THE BROADER ASPECTS OF VALENCE: ITS APPLICATION TO COLLOID COMPOUNDS

VICTOR COFMAN

Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware

The classical idea of valence was developed to explain the properties and behavior of "pure" chemical compounds.[1] Even in that field it does not at present completely account for the facts. As Sidgwick puts it: "The modern distinction of different types of valency shows that the combining power of an atom may be due to more than one cause and may arise in more than one way, and it is not possible to express all the variations of this power as numerical values of a single constant" (1).

CHEMICAL COMPOUNDS AND COLLOID COMPOUNDS

True chemical compounds are usually crystalline or crystallizable substances, of constant composition, with discontinuous properties (entirely different from those of their constituents). They are brittle when solid and usually not very sensitive to light.

On the other hand colloids are typically gel-like, have curved forms, variable composition, and properties changing continuously with outside conditions. They are generally elastic and

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[1] The valence concept was originally introduced to account for certain whole number relations in the combining ratios of atoms and groups. A. W. Williamson's "monad" and "diad" groups, Frankland's "affinities (1852), Gerhardt's "atomicity" (1853), Odling's "replaceable values" and Kekulé's "saturation capacity" (1857), laid the foundations of the doctrine of valence. Since that time numerous types of valence have been described: Polar, electro- or ionizable; non-polar, neutral or non-ionizable; normal or positive, contra- or negative; principal and subsidiary, primary and secondary, auxiliary, coördinate; absolute or maximum, active, actual, free or effective, passive, dormant, crypto- or unsaturated; electrical-double, dative or co-valence; conjugate, semi-, partial, virtual partial, latent, residual, potential; unsymmetrical, forced, absolute polar, homopolar, heteropolar; and no doubt many others.

extensible and more readily affected by light. Colloidal dispersions possess only part of these properties and may be considered as imperfect colloids.

TABLE 1

	HOMOGENEOUS					HETEROGENEOUS		
	Chemical compounds } →		Physical compounds } →				Physical mixtures	
	Chemical compounds	Dissociable compounds	Hydrates and alloys	Hydrous oxides; oxy-salts	Colloid compounds (elastic gels)	Solutions	Fine dispersions or suspensions	Course dispersions or physical mixtures
Crystalline form	+ +	+ +	+					
Constant composition	+ +	+ +	+	(+)				
Unlike their constituents (discontinuity in properties)	+ +	+ +	+	(+)				
Elastic, but not extensible	+	+	+	(+)				
Energy change accompanying formation	+	+	+	+	+	+	(+)	
Composition varies with external conditions		(+)	(+)	+	+ +	+ +	+ +	
Properties depend on P, V, T variables			+	+ +	+ +	+		
Curved outline; extensibility				+	+ +			
Constituents can be separated by gravitation						(+)	+	+ +

In order to study the forces that act in colloid systems, we may either render our concept of valence more flexible or we may consider valence as a limiting case of a more extensive type of physico-chemical affinity.

One can devise a scheme—as in table 1[2]—showing the transition from definite chemical compounds, through dissociable compounds, hydrates and alloys, hydrous oxides and oxysalts, elastic gels and adsorption compounds, solutions and dispersions—on to coarse physical mixtures. In many of the above systems it is difficult to state whether the forces that hold the atoms together are of the valence type or are due to some other kind of affinity.

For convenience' sake one may consider the current picture of the true chemical combination—namely, the transference or sharing of electrons. In sodium hydride the sodium is assumed to have lost an electron to hydrogen, the latter being therefore negatively charged:

$$\overset{+}{\mathrm{Na}}\ \overset{-}{\mathrm{H}}$$

This is chemical combination.

Now, consider a negatively charged gold particle containing adsorbed sodium ions (see fig. 1). Here, too, the sodium ions have a deficiency of electrons and the gold particle has an excess of electrons. But what we know of the freedom of movement of electrons in metals constrains us to admit that the excess electrons do not belong to any particular atoms of gold, but to the particle as a whole. Consequently one must say that there are cases in which the primary valence forces of a group of ions are satisfied by the electrical field of force of another group of ions, in non-equivalent proportion.

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[2] Table 1 indicates that properties change gradually from one group to the next and no property belongs exclusively to one group (2). For instance, the change in energy accompanying formation—often supposed to be typical of chemical compounds,—is in reality common to all groups, but varies greatly in degree. Again, physical mixtures are characterized by ease of separation with simple methods involving gravitational or centrifugal forces; but gravitation will also cause partial separation of dispersions or even solutions, and it is possible that in some celestial bodies at high temperatures it may break up compounds owing to difference in the weight of their component atoms.

It is equally true that a substance of given composition may exist in different states. Chemical compounds, at high temperatures, may dissociate completely and become physical mixtures, while colloidal substances, under certain conditions, may assume crystalline form.

THE "LAW" OF CONSTANT PROPORTIONS

How does this conclusion affect the law of constant proportions? It merely shows it to be one more of those "laws of nature" which state that there are three feet to the yard. If, out of the infinite variety of substances in nature one chooses to call chemical compounds only those in which stoichiometric relations exist, one has made a useful definition. By saying, further, that substances can only combine chemically in definite proportions, one merely *restates* the definition of chemical compounds. This restatement has been given the form of a "law" and invested with possibilities of good and evil.

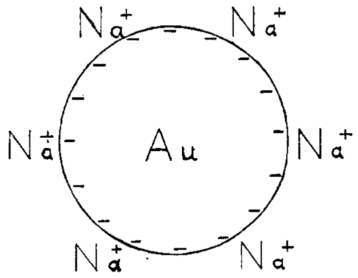

Fig. 1. Combination (Adsorption of Ions) in Non-Stoichiometric Proportions

Consider its good effect first: Coming at a time when technical skill and knowledge of the properties of matter were rather limited, it was a distinct advantage to restrict the field of investigation of chemists to substances of constant composition. Such substances can generally be crystallized and are readily identifiable by definite properties. Even today with a greatly increased knowledge of nature and with the help of specialized apparatus, investigators find themselves baffled by many colloid problems. Had our predecessors attempted to study these difficult systems instead of the readily purified chemical compounds, they may well have become discouraged.

The law of constant proportions enabled them to build a truly magnificent edifice of chemical knowledge and to prepare and describe hundreds of thousands of chemical species. However, in the enthusiasm of their great success, forgetting that they simply discovered in Nature only what they were looking for, chemists endowed the statement of constant proportion with universal validity; later, when they began to study less definite substances like proteins, soap, cellulose, etc., the ideas of constant proportion and discontinuous valence were so deeply entrenched, —and they still are,—that to some chemists it seems almost sacrilegious to discuss the limitations of these concepts (2). Yet a simple analogy will show how arbitrary such a view is.

Suppose that some superpower were interested to know how much a chemist drinks, in other words, the affinity of, say, American chemists for water, beer or wine. If this superpower were to follow the example set by chemists it would proceed somewhat along the following lines: It might begin with a very large number of chemists and start a race, rejecting those who reach the goal first and those who are left behind, retaining only those that run at about the same speed. This would correspond to fractional distillation, and would eliminate many of the stout chemists and leave a more homogeneous crowd. Next, this superpower might resort to crystallization by arranging the chemists into such patterns that it would necessarily place those of the same size together, and thus eliminate those that are too tall, or too short. After a few more "purifications" which would render the group as uniform as possible, the superpower would be ready to investigate the drinking capacity of the individuals; however, instead of doing so with each one separately this superbeing would calculate how many barrels the group, as a whole, needs. Under such circumstances the probability is that, no matter what group of chemists this superbeing began with, it would obtain the same *per capita* consumption of liquid; thus it could prove as a law of nature, that the combining affinity of chemists for water, or beer, or wine, has a constant value.

This analogy may seem fantastic, but proofs of the constancy of composition of many compounds (e.g., sodium caseinate or hydrated magnesium oxides) are, in my opinion, no less forced. The methods which are used in the so-called purification of these substances, and the restrictions placed upon the conditions of the system are such as to make the law of constant composition necessarily true. No one would deny that the beautiful crystalline substances and the constant-boiling liquids that adorn the shelves of the chemical laboratories are examples of stoichiometric compounds and that their structure can be simply and plausibly explained by our present views of valence. There is no sufficient reason, however, to assume that theories which have been found useful for those specially prepared substances will be found convenient for the rest of nature. From the fact that telegraph poles are of standard sizes, it is not safe to generalize that all trees in the forest grow to the same height.

For the sake of uniformity and simplicity we should, of course, apply as far as possible, the same pictures and theories to all substances in nature. It should be apparent, nevertheless, that the differences between typically crystalloidal and typically colloidal substances are sufficiently great to warrant a new and more flexible viewpoint.

COMBINING RATIO (? VALENCE) AS A CONTINUOUS VARIABLE

From a purely experimental point of view, the valence or combining ratio of atoms, or groups, can be determined from the molar ratio of substances liberated at the electrodes on electrolysis. With chemical compounds this ratio is generally a simple whole number, but with colloidal compounds, like proteins and soaps, the ratio of acid to base liberated by the current varies with experimental conditions (pH, concentration, etc.). This abnormality is usually explained, as due to the presence of micells or complex ions (3). Independent of these views, however, it is possible to deal with this variable ratio—which, when constant, is called valence—as a continuous variable, depending on external conditions.

In the case of ions attached to a charged particle (fig. 1) the affinity—or valence, if one chooses to extend the meaning of that word—can also vary. The number of ions associated with the particle will depend on the charge of the particle, therefore on its electrical potential. If this increases above a certain value—the critical potential of the adsorbed ion—then the latter will have its charge neutralized and will be liberated in the atomic state.

Another instance of adsorption, which is even more difficult to distinguish from chemical combination is afforded by a monomolecular film of oleic acid floating on water containing a little sodium hydroxide. It has been proven by Hartridge and Peters (4) that the amount of sodium hydroxide combined with the oleic acid varies continuously with the pH—and Rideal (5) has even calculated this so-called combination from Gibbs' law of surface adsorption.

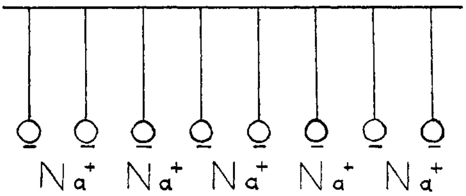

FIG. 2. ADSORPTION OF SODIUM IONS BY OLEIC ACID FILM FLOATING ON WEAK NaOH SOLUTION

The aptitude to combine in all ratios is not restricted to surface adsorption. Figure 3 shows how the composition of a soap gel or solution varies with pH. There is no reason whatever to suppose that the neutralization of oleic acid by sodium hydroxide is not uniform, in these instances. In other words, the composition of the gel and the affinity of sodium ions for oleate ions depends on the pH, which is an electrochemical potential.

The idea that combining capacity might be considered from a dynamic point of view, occurred to the writer originally from a different set of considerations: There are numerous physical laws which can be conveniently expressed in terms of an intensity factor, like pressure, and an extensive factor, like volume. These laws tell us how a change in the value of one of these factors, in one phase or system, affects the corresponding factor in a related system. For instance, the change in vapor pressure of a liquid

(dp) with change in total pressure on the liquid (dp') may be expressed thus

$$Vdp = V'dp'$$

where V and V' are the specific volumes of vapor and liquid respectively.

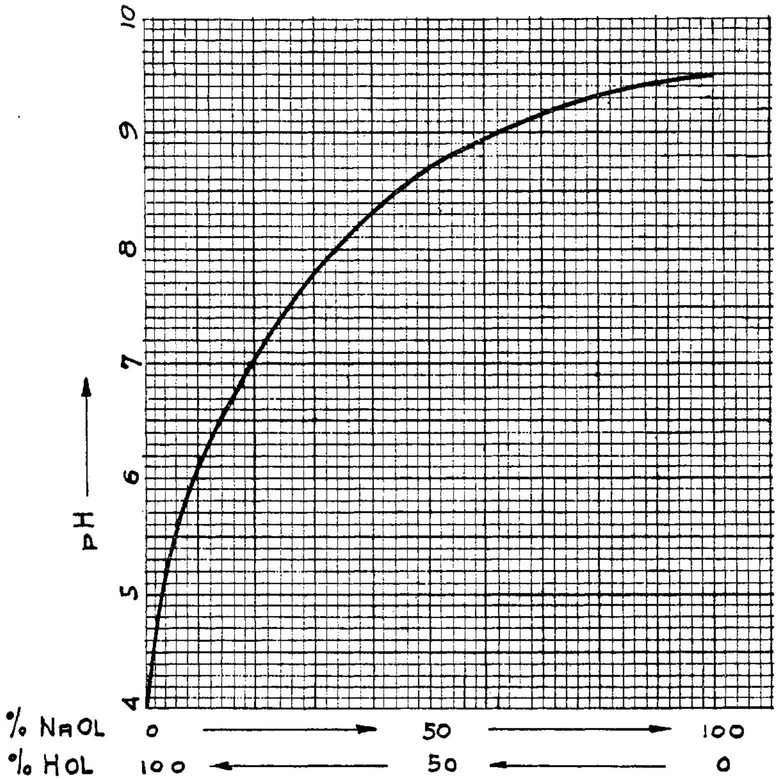

Fig. 3. Relation between pH of 0.3 Per Cent Sodium Oleate Solution and Per Cent Composition

Note: pH determined by means of indicators

The relations between vapor pressure and osmotic pressure or swelling pressure, of osmotic pressure and surface pressure, can be expressed in an identical manner (6).

Similarly the relation between electromotive force and ionic pressure is given by

$$(Fn)dE = Vdp$$

where dE = change in pressure of electrons (e.m.f.).
dp = change in pressure of molecules or ions.
F = Faraday's constant.
n = valence; it corresponds to gas volume or space distribution of molecules and may, indeed, be considered a function of the *space distribution of electrons*.

Those who care to have a picture in terms of electrons may imagine that in the case of colloid compounds the electrons lost by the positively charged atom do not go to a single other atom but are shared, or revolve around a number of atoms or molecules. With this crude picture as a beginning one would be led to inquire about the orbits, the number, and the frequency of these electrons that move around several molecules. Investigations on particle size, extensibility and sensitivity to light of various wave length would naturally follow.

THE PRACTICAL IMPORTANCE OF A THEORY

Let us suppose that two young chemists are asked to carry out research work in an industry dealing with colloidal substances like rubber, soap, cement or cellulose. One of these young men has been taught, and believes, that atoms can only join in definite ratios. The other believes that they can combine in all proportions. How will these hypotheses influence their work?

We know what the classically trained chemist would do. If engaged in the investigation of soaps, he would begin to purify and separate various fatty acids and prepare their salts; he would succeed eventually in obtaining crystals of sodium oleate, dioleate, and tetra oleate. If working with gelatin, the stoichiometrist would try to obtain crystals and spend most of his time in proving that such compounds as sodium gelatinate and gelatin chloride, have constant ratios between their constituents (7). If he were in the nitrocellulose industry, the man who believes in constant ratios would continue to discuss mono-, di-, and tri-nitrocellulose and attempt to prepare them pure, as others have done for the last half century.

Now, this point of view is entirely correct. By trying hard enough, and long enough, one may succeed in preparing, under special conditions, crystals of gelatin chloride (8) or nitrocellulose. Unfortunately, such crystals would not have the properties of the common substances which go by that name.

A soap manufacturer may have been in business a lifetime without ever having seen crystals of sodium oleate. He is not interested in that aspect of his material; therefore he does not appreciate the efforts of the classical chemist and trusts the production in the hands of technical men. On the other hand, it so happens that the man who takes the view that atoms can combine in all proportions will necessarily be led to investigate those properties of colloid systems which are of greatest practical value to biology and industry. He will inquire how the ratio between oleic acid and alkali affects the properties of the system, e.g., its pH, its power of absorbing water, its elasticity, etc.

In biology he would find out the relation between the amounts of the constituents and factors like pH and rH (oxidation-reduction potential), swelling pressure and other important physiological facts.

In dealing with cellulose and nitrocellulose the careful investigator would not simply determine, say, the copper value, and forget that the intensity of oxidation is just as important as the amount of oxidation. He might be led to inquire into the intensity of nitration of nitrocellulose rather than the relative proportions of mono-, di-, and tri-nitrocellulose. Also, as already pointed out, his attention would be forcibly drawn towards properties like polymerization, elasticity and sensitivity to light.

It has been retorted, with perfect truth, that there is nothing in the doctrine of valence or the law of constant proportions that will prevent a man from carrying out the same kind of experiments; that, in fact, much of the advance in our knowledge of colloids has been made by people who held strictly orthodox stoichiometric views. This is true but not sufficient. If one man has learned Chinese and another French, there is nothing to prevent the one who knows Chinese from going to France or the one who speaks French from visiting China. But the immense probability is that, if they had leisure and means, the one who has read about China will cross the Pacific to see the Chinese wall while the other who has studied French history will cross the Atlantic to see the Cathedral at Rheims. There is no question here as to whether Chinese or French is the truer language, and similarly, the point is not whether valence and combining power are continuous or discontinuous. The essential fact is that these two views direct our attention to different problems.

TABLE 2

	BOUNDED BY PLANE FACES	SOLID	SHOW DOUBLE REFRACTION	GIVE X-RAY DIFFRACTION IMAGE
True crystals	+	+	(+)	+
Fine grained rocks or crystalline powders		+	+	+
Liquid crystals			+	(+)
Stretched gelatin, rubber, etc			(+)	+

CRYSTAL FORMS AND COLLOID FORMS

As an example of the tendency to apply to colloid systems ideas derived from the study of chemical compounds—and in doing so to neglect the intrinsic properties of colloids—we may consider the use of the word "crystal" in connection with substances like rubber or cellulose. The term "crystal" originally defined a solid substance bounded by plane faces. Subsequent work with the microscope showed that most crystals are double-refracting and, more recently, Laue and Bragg have shown that all crystals give definite x-ray diffraction patterns. Mineralogists found it convenient, in the identification of minerals, to rely more upon optical behaviour than external shape as a criterion of crystallinity. Further, Lehmann (9) showed that certain liquids exhibit a property in common with crystals, namely double-refraction, and the term "liquid crystals" was used to show this similarity. Finally x-ray patterns were ob-

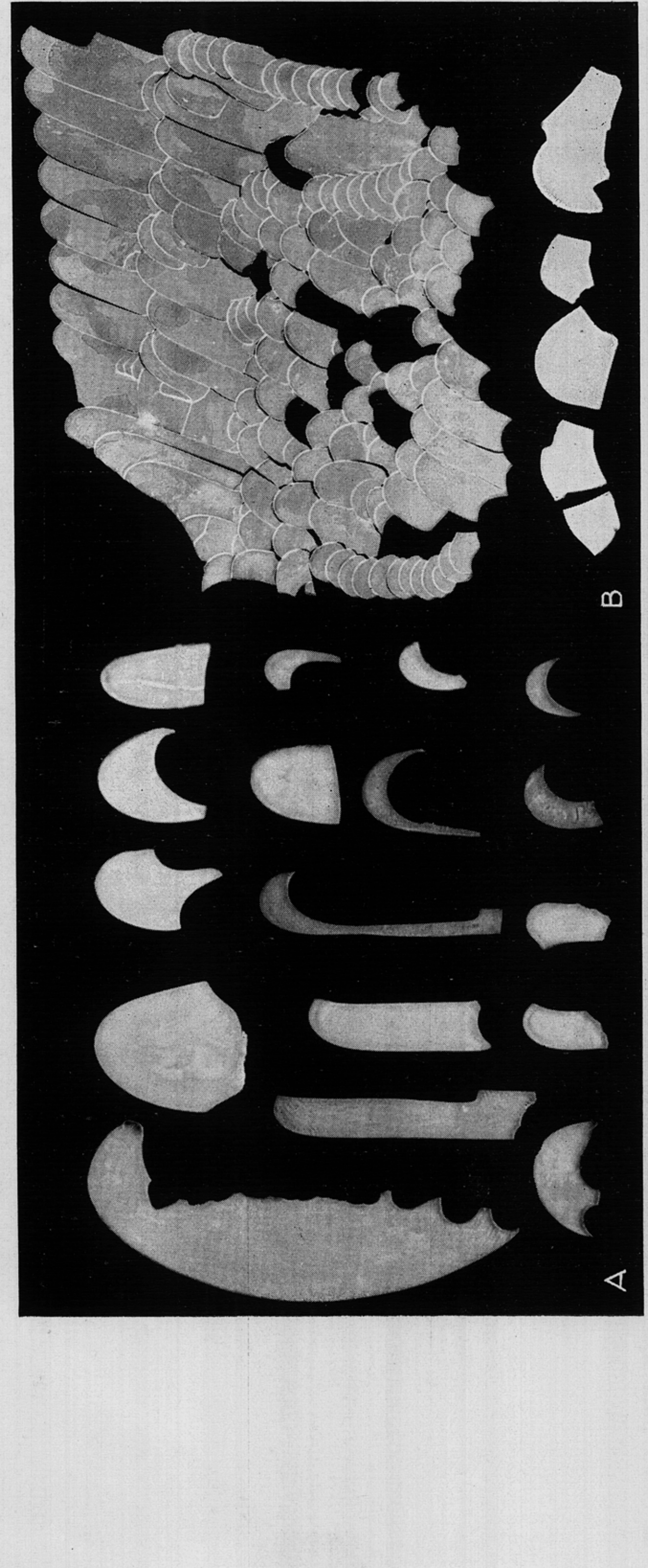

FIG. 4. COLLOID FORMS OBTAINED WITH ETHYL CELLULOSE

tained from rubber and some other colloids, frequently under tension, which showed that a certain similarity exists between colloids and crystals (10). The x-ray diffraction pattern can be obtained by the uniform arrangement of very small particles that are not necessarily bounded by plane faces. Thus the x-ray diffraction method is more inclusive than the former methods of judging crystallinity, and the use of limiting terms to describe the original conception of crystallinity becomes necessary. G. L. Clark (11) has recognized this by defining two states: "the *paracrystalline* state, involving the true, incipient and transition processes which ultimately yield the true crystal with its permanent symmetrical disposition in direction and space" and "the *metacrystalline* state, a transient symmetrical arrangement of diffracting centers under special external conditions, which is not a transition towards a true crystal." All that the x-ray patterns indicate is a certain regularity in the arrangement of the constituent particles—and this is but one out of four important properties of a true crystal. It would be hardly correct to state that a book is crystalline because its leaves are arranged in definite order.

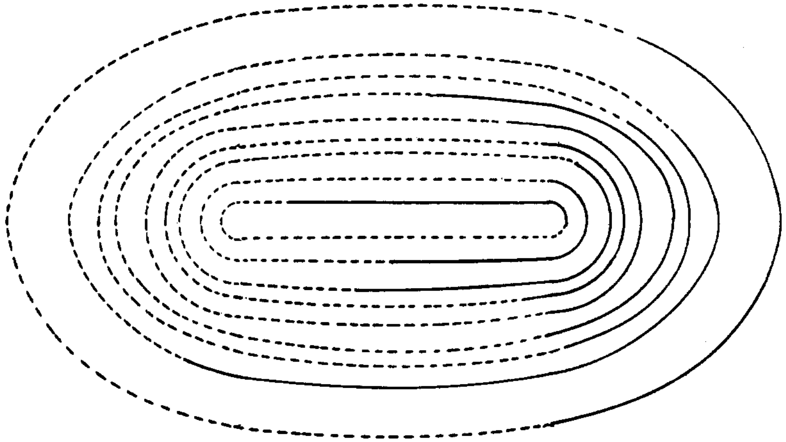

FIG. 5. REGULARITY OF COLLOID FORMS

The chief objection to the use of the word "crystalline" in connection with colloid compounds like cellulose is that it directs our attention to straight lines and solid angles. In reality, a curved shape appears to be typical of colloids, just as the crystal is the normal form of a chemical compound. Figure 4 shows colloid forms obtained in films of ethyl cellulose.[3] It will be seen that the curves can be fitted in a series of ellipses with common foci (fig. 5). This suggests that colloid forms follow as definite and simple laws as crystalline forms do, and reveals a valuable avenue of approach to the study of the shapes of bio-colloids such as leaves and flowers,[4] a field which has been completely ignored by stoichiometrists. "Of all problems in physiology that of form is least approachable" states Warburg (12) and, we may add, "from the classical point of view."

CONCLUSION

The history of science supplies many examples of the limited usefulness of theories. A new theory is generally based upon a few simple hypotheses; it coördinates known facts and leads to new knowledge. As the number of facts to be explained by a given theory increases, it is often found that the original simple hypotheses no longer suffice. This is the position reached by valence theories with reference to the study of colloids.

The study of colloid behaviour is of relatively recent growth. Many of its most important aspects like the laws that regulate colloid forms and the action of light on colloids have hardly been touched upon. It is important that we approach this study with an open mind. If necessary, let us be ready to accept the viewpoint of variable affinity which broadens our concept of valence by removing an unnecessary restriction. It is probable, moreover, that we shall eventually be constrained to give up

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[3] These were obtained on pouring a 10 per cent dispersion of ethyl cellulose in butyl acetate on a glass plate, so as to form a layer 3 mm. thick, and evaporating at 60°C.

[4] Examples of leaf-like forms taken up by inorganic salts (NH_4Cl, $MgSO_4$), etc.) are illustrated in Kapacewski's book "L'état colloidal et l'Industrie," Paris 1927, p. 282.

our cherished views of the electron as a definite particle, and picture it as a system of waves defined by a set of equations. It is to be expected that these new ideas will agree better with a continuously variable affinity than with a fixed valence.

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