtain at all comparable results, a thoroughly homogeneous sample of charcoal should be used.

Pickle[61] gives no information as to his method of preparing the adsorbent. The varieties of charcoal used were fruit-stone dust, animal charcoal containing 21 per cent carbon, birch dust and coarse birch. He concludes that the value of 'n' in the equation, $\frac{c^n_{charcoal}}{c_{water}} = K$, giving the most consistent values of K, vary with the charcoal used and also with its state.

The method followed by the present writer in the preparation of an adsorbent was one which took into consideration the following points:-

(1) Purity and uniformity of raw material - thus insuring purity and uniformity of adsorbent obtained.

(2) A fair degree of adsorptive capacity.

(3) Uniformity of size of particles of adsorbent.

Animal charcoal, because of its high degree of adsorptive capacity for materials from solution, presented itself as a possible choice. But since such a choice would have meant no guarantee as to the purity and uniformity of the adsorbent, cane sugar charcoal in spite of its lesser adsorptive capacity, was the selection made. To increase its value as an adsorptive agent, recourse was had to the so-called process of "activation".

Here, I hope, the writer may be allowed a slight digression. The work of chemists during the recent war upon the preparation of highly efficient adsorbents to be used in gas masks has done much to enlarge our knowledge as to the character of the surface of charcoal and as to its mode of action. Many years ago De Saussure had called attention to the fact that fine pores in the adsorbent were essential to assure a high degree of adsorption. "The greater the ratio of the charcoal's surface to its mass, that is, the more highly developed and fine-grained its porosity, the greater its value."[62] But in addition to the extent of the surface of the charcoal, Chaney[63] recognized another factor as entering into the evaluation of charcoal as an adsorbent. He distinguished between two forms of carbon, active and inactive. The first is formed whenever carbon is deposited at a relatively low temperature by chemical or thermal decomposition of carbon-bearing materials, generally below 500° - 600°. It is characterized by the ease with which it is attacked by oxidizing materials, and its high specific adsorptive capacity. Inactive carbon, on the other hand, is formed by a similar decomposition but at higher temperatures, above 600° or 700°. Its properties are stability towards oxidizing agents and a low adsorptive capacity. "Primary" amorphous carbon, or the original product first formed in low temperature distillations of carboniferous materials, is a stabilized complex of hydrocarbons adsorbed on a base of active carbon, and is the starting point in the preparation of active carbon. "Secondary" carbon is primary carbon partially or completely broken up with the formation or introduction of inactive carbon by decomposition of its hydrocarbons at high temperatures. "This primary carbon[64] has little or no apparent adsorptive power. It is evidently a complex of materials, consisting of hydrocarbons adsorbed on a base of active carbon. These hydrocarbons, being difficulty volatile, prevent the adsorption of other gases or vapors upon the active material. They can be driven off by heating and particularly by the application of a high vacuum at elevated temperatures, but, like any adsorbed material, they require temperatures well above their boiling points to accomplish this".

The authors of the following quotation summarize the specifications of a good adsorbent charcoal as follows:

"1. It must have high and fine-grained porosity.
2. It must consist of amorphous base carbon.
3. It must be free from adsorbed hydrocarbons."

The removal of these adsorbed hydrocarbons is attended by considerable difficulty. If heating alone is employed, the danger of deposition of inactive carbon upon the surface of the charcoal, due to the cracking of the hydrocarbons, is to be feared. Hence the process resorted to is one of combined oxidation and distillation, by which process the hydrocarbons are removed at a much lower temperature. Two methods are available, depending upon the selection of the oxidizing agent. Either air or steam may be used. In the first case the optimum activation temperature is between 350° and 450°, in the second case between 800° and 1000°.

It was in the light of this more recent work upon the preparation of adsorbent charcoals that a method was developed for the preparation of the adsorbent used. Activation of the charcoal by air at a temperature between 320° and 360° was an important step in this process. For an exact description of the method employed, see under heading "Experimental", page 62.

The second point of comparison as indicated in a preceding page was the procedure used in each case. The general method for carrying out adsorption experiments, a method inaugurated by Freundlich[13] and adhered to by later investigators, was somewhat as follows. A weighed quantity of adsorbent was allowed to come in contact with a given volume of solution of known concentration in a glass stoppered vessel. This was shaken for a length of time in a thermostat. The charcoal was allowed to settle, the clear supernatant solution removed by pipetting, and this solution titrated against either barium hydroxide or carbon dioxide free sodium hydroxide, depending upon the concentration of acid used in the experiment.

The procedure used by the present writer was one which differed in certain essentials from that of preceding investigators.

(1) No attempt was made to accurately regulate the temperature. Since the temperature coefficient for adsorption from solution is very small, variations in adsorption due to slight variations in temperature would be practically negligible.

(2) Shaking was avoided. This was done primarily so that

the data thus obtained could be carried over to the work on percolation included in the latter half of this paper. Then too, the vigorous shaking employed by Freundlich and others would have had a tendency to break the particles, thus making the preliminary sifting of little avail, and accurate comparisons impossible.

(3) Greater attention was directed to the question of the reality of the equilibrium obtained. Contrary to the observations of Freundlich, it was found that equilibrium was not attained instantaneously. True equilibrium values for $\frac{x}{m}$ and c were derived indirectly, by plotting concentration against the cube root of the time, multiplied by 10,000, and exterpolating to $\sqrt[3]{\frac{1}{10,000T}} = 0$.

(4) To hasten adsorption the charcoal was first subjected to the vacuum of an oil suction pump.

The results of the investigators may be summarized under the following captions:-

(1) As to the speed at which equilibrium is reached. Freundlich found this to be practically instantaneous, and equally rapidly reached from either side. He cites the following experiment in confirmation of the instantaneousness of the process.[65] 0.871 grams of blood charcoal were allowed to act upon 50 cc. of an acetic acid solution of .06832 normality, the mixture shaken once, and allowed to settle for 20 minutes. An equilibrium concentration of

0.0561 moles per liter was obtained. Shaken again, and allowed to settle for the same length of time, an equilibrium concentration of 0;05552 moles per liter resulted. Another attempt (starting presumably with similar concentrations of acetic acid and weights of charcoal), in which the mixture was shaken for 30 minutes and allowed to settle for another 20 minutes, gave an equilibrium concentration of 0.05582 moles per liter. It is doubtful, however, whether one can consider cessation of shaking as meaning cessation of the process of adsorption, as Freundlich apparently did; and if one can not, the time interval selected was too great to admit of any conclusions as to the instantaneousness of the process of adsorption.

Schmidt[27] came to different conclusions as to the rate at which equilibrium was reached. This rate was dependant upon (1) the variety of charcoal used, (2) the temperature - it was hastened by a rise in the temperature, (3) the difference in the original concentration and the equilibrium concentration and varied directly as did this difference.

Pickle[61] takes adsorption as complete after the expiration of twenty-four hours.

My own investigations were such as to lead me to believe that equilibrium had not yet been reached after twenty-four hours, but that the differences from equilibrium concentration were relatively small after thirty minutes.

Values for β and p in the adsorption isotherm $\frac{x}{m} = \beta c^{1/p}$, differ from investigator to investigator. The following table will make comparisons possible:

Freundlich[13]	2.35	(25°)	2.606	(25°)
Schmidt[27]	2.00	(15°)		
Pickle[61]	1.77-2.6	(12°)		
Present Investigator	(2.00)	(20°)	2.905	(20°)

The K determined by Pickle which is Freundlich's β raised to the p power, cannot be compared with Freundlich's since Pickle's concentrations are expressed in different units. The real density of the charcoal was determined and the concentration expressed in moles per c.c. of charcoal, and in moles per c.c. of solution. The data[61], however, is interesting in that it shows variations of K and n (where n = p), with the variety of charcoal used and with the temperature. Such values as n were chosen as would give most consistent values for K.

Variety of charcoal	n 12°	 30°	 50°	K 12°	 30°	 50°
Fruit stone dust Density = 1.70	1.97	1.8	1.76	0.202- 0.208-	0.142- 0.145	0.135 0.139
Animal charcoal Density = 2.8 % C = 21	2.4	2.1	2.0	0.307- 0.360	0.219- 0.225	0.209- 0.210
Birch dust Density = 1.96	2.6		2.3	0.197- 0.201		0.245- 0.281
Coarse Birch Density = 1.47	2.1		2.0	0.205- 0.207		0.184- 0.197

Freundlich's data show quite consistent values for K. Distribution of Acetic Acid Between Water and Blood Charcoal.[66.67]

$(x/m)^p = kc$ $\qquad$ $p = \overline{2.35}$ $\qquad$ $\log k = 0.98$

c in moles per liter, x/m in millimoles per gram charcoal

c	x/m (found)	x/m (calc.)	K
0.0181	0.467	0.474	9.247
0.0309	0.624	0.673	10.69
0.0616	0.801	0.798	9.638
0.1259	1.11	1.08	10.14
0.2677	1.55	1.49	10.72
0.4711	2.04	1.90	11.35
0.8817	2.48	2.48	9.572
2.785	3.76	4.04	8.054

Here $k = \beta^p$.

Values for K determined by the present writer show considerable variation over the range of concentration employed. The following table will give the values.

Normality of acid	$\frac{x}{m}$ in grams per cc. charcoal	c in grams per cc. solution	K
.1058	.06125	.002679	1.4010
.9895	.12625	.051825	.3076
1.5535	.12850	.085550	.1930
5.1575	.19500	.297800	.1276
		Mean	.5073

The mean value of K as expressed in the same units as Freundlich's K is 8.44 as against Freundlich's 9.55.

12. Additional Studies on Adsorption

a. The system bromine, water and charcoal.

An attempt was made to study the adsorption from water solution of substances other than acetic acid. Bromine in aqueous solution was chosen as a material which would be apt to be strongly adsorbed. It was found, however, that the selection was an unhappy one, since bromine shows a marked tendency to be adsorbed by glass. Also at room temperature charcoal probably accelerates the reaction — $2Br_2 + 2H_2O \longrightarrow 4HBr + O_2$.– thus making a study of the kinetics of adsorption unnecessarily complex.

The following data, on the relation of time to the adsorption of bromine by charcoal, will indicate how tremendous is the decrease in concentration after the lapse of a twenty-four hour period.

$m = 1$ gm.

t in min.	concentration in water solution milligram equivalents per cc.
0	.09243
2	.04364
5	.03388
30	.02717
1440	.0006398

b. Aqueous solutions of aromatic acids and charcoal.

Since bromine proved to be unsuitable for experimentation, attention was turned to the aromatic acids. The

The experiments of Walker and Appleyard indicated that aromatic acids would be more strongly adsorbed than aliphatic. The choice rested first upon ortho-phthalic acid, due to the greater solubility of this acid as compared with either salicylic or benzoic. The attempt however was abandoned in that the acid showed very meager adsorption. Salicylic acid was then selected. Here, as in the case of the bromine, a marked decrease in concentration after twenty-four hours was noticed, as the following table will testify.

m = 3 gms.

time in min.	conc. in solution in grams per cc.
0	.001623
2	.001190
5	.000847
30	.000626
1440	.0000501

It was therefore thought wise to abandon the use of salicylic acid, since so slow a rate of adsorption would prove unsuitable for percolation experiments.

B. Percolation

It would be well to define at the outset in what sense the term "percolation" is used. The process of percolation is usually understood to mean the extraction of a soluble material from a powdered or otherwise finely divided substance by the use of successive quantities of a solvent. In the experiments included in this work, however, the term is intended to signify the removal of a soluble material from solution by the passage of successive quantities of this solution through a layer of adsorbent.

The literature on the subject of percolation, (percolation as defined above) indicates that few people have asked themselves the question as to whether there exists an exact relation between the concentration of the percolate at any given point and the volume of solution passed through a standard layer of adsorbing agent. One of the few attempts along an analogous line is that of J. G. C. Vriens[68], who showed that the change in concentration occurring in a solution when passed through a successive number of filter papers was a constant function of the number of filter papers passed through.

Whereas it was hoped to be able to use the adsorption data obtained, and apply the quantitative relationship of the adsorption isotherm to the process of percolation, the complexity of the equation involving the velocity constant made the fruition of that hope impossible.

Recourse was therefore had to an equation which was purely empirical in character. It follows:-

$$K = \frac{1}{M^{1/2}} \cdot \frac{1}{v} \cdot \log \frac{M}{M-m}$$

where v = number of cc. of percolate,

M = concentration of acetic acid in standard solution,

m = concentration of acetic acid at point v.

The expression holds good if the weight of charcoal employed from experiment to experiment is constant, as also the velocity at which the acetic acid percolates through the adsorbent. The equation may be said to possess merits in that it holds good throughout the entire range of percolation, i.e., when $v = 0$, and $v = \infty$.

The tables below give K calculated from the data obtained.

v in cc.	M in milligram equivalents per cc.	m in milligram equivalents per cc.	K
25	.5194	.2121	.01266
75	.5194	.4875	.02242
125	.5194	.5086	.01866
175	.5194	.5129	.01509
217	.5194	.5140	.01268

v in cc.	M in milligram equivalents per cc.	m in milligram equivalents per cc.	K
25	.9996	.6428	.01790
75	.9996	.9720	.02078
125	.9996	.9791	.01351
175	.9996	.9901	.01155
217	.9996	.9946	.01060

v in cc.	M in milligram equivalents per cc.	m in milligram equivalents per cc.	K
25	1.549	1.1396	.01858
75	1.549	1.5232	.01905
125	1.549	1.5409	.01467
175	1.549	1.5429	.01104
217	1.549	1.5435	--

v in cc.	M in milligram equivalents per cc.	m in milligram equivalents per cc.	K
25	1.4570	1.0838	.02007
75	1.4570	1.4372	.02062
125	1.4570	1.4452	.01387
175	1.4570	1.4522	.01175
217	1.4570	1.4540	

Mean value of K = .01584 ± .00352

Summary

The following may be regarded as a summary of the original work included in this paper:-

(1) Contrary to the observations of Davis, the use of a vacuum decidedly hastens the establishment of equilibrium in adsorption phenomena.

(2) An equation expressing the kinetics of adsorption was developed and experimentally verified. The equation, whereas it does not claim any theoretical foundation, indicates progress over preceding equations, in that:

(a) It holds over the whole range of adsorption, and does not reduce to an absurdity when $t = 0$, and $t = \infty$.

(b) It emphasizes the reversibility of the phenomenon of adsorption, giving place as it does to the equilibrium constant.

(c) It fits the facts over a wider range of concentrations then worked with before.

(3) Adsorption is far from being an instantaneous process as experimentation on the following indicates:

(a) Acetic acid in water solution, and charcoal; incomplete after 24 hours.

(b) Ditto for water solutions of salicylic acid and bromine, with charcoal as adsorbent.

(4) Ortho-phthalic acid in water is poorly adsorbed by charcoal, while bromine and salicylic acid in water are strongly adsorbed by charcoal.

(5) The adsorption of bromine by charcoal occurs slowly. The process is complicated, however, in that charcoal most probably catalyzes the reaction $2Br_2 + 2H_2O \longrightarrow 4HBr + O_2$.

(6) Salicylic acid is also slowly adsorbed by charcoal. It is doubtful whether any reactions, other than pure adsorption, occur here.

(7) Experimental values for the equilibrium constant as obtained from the adsorption data on acetic acid indicate that it is far from being a constant. The mean value for K, however, closely approximates that obtained by Freundlich.

(8) An empirical formula relating the concentration of the percolate to the volume of solution percolated was developed and experimentally verified, although only approximately.

Appendix

Effect of vacuum upon hastening the speed of attainment of equilibrium

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Normality of acetic acid = .9895   m = 3 grms.

	time=2 min.		time=5 min.		t = 30 min.		t = 1440 min.	
	a	b	a	b	a	b	a	b
Normality	.9216	.9391	.9149	.9307	.8835	.8992	.8678	.8678
Grms. adsorbed per cc. charcoal	.068	.050	.075	.058	.106	.090	.122	.122
Percentage decrease in water solution	6.834	5.084	7.544	5.891	10.68	9.09	12.28	12.28

a = at 10 - 12 mm pressure

b = at atmospheric pressure

Experimental

A. Preparation of Materials

1. Preparation of adsorbent

Sugar charcoal, although a less active adsorbent than either animal charcoal or coconut charcoal, was preferred because of the purity of the material from which it could be prepared, thus insuring purity of product. The sugar used was in all cases the Domino lump sugar (American Sugar Refining Company). 1000 grams of sugar were placed in a large evaporating dish, to this 240 cc. of C. P. concentrated sulphuric acid added, the mixture stirred and allowed to remain standing until the fuming had died down. The black mass was then transferred to large silica crucibles of 500 cc. capacity, covered with silica lids, and heated for thirty minutes at a red heat in a gas furnace. Upon removal the charcoal was allowed to stand in the covered crucible until cooled to room temperature. It was then tested for sulphuric acid. Well ground up portions placed in a small beaker and allowed to soak in water, were tested with litmus. No red coloration resulted. Also, when small pieces were chewed, no acid taste could be noticed. The charcoal was broken up into small lumps and allowed to stand from 3 - 12 hours with 6 N ammonium hydroxide (previously filtered) in a large glass jar. It was then filtered on a Büchner funnel, and thoroughly washed with distilled water . It was then reheated in the gas furnace at a red heat for twenty minutes and allowed to cool in the same manner as before. Grinding in a mortar and sifting followed. The sizes of charcoal used were those sizes retained by a twenty and fourty mesh sieve. The sifted charcoal was then placed in a 1000 cc. round-bottomed distilling flask, which was packed up to the neck in asbestos and heated by an electrical furnace. A slow stream of air was passed through at a temperature between 320°C and 360°C, for a period of three hours. The charcoal was then heated in vacuo for three hours, again at a temperature above 300°C. After cooling the charcoal was re-ground and re-sifted, this time to a uniform size, the size retained by a fourty mesh sieve. The large bulk of the charcoal was kept in a large glass-stoppered bottle, smaller portions having been transferred to small two ounze glass-stoppered bottles. An analysis for the ash content of the charcoal gave the following results:

	I	II
% ash in 1.5 gm. samples	.3070	.2727.

Revivification of charcoal. The charcoal after use was revivified as follows: It was thoroughly washed on a Büchner, and then reheated in the gas furnace at red heat for thirty minutes. Sifting followed, all of the material passing beyond a fourty mesh sieve being discarded.

2. Preparation and Standardization of solutions used.

a) Preparation of standard acid.

The hydrochloric acid used for standardizing the barium hydroxide was prepared from concentrated C. P. hydrochloric acid. Approximately .5 N and .1 N acids were used. Standardization against sodium carbonate, according to the usual analytical procedure, was the method followed.

b) Preparation and standardization of the barium hydroxide solution.

Carbonate-free sodium hydroxide solution was found difficult to handle, and therefore recourse was had to barium hydroxide. The maximum concentration of the barium hydroxide was approximately .4 N. The solution was made from a saturated barium hydroxide solution, which was diluted and transferred to a bottle fitted up with a syphon and soda-lime tube. The alkali was always standardized before use against the standard acid, since small variations in the factor were apparent in twenty-four hour periods. In this way trustworthy results could be guaranteed.

c) Preparation and standardization of sodium thiosulphate solution.

The solution was prepared from sodium thiosulphate of Kahlbaum origin. Freshly boiled distilled water was used. It was standardized against C. P. potassium dichromate, after having been allowed to stand for two weeks. A constant factor was thus obtained.

d) Preparation and standardization of solutions used in the adsorption and percolation experiments.

1. Preparation and standardization of the acetic acid solution.

Solutions varying in strength from .1 N to 5 N were used, and were in each case prepared from the same C.P. glacial acetic acid. These were standardized against the alkali by using the same pipettes used for measuring out samples from the residues of the adsorption and percolation experiments. Thus accurate comparisons were possible.

2. The preparation and standardization of the phthalic and salicylic acid solutions.

The phthalic acid was prepared from Kahlbaum's phthalic anhydride by solution in hot water. The salicylic acid used was Kahlbaum's. Solution in hot water and then dilution was the procedure followed. The acids were standardized as above.

3. The preparation and standardization of the bromine solution.

This was prepared from a saturated bromine solution by diluting to four times its original volume. After standing several days it was standardized against the thiosulphate as follows:

Two 5 cc. portions of KI solution (approximately twice as concentrated as the bromine solution - thus guaranteeing an excess) were pipetted into two 250 cc. Erlenmeyers.

To each 50 cc. of water were added and 10 cc. of a one per cent acetic acid solution. 5 cc. portions of the bromine solution were carefully added to each, the mixtures shaken, and immediately titrated against the standard thiosulphate, freshly-prepared starch solution being used as indicator.

B. Apparatus and Procedure

1. Apparatus and Procedure for Adsorption Experiments

The weighed amount of charcoal was placed in a 100 cc. round-bottomed distilling flask. It was clamped to a ring stand and in it placed a tightly fitting rubber stopper through which a 50 cc. dropping funnel had been inserted. The flask was then connected up with an evacuating train, consisting of two stopcocks, the first two-way, the second three-way, a manometer, a filtering flask which acted as a safe-guard for back flow of the oil from an oil suction pump, and the pump. 50 cc. of the solution used was measured from a pipette into the dropping funnel. Then, after a pressure from 5 - 10 mm. had been established, the first stopcock was closed, the pump stopped and the second stopcock opened so as to allow normal pressure to become reestablished in the train. The liquid was then allowed to flow in until approximately 10 cc. remained, normal pressure reestablished in the distilling flask, and the remainder of the solution allowed to flow in. The time from complete entrance of the liquid to the time limit set was noted on a stop watch. The dropping funnel was allowed to drain 30 seconds after the stop watch was set going, and the stem then touched to the side of the vessel. The distilling flask was then well corked and set aside. 30 seconds before the time limit had elapsed, a 50 cc. pipette was placed in the distilling flask and the solution pipetted off within from 15 - 25 seconds. The solution thus obtained was transferred to a dry 50 cc. glass-stoppered bottle. By an exact observation of the above directions, the results obtained could be considered as comparable.

The time intervals used were 2 min., 5 min., 30 min., and 24 hrs. The experiment was always carried out in duplicate and 2 samples (or more if checks were not obtained) of either 5 or 10 cc. portions used from the volume of solution removed from the charcoal.

The titrations were carried out as follows:- 5 cc. or 10 cc. portions were diluted to 50 cc. and 1 drop of thymolphthalein indicator solution added. The end was very sharp and easily distinguished.

In the case of the 5 N acid the procedure was slightly modified in that two 10 cc. samples of the solution removed from the charcoal were diluted to 50 cc., well mixed, and 5 cc. portions of the diluted solutions used. The 5 N acid was standardized after the same fashion.

The procedure for the bromine was similar to that for the dilute acids, except that the solutions were transferred to brown bottles and titrated immediately against standard thiosulphate.

2. Apparatus and Procedure for Percolation Experiments

10 grams of charcoal were placed in a burette, of length 60 cm. and diameter of cross-section 1.2 cm. The charcoal was prevented from passing through by the use of a small silver sieve, cut to fit the burette. The length of the column of charcoal was approximately 54 cm. . The burette was connected by a piece of wide rubber to what was originally the neck and side-tube of a distilling flask. Into the upper end of this neck was fitted a rubber stopper through which had been inserted the stem of a 250 cc. dropping funnel. To the side-tube of distilling flask was attached a piece of pressure tubing which connected the percolation apparatus with the evacuating train previously described.

250 cc. of the solution to be used was measured into the dropping funnel. The pump was started and when a pressure ranging between 5 - 10 mm. was established, the stopcock was closed. The pump was stopped, normal pressure reestablished in the evacuating train. The solution was then allowed to enter dropwise into the burette, its flow so regulated that the burette would be completely filled in 15 minutes. Normal pressure was then reestablished and the solution allowed to stand with the charcoal for 25 minutes. Whereas it would have been better to have so regulated the flow of solution that first entered the burette so that its rate of inflow would have approximated the rate of out-

flow, yet it was found impossible to maintain a diminished pressure in the burette successfully for longer periods of time than 15 minutes. After the lapse of fourty minutes (noted on the stop watch), the stopcock was opened and the solution allowed to drop into a 50 cc. graduate, at such a speed that 50 cc. would flow through in 30 minutes (approximately). This process was continued until the last portion of solution flowed through. To drain the column of charcoal more completely, suction was applied towards the end. The number of cc. of solution delivered was noted. The 50 cc. portions, which had been in the mean time, after thorough mixing, transferred to dry glass-stoppered bottles, were then titrated as described under the adsorption experiment.

Percolation experiments were always run either in duplicate or triplicate.

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