

## COLLOIDAL PHENOMENA AND THE ADSORPTION FORMULA.

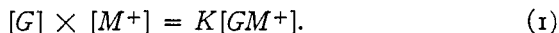
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The theory of the molecular mechanism of protein swelling recently presented by Tolman and Stearn<sup>1</sup> stands out in marked contrast to that evolved by Procter and Wilson.<sup>2</sup> According to the former, the force causing swelling is one of electrostatic repulsion, while in the latter theory this force is ascribed to the diffusion pressure of the necessary excess concentration of diffusible ions of the jelly phase over that of the external solution. Grounds for discussion have been furnished and the importance of the subject demands the attention of physical chemists in general. While this work is of great biological importance, it also has an enormous bearing upon the application of modern science to industry. It is not our purpose in the present paper to criticize the work of Tolman and Stearn, but rather to summarize briefly and to extend the theory of Procter and Wilson and to examine the widely-accepted, empirical formula for adsorption, as regards its reliability as a criterion of physical phenomena.

**The Consequence of Chemical Combination between a Binary Electrolyte<sup>3</sup> and a Colloid Jelly.**

Let us consider a purely hypothetical substance  $G$  which has the following properties: It is a colloid jelly, is completely permeable to water and all dissolved electrolytes, is elastic and under all conditions under consideration follows Hooke's law, and combines chemically with the positive, but not the negative ion of a binary electrolyte  $MN$ , according to the equation



(In other words, the compound  $GMN$  is completely ionized into  $GM^+$  and  $N^-$ .)

Now take one millimole of  $G$  and immerse it in an aqueous solution of  $MN$ . The solution penetrates  $G$ , which thereupon combines with some of the positive ions, removing them from solution, and consequently the solution within the jelly will have a greater concentration of  $N^-$  than of  $M^+$ , while in the external solution  $[M^+]$  is necessarily equal to  $[N^-]$ . The solution thus becomes separated into 2 phases, that within and that surrounding the jelly, and the ions of one phase must finally reach equilibrium with those of the other phase.

At equilibrium, in the external solution, let

$$x = [M^+] = [N^-]$$

and in the jelly phase let

<sup>1</sup> THIS JOURNAL, 40, 264 (1918).

<sup>2</sup> J. Chem. Soc., 109, 307 (1916).

<sup>3</sup> Meaning exclusively an electrolyte which dissociates into two monovalent ions.

$$y = [M^+]$$

and

$$z = [GM^+]$$

whence

$$[N^-] = y + z.$$

(All concentrations are taken in moles per liter.)

The relation existing between the concentrations of diffusible ions of the 2 phases at equilibrium can be derived from the consideration of the transfer of an infinitesimally small amount,  $dn$  moles, of  $M^+$  and  $N^-$  from the outer solution to the jelly phase, in which case, since no work is actually done,

$$dn RT \log x/y + dn RT \log x/(y + z) = 0,$$

whence

$$x^2 = y(y + z). \quad (2)$$

But in this equation, the product of *equals* is equated to the product of *unequals*, from which it follows that the sum of those unequals is greater than the sum of the equals, *i. e.*,

$$2y + z > 2x.$$

This is a mathematical proof that the concentration of diffusible ions of the jelly phase is greater than that of the external solution and makes possible the derivation of a second equation involving  $e$ , which is defined as the excess of concentration of diffusible ions of the jelly phase over that of the external solution

$$2x + e = 2y + z. \quad (3)$$

Since  $[N^-]$  is greater in the jelly than in the surrounding solution, the negative ions of the colloid compound will tend to diffuse outward into the external solution, but this they cannot do without dragging their colloid cations with them. On the other hand, the cohesive forces of the elastic jelly will resist this outward pull, the quantitative measure of which is  $e$ , and according to Hooke's law

$$e = CV \quad (4)$$

where  $C$  is a constant and  $V$  the increase in volume in cubic centimeters of one millimole of the colloid.

Now since we have taken unit quantity of the substance  $G$

$$[G] + [GM^+] = 1/(V + a)$$

or

$$[G] = 1/(V + a) - z \quad (5)$$

where  $a$  is the initial volume of the colloid.

From (1) and (5)

$$(1/(V + a) - z)y = Kz \quad (6)$$

and from (2) and (3)

$$z = e + 2\sqrt{ey}$$

or

$$z = CV + 2\sqrt{CVy}. \quad (7)$$

From (6)

$$(V + a)(K + y)z = y$$

and substituting the value for  $z$  in (7)

$$(V + a)(K + y)(CV + 2\sqrt{CVy}) - y = 0 \quad (8)$$

where the only variables are  $V$  and  $y$ .

Since volumes are usually plotted as functions of  $x$ , it might seem preferable to substitute for  $y$  its equivalent function of  $V$  and  $x$ , for

$$2y = 2x + CV - \sqrt{4CVx + C^2V^2}.$$

But by so doing the equation becomes unnecessarily involved, since the Curve  $V = f(x)$  can be plotted indirectly by giving successive values to  $y$ , solving for  $V$ , and then determining  $x$  from

$$x = y + \sqrt{CVy}.$$

It is evident that where any 2 variables are known all others can be calculated.

If the molecules or atoms of the colloid are not themselves permeable to all the ions considered, we believe that the quantity  $a$  should not be taken as the whole of the initial volume of the jelly, but only as the free space within the jelly through which the ions may pass. For our hypothetical substance, then, we shall consider the limiting case where the value of  $a$  is zero. Equation 8 thus reduces to

$$V(K + y)(CV + 2\sqrt{CVy}) - y = 0. \quad (9)$$

TABLE I.—SHOWING INTERRELATION OF VARIABLES AT EQUILIBRIUM.

$y$ .	$V$ .	$x$ .	$e$ .	$z$ .	$y + z$ .	$Vz$ .
0.0005	44.7	0.00199	0.00447	0.0074	0.0079	0.333
0.0008	49.7	0.00279	0.00497	0.0090	0.0098	0.445
0.0009	50.7	0.00304	0.00507	0.0093	0.0102	0.474
0.0010	51.6	0.00327	0.00516	0.0097	0.0107	0.501
0.0020	55.0	0.00530	0.00550	0.0120	0.0140	0.662
0.0024	55.170	0.00604	0.00552	0.0128	0.0152	0.706
0.0025	55.176	0.00621	0.00552	0.0129	0.0154	0.712
0.0026	55.168	0.00638	0.00552	0.0131	0.0157	0.723
0.003	55.0	0.00706	0.00550	0.0136	0.0166	0.750
0.004	54.3	0.00866	0.00543	0.0147	0.0187	0.801
0.005	53.3	0.01016	0.00533	0.0157	0.0207	0.834
0.010	48.5	0.01696	0.00485	0.0188	0.0288	0.911
0.050	33.6	0.06296	0.00336	0.0293	0.0793	0.984
0.100	27.5	0.11658	0.00275	0.0360	0.1360	0.990
1.000	13.4	1.03661	0.00134	0.0745	1.0745	0.999

Table I and Fig. 1 were prepared by taking the arbitrary values  $C = 10^{-4}$  and  $K = 10^{-3}$ , substituting successive values for  $y$ , and solving by a

method of approximation for one real root, the corresponding root being taken in each case; from  $V$  and  $y$  all other variables were obtained by

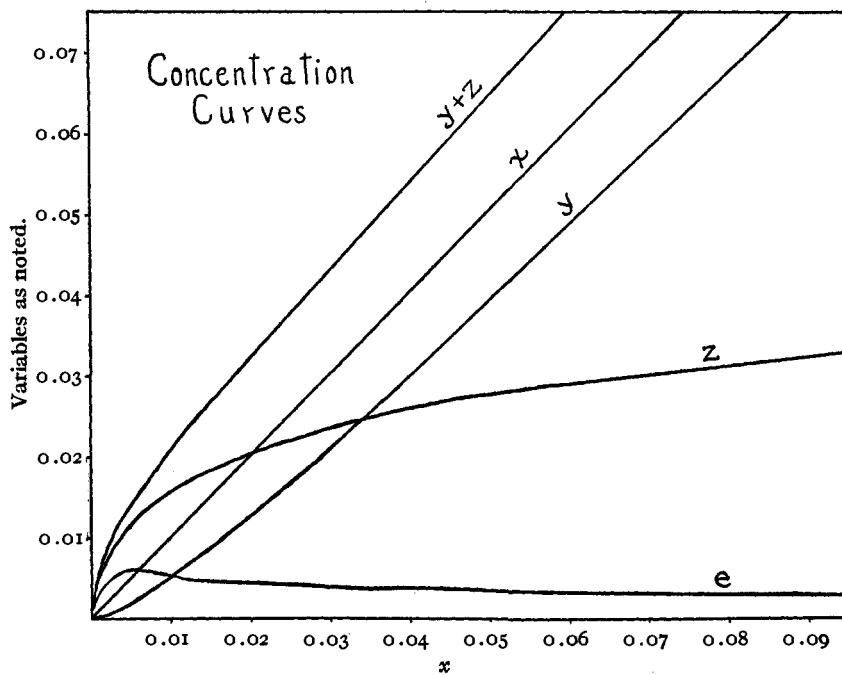


Fig. 1.

substituting in equations already given. A similar method was used in plotting the family of curves in Fig. 2, which is self-explanatory.

All of these curves are of the same nature as many corresponding ones obtained by experiment upon various colloid jellies and electrolytes.<sup>1</sup>

#### The Case of Several Binary Electrolytes and a Colloid Jelly which Combines with Some, but not All, Ions of One Sign.

From the derivation of Equation 2 it is evident that the product of concentrations of the oppositely-charged ions of any electrolyte must be the same in both phases, making it possible to broaden the system of notation so that in the external solution

<sup>1</sup> Since writing this paper, one of us has prepared a reply on the theory of tanning, which has been sent to the *Journal of the American Leather Chemists' Association* for publication. In this paper it is mentioned that Procter and Wilson obtained the value  $K = 1.5 \times 10^{-4}$  for gelatin and hydron by adding successive portions of HCl to a gelatin solution and determining the hydron concentration after each addition by means of the hydrogen electrode. They obtained the value  $C = 3 \times 10^{-4}$  from experimental values for  $e$  with Coignet's gelatin at 18°. Using these 2 constants in Equation 9 and solving for all variables, curves were obtained which are in rigid quantitative agreement with all of the experimental curves for gelatin and HCl solutions at 18°.

$x$  = sum of concentrations of all positive or negative ions and in the jelly phase.

$y$  = sum of concentrations of all diffusible ions of the same sign as that of the colloid ions.

$z$  = sum of concentrations of colloid ions.

Equations 2 and 3 can now be re-derived and their simultaneous solution gives

$$e = -2x + \sqrt{4x^2 + z^2}$$

or

$$CV = -2x + \sqrt{4x^2 + z^2}. \quad (7)$$

Whenever an electrolyte is added to the system, if it combines with  $G$ , then the value of  $z$  is increased; otherwise  $x$  is increased. If the value of  $x$  is raised while  $z$  remains constant, the volume must fall. Likewise the volume will increase if  $z$ , but not  $x$ , is augmented. By applying the calculus, it is found that to effect an increase in volume the rate of in-

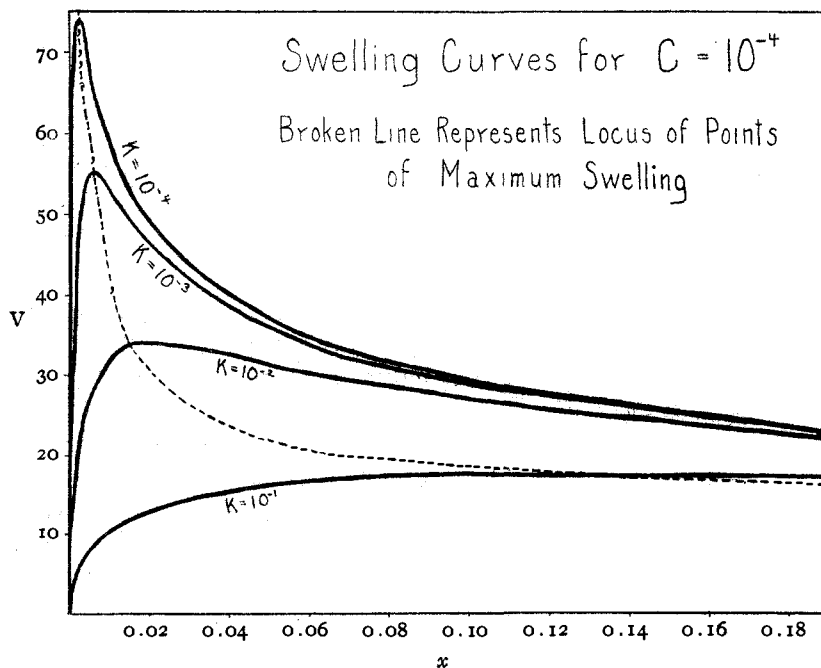


Fig. 2.

crease of  $z$  must be made greater than  $2e/z$  times that of  $x$ . The addition of any electrolyte which does not combine with  $G$  must cause contraction of the swollen jelly to the extent to which it increases the ionic concentration, while adding one which does combine with the colloid will produce either swelling or contraction depending upon the value of  $dz/dx$ . This

statement would have to be modified, however, if any one of the colloid compounds were not wholly ionized. Any combination between the colloid ion and a diffusible ion of opposite sign would decrease the value of  $z$  and cause contraction of the jelly.

#### The Presence of Polyvalent Ions.

Suppose that  $G$  were to combine with the positive but not the negative ion of the electrolyte  $MaN$ . Using the method by which Equation 2 was derived,

$$x^{a+1} = y^a(y + z)$$

from which it is mathematically apparent that

$$(a + 1)y + z > (a + 1)x$$

or that

$$(a + 1)y + z = (a + 1)x + e.$$

Although the relations are now more complex, it is still clear that the addition of  $MaN$  to  $G$  will produce swelling and that when  $G$  becomes nearly saturated, contraction of the jelly is the necessary concomitant of any further addition of electrolyte. As a matter of fact, however, we should not expect this colloid salt with a polyvalent negative ion to be highly ionized, and if it were not, the value of  $z$  would be correspondingly smaller, there would be less swelling, and our equations for the volume would be worthless unless we took into consideration the actual degree of ionization of the colloid salt.

A general mathematical treatment of the whole subject is desired and it is to be hoped that it will soon be undertaken, but in the present paper it has been deemed sufficient to derive volume equations only for binary electrolytes, as the purpose in view is only to give an outline of the general mechanism of the swelling of colloid jellies rather than to explain the peculiarities in the swelling curves of polybasic acids upon certain proteins.

#### General Nature of the Equations.

Equations 2, 3 and 7 were not derived upon the assumption that any chemical combination had taken place, but that  $[M^+]$  and  $[N^-]$  were unequal in one phase and equal in the other and they are therefore applicable to any such 2-phased systems. The particular curve for  $z$  in Fig. 1, on the other hand, does assume actual combination because it is taken as proportional to the product of the concentrations of the combining substances. The volume curves in Fig. 2 also assume chemical combination.

#### Relation of Physical Constants to the Point of Maximum Swelling.

The broken line in Fig. 2 represents the locus of all points of maximum swelling for one millimole of  $G$  whose value for  $C = 10^{-4}$ . By the variation of  $C$ , an area is generated which is a function of  $C$ ,  $x$ , and  $V$ , and repre-

sents the locus of all points of maximum swelling for one millimole of every colloid jelly with the properties of  $G$ , when immersed in solutions of  $MN$  of varying concentration. This standard curve might be used to test the validity of the assumptions. Suppose the bulk modulus of a certain protein had been determined by elasticity experiments to correspond to  $C = C'$ , and that when immersed in varying strengths of a binary electrolyte its maximum volume per milligram was found to be  $V'$  cubic centimeters at  $x = x'$ . Erect a perpendicular to the plane  $Cx$  at the point  $C', x', o$ . It will intersect the standard curve at  $V$ , the maximum volume of one millimole. The equivalent weight of the protein is  $V/V'$ , which should equal the numerical value of the number of grams of the protein which combine with a maximum of one mole of  $MN$ .

### Continuity of the Phases.

In the foregoing discussion of 2-phased systems, each phase has been assumed to be continuous. This is not the case when the system becomes a sol, and it is therefore interesting to examine the transition from one state to the other. In the colloid ions  $GM^+$ , the  $M^+$  ions will be in direct combination only with certain isolated atoms (say  $A$ ) and consequently the negative ions cannot diffuse to more than a certain average distance from their corresponding positive colloid ions unless replaced by their equivalent value of ions of the same sign. Consider a cross-section of

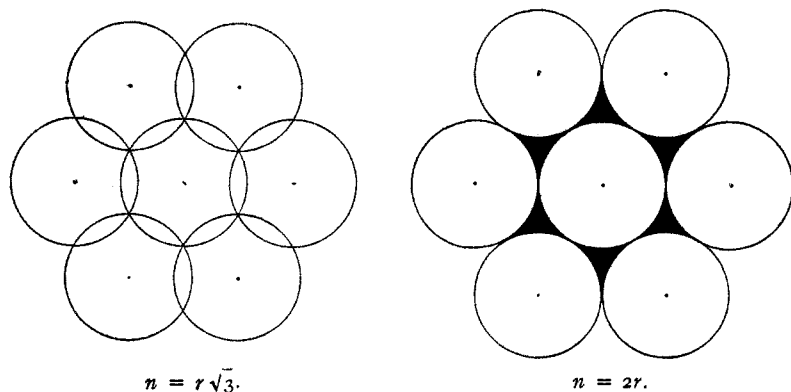


Fig. 3.

the jelly and assume for the sake of simplicity that each positively-charged  $A$  atom is immediately surrounded by and equidistant from six others, which distance we may call  $n$ . Denote the average distance which a negative ion may move from its corresponding  $A$  atom by  $r$ , which might be termed its radius of action. A glance at Fig. 3 will show that so long as  $n < r\sqrt{3}$ , the jelly-phase as well as the external solution will be continuous. It will be seen, however, that between  $n = r\sqrt{3}$  and  $n = 2r$ , the jelly-phase will still be continuous, but the solution phase will be dis-

continuous. The black regions in the figure show isolated sections of external solution distributed throughout the jelly. It is suggested that certain microscopic pores found in hardened jellies may have had their origin in these isolated portions of solution. When  $n > 2r$ , the solution phase again becomes continuous, the jelly-phase discontinuous and the system a sol.

### The Empirical Adsorption Formula.

The voluminous literature which has appeared dealing with "adsorption isotherms" lends an added significance to the curve for  $z$  in Fig. 1, which by its derivation represents the concentration of electrolyte chemically combined with the colloid, *i. e.*,  $[GM^+]$ . Not being aware of this, one might be tempted to try to fit it to the empirical adsorption formula  $z = ax^{1/n}$ , and assuming slight discrepancies to be due "to experimental error," to announce that the phenomenon had been proved to be purely physical. By substituting 2 sets of values for  $z$  and  $x$  in this equation and solving for the constants, we get  $a = 0.073$  and  $1/n = 0.335$ . In Table II there are given actual values of  $z$  taken from the curve, together

TABLE II.—COMPARISON OF VALUES CALCULATED FROM EMPIRICAL ADSORPTION FORMULA AND THOSE CALCULATED FROM EQUATIONS GIVEN IN THIS PAPER.

$x$ .	$z$ .	$0.073x^{0.335}$ .	$V(y+z)$ .	$14x^{0.66}$ .
0.003	0.009	0.010	0.52	0.54
0.006	0.013	0.013	0.84	0.80
0.010	0.016	0.016	1.10	1.06
0.017	0.019	0.019	1.40	1.43
0.063	0.029	0.029	2.66	2.98
0.117	0.036	0.036	3.74	4.21
1.000	0.074	0.073	14.4	14.0
10.000	0.159	0.158	64.0	50.8
100.000	0.341	0.341	191.0	185.0

with values calculated from the adsorption equation upon the assumption that

$$z = 0.073x^{0.335}.$$

The results are in fully as close agreement as is general when observed results are compared with calculations from the empirical formula.

Examination of an earlier paper<sup>1</sup> by one of us will show that the above relations are equally applicable to suspensoids or any other colloids, even when these are impermeable to water. Suppose that a suspensoid  $S$  is impermeable to water, but that its surface molecules will combine chemically (say by reason of their residual valencies) with the positive ion of a binary electrolyte forming the completely ionized compound  $SMN$  only at the surface of  $S$ . The surface film of solution surrounding the particles will have a greater concentration of  $N^-$  than of  $M^+$  and consequently

<sup>1</sup> THIS JOURNAL, 38, 1982 (1916).



when equilibrium has been established, the relations existing between the concentrations of the ions of the surface film and those of the bulk of solution will be expressible by Equations 2 and 3 given above, but where in the bulk of solution

$$x = [M^+] = [N^-],$$

and in the surface film

$$y = [M^+], \text{ and } y + z = [N^-]$$

and  $e$  = the necessary excess concentration of diffusible ions of the surface film over that of the bulk of solution. One millimole of  $S$  is defined as that weight of  $S$  whose surface molecules can combine with a maximum of one millimole of  $MN$ , and this weight will naturally vary with the degree of dispersion.  $V$  is defined as the volume in cubic centimeters of the surface film surrounding one millimole of  $S$ . As  $e$  becomes greater, the resulting increase of outward diffusion pressure will cause an increase in the size of the particles with a corresponding increase in  $V$ . It is now clear that the relations derived for colloid jellies differ from those of other dispersoids only in degree.

Since, according to the empirical formula,  $z$  becomes continually greater as  $x$  increases without limit, this formula is quite incompatible with that for chemical combination where only one phase and no alteration in volume are concerned, for in

$$z = ay/(K + y),$$

as  $y$  increases without limit,  $z$  approaches the constant  $a$ . If  $V$  be assumed constant and  $z$  be plotted against  $x$ , the curve will be rounded off, since  $x$  increases at a greater rate than  $y$ , and therefore within certain fixed limits  $z$  may more nearly approximate values obtained by use of the empirical formula, but the formulas are still incompatible since  $z$  has a finite limit. But according to the reasoning given for colloid jellies, the limit of  $V$ , as  $x$  increases without limit, is zero and consequently  $z$  has no finite limiting value and the above-mentioned incompatibility between the 2 formulas vanishes.

Since the empirical formula is concerned rather with the total quantity of electrolyte adsorbed, whether chemically combined with the colloid or merely in solution in the surface layer, the curves from this formula should be compared with those for the quantity  $V(y + z)$ . In Table II are given values for this quantity taken from Table I along with the corresponding values for  $14x^{0.56}$ , from which it will be seen that the two values do approximate each other over wide ranges of concentration. The authors believe that further development of the above reasoning will finally result in the derivation of a formula for adsorption which will be more satisfactory than the one now so widely employed.

### Summary.

The radical difference between the theory of the molecular mechanism of protein swelling presented by Tolman and Stearn and that evolved by Procter and Wilson is pointed out.

It is shown that if a colloid jelly combines chemically with a given electrolyte forming a highly ionizable colloid salt, the jelly must swell to a maximum and then contract indefinitely as the concentration of ionized electrolyte in the solution is increased.

It is shown further that the addition to the system of any electrolyte which does not combine with the colloid will produce contraction of the swollen jelly to an extent depending upon the resulting increase in ionic concentration.

A suggestion is given as to the origin of microscopic pores observed in certain hardened jellies.

Upon the assumption that a colloid combines chemically with ions of one sign of a dissolved electrolyte, both the concentration of chemically combined electrolyte and the total quantity of electrolyte either combined with or present in the solution in contact with the colloid are represented as functions of the concentration of electrolyte in the solution. The curves for these functions are approximately the same as those obtained by use of the empirical adsorption formula. It is believed that further development of the reasoning given in this paper will result in a more satisfactory formula for adsorption than the one now so generally used.

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## THE USE OF HYDROFLUORIC ACID IN ANALYSIS:

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### Introduction.

In recent years a number of new analytical procedures have been developed which are based upon the behavior of certain fluorides in neutral and acid solution. The main chemical facts of which use is made in these procedures are:

First, by choosing the proper solvent true solutions of the metals of the copper-tin group, or of the metals chromium, tungsten, and molybdenum, may be obtained. Indeed, nearly all of the metals, especially those most frequently found in alloys, are readily soluble in a mixture of nitric and hydrofluoric acids.

Second, having obtained such solutions, a number of separations which are difficult, or impracticable by any other known method, may be effected quickly and completely by the use of reagents commonly employed in analysis.