Some Fundamental Principles of the Author's Theory of the Dispersoid (Colloid) State.

Ву

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A. General Principles.

- 1. All the properties (both chemical and physical) which earlier were considered as specific of the colloid substances, appear spontaneously with *every* solid substance as its subdivision progressively increases, irrespective of the means by which this subdivision is brought about (e. g. whether they be chemical, physico-chemical, physical, mechanical, and the like).
- 2. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on dissolving, through a *colloid stage of solution*.

¹ The terms: "Dispersoid", "Dispersoidal" were in due time suggested by myself to be used instead of the terms: "Colloid", "Colloidal" which latter have entirely lost, according to my opinion, their original value. The general science dealing with the dispersoid state I proposed to call "Dispersoidology", to be conveniently subdivided further into Dispersoid Physics and Dispersoid Chemistry, or still shorter: Dispersoidics and Dispersoidy correspondingly / The corresponding German terms are:

Dispersoidologie Dispersoidophysik = Dispersoid(phys)ik = Dispersoidik. Dispersoidohemie = Dispersoid(chem)ie = Dispersoidie. It should be noted here that the term "Dispersoidik" was suggested for the first time by Wo. Ostwald (see: Koll.-Zeitschr. 33, 300. 1923), but somewhat in a different sense. I maintain that the short terms: "Dispersoidics" and "Dispersoidy" are most convenient for designating correspondingly the physics and the chemistry of the dispersoids.

² Compare the present paper with my paper of analogical contents in "News of the Ural Mining Institute", Vol. 1 (1918/19); Section III; pp. 65-69.

And in fact, if, with a size of the crystalline grains falling below the limits of microscopic resolvability, the colloid properties (Principle I) begin to assert themselves somewhat sharply, it is obvious that, were we to stir up a pinch of some powdered substance in a liquid in which it is able to dissolve, the grains of this powder must necessarily pass through a colloid stage of solution, antecedent to their complete dissolution, i. e. before they break up into molecules (in special cases – into atoms).

For the cases of solid substances rapidly dissolving in the liquids selected, the time intervals during which this colloid stage of solution would persist, will naturally be very small; but nevertheless, even for these cases, the existence of a colloid stage of solution is beyond any doubt.

3. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on crystallizing, through a colloid stage of crystallization.

For the cases of a *rapid* increase in size, i. e. of rapid growth of the vanishingly small crystals initially formed, the time intervals during which the *colloid stage* of crystallization would persist, will naturally be very small, but nevertheless, even for these cases, the existence of a *Colloid stage of crystallization* is beyond any doubt.

- 4. For any substance such physico-chemical conditions of crystallization and solution may, according to one's wish, be realized, at which the colloid stages of crystallization and solution would last for periods of time, of which the corresponding durations may be varied, according to the above mentioned conditions, within extremely wide limits, viz.: from such practically vanishingly small values as amount to e. g. fractions of a second and seconds, up to such large values as are measured by years, decades and even centuries.
- 5. For any given solid substance, suitable solvents and such temperature conditions may be found, at which, in the solutions of this solid substance in the above solvents, large molecular complexes will form by way of association and

solvation, subsequently to persist in a state of kinetic equilibrium,—which will not be inferior in size to the particles existing during the colloid stages of solution and crystallization of substances (vide: Principles 2, 3 and 4).

To the same species of the colloid state the solutions also belong of such solid substances, of which the molecules contain a large number of atoms condensed by ordinary chemical forces (e. g. the proteins and the like), or — to put it in a different way — the solutions of substances of composite chemical nature.

All the above enumerated principles hold equally for the case of the coexistence of phases other than solid and liquid¹ (e. g.: liquid and liquid).

B. Principles on the Temperature-Irreversible Dispersoid State (the Dispersoid State of Substances Present under the Conditions of Slight Solubility)².

I. ON THE DISPERSOID SOLUTIONS OF SMALL CONCENTRATIONS.

On realizing the reaction, which is practically instantaneously completed, of the formation of any substance in a dispersion medium in which this substance is little soluble, there arises a dispersoid solution of this substance, which is sufficiently stable with small concentration of the reacting solutions; however insignificant the solubility of the substance in the dispersion medium selected, and however indifferent this latter might be toward the substance, it is still possible

This I had pointed out in my communications read before the Russian Chemical Society on Dec. 7, 1906, and April 5, 1907, and so on. / Journ. Russ. Chem. Soc. 38. 1400 (1906); 39. 619-621 (1907)/. Quite independently from my works, Wo. Ostwald arrived in 1907 at his teaching of disperse systems, and gave them a rational classification (Koll.-Zeitschr. 1. 331-341/1907/) /April-May issues/.

I confine myself to adducing the principles pertaining to the preparation of dispersoid solutions and dispersoid precipitates of solid substances in liquids by the crystallization method.

to prepare, with sufficiently small (sometimes-insignificantly small) concentration of the reacting solutions, a sufficiently stable dispersoid solution of this substance.

II. ON THE DISPERSOID SOLUTIONS OF CONSIDERABLE CONCENTRATIONS.

- 1. The dispersoid solutions of considerable concentrations will immediately coagulate in such dispersion media as are practically altogether indifferent toward the disperse phase.
- 2. For the preparation of dispersoid solutions of considerable concentration, the presence is requisite of conditions for dispergation¹

¹ The fundamental conditions for dispergation (peptisation). The conditions for dispergation are as follows: (Compare e.g. P. P. von Weimarn. Journ. Russ. Chem. Soc. 40, 1785 / 1908 /; Koll.-Zeitschr. 4, 127 / 1909 /; Grundzuge der Dispersoidchemie. 76 / 1911 /; Kolloidchem. Beih. 1, 105 / 1910 /; Kolloides und kristalloides Loesen und Niederschlagen. 554-638. Kyoto 1921.)

a). The dispergator, that in the substance which is introduced into the dispersion medium in order to obtain a stable dispersoid solution, must form, when present in sufficiently high concentration, a soluble chemical compound with the disperse phase in question; with small concentration of the dispergator, no such compound must be formed, or else it must be strongly dissociated, so that the disperse phase be also the saturating substance.

b). Previous to the introduction of the dispergator, the dispersion medium must practically not resolve the disperse phase.

If, in preparing a dispersoid solution, one starts from a precipitate, the degree of dispersity of this precipitate must be near to the dispersoidal degree of dispersity.

The experimental material from which these conditions were derived is very extensive: not only had I repeated A. Lottermoser's experiments with silver salts in aqueous media, but I have additionally carried out investigations on the peptisation of the precipitates of these salts in mixtures of water and alcohols of the fatty series, as well as of many other salts of the alcalineearth and the heavy metals, and also of elementary substances (such as: Ag, Au) and hydroxides (e.g. of Fe, Al, Si). Notwithstanding the multifariousness of the substances, the general results obtained were thoroughly equal. Owing to the progressively decreasing capacity of the alcoholicaqueous media to produce dissociation, it was possible, easily to regulate the processes which are taking place at the surfaces of the dispersed particles; I was thus able to establish that the dispergation ability is directly dependent on the energy with which the soluble chemical compounds arising at corresponding conditions are retained by the dispersion medium; this energy is varying, in most cases, as a first approximation, in the same sense as varies the solubility of the dispergator, and series of dispergators are thus obtained (similar to those by Hofmeister), closely connected with the solubility and the solvation capacity.

(peptisation) and for dispersoidal parasitism¹. If these conditions are present, then any substance can be obtained in the state of extremely stable (for years, decades, and possibly—centuries) dispersoid solutions, of which the concentration may attain—to the detriment of stability, of course—several percent, or even several tens percent.

3. The complex compounds, which exist for every substance, make it possible to realize, for any substance, the conditions necessary and sufficient for dispersation (peptisation) and for dispersoidal parasitism, and to prepare stable dispersoid solutions of high concentrations.

For this purpose, it is necessary to select such a dispersion medium and such temperature conditions, which would make easy the regulation of the dissociation of the above complex compounds.

A mixture of water and alcohols of the fatty series offers an especially convenient dispersion medium for preparing dispersoid solutions at the expense of a dissociation of complex compounds, and of the presence of dispersoidal parasitism: elementary substances (e. g. Ag, Au and others), hydroxides (Si, Al, Fe, and others), salts (sulphates, chromates, carbonates, phosphates, arsenates, phosphites, arsenites, tungstates, molybdates, silicates, sulphides, fluorides, chlorides, bromides, iodides, borates, oxalates, tartrates, citrates, and so on) of the alcalineearth and the heavy metals, can easily be prepared in the state of stable dispersoid solutions in alcoholic-aqueous media².

III. ON THE DISPERSOID PRECIPITATES.

1. Any substance whatever can be obtained under the form of

The dispersoidal parasitism / Compare e.g. P.P. von Weimarn. Kolloidchem. Beih. IV. 125; 188 (1912–1913) / consists in increasing the stability of dispersoid solutions by way of a linking together of the particles of the disperse phase with the molecules or, more generally, with the particles of substances which are more soluble or more strongly tied up with the dispersion medium than is the pure disperse phase. This linking together is mostly not of a static, but of a dynamic character.

Whenever the above explained conditions of dispergation are present in the disperse systems, dispersoidal parasitism takes place to a greater or smaller extent.

² These solutions can be obtained either through condensation, or through dispergation (peptisation) of precipitates.

dispersoid precipitates, whenever the practically instantaneous reaction of its formation is realized in dispersion media, in which the substance in question is extremely slightly soluble. (The precipitation curves for *normal* cases are given in the drawing on p. 7).

- 2. The less the dispersion medium selected is able to dissolve the substance in question, and of the more this latter is indifferent toward the dispersion medium, the longer will the high degrees of dispersity of the dispersoid precipitates persist.
- 3. The homochemical and heterochemical cohesion of the dispersion medium and of the substances either "colloidally" or "truly" dissolved therein, with the disperse phase, makes, under suitable conditions, the process slower, of union of the disperse particles (e. g. into aggregates, flakes, crystals), and reduces the rate of the recrystallization process.

This cohesion makes for an increase, under suitable conditions, of both the stability of colloid solutions of considerable concentrations, as well as the stability of supersaturated true solutions with large absolute supersaturation, e. g. of supersaturated solutions of well-soluble substances in water or in other solvents.

IV. ON THE FORMS AND THE CHEMICAL COMPOSITION OF THE PARTICLES PRESENT IN THE DISPERSOID SOLUTIONS AND IN THE DISPERSOID PRECIPITATES.

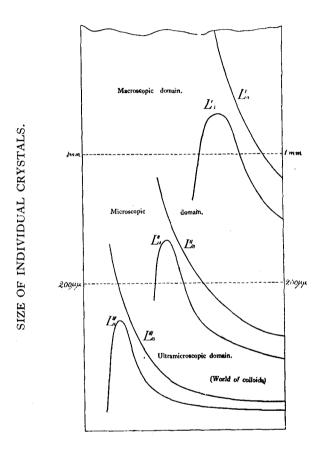
(see: Figs. 1-3).

- a. On the forms of the particles.
- 1. The particles in the dispersoid (suspensoid) solutions can

P. P. von Weimarn. Journ. Russ. Chem. Soc. 39. "On the Chemical Composition of Microcrystalline and Ultramicrocrystalline Precipitates" 650 (1907); "On Indetermined Chemical Compounds" 1461 (1907). News of the St. Petersburg Mining Instit. 1. 255 (1908) etc.; Koll.-Zeitschr. 2. 206 (Fig. 3); 327-328 (1908). 6. 32 (1910). 7. 156, Fig. 1 (1910); 12. 308 (1913) and so on; Kolloidchem. Beih. 1. 399, Fig. 1 (1910); 4. 88, "Selbstreinigung' (Selfpurification) 111 and following. Grundzuege der Dispersoidchemie 15-20 (1911). Verlag von Theodor Steinkopff. Dreseden, and so on. For a most detailed account, see: P. P. von Weimarn. "Kolloides und kristalloides Loesen und Niederschlagen", Kyoto 1921. Compare: Presentation of this part of my theory of the colloid state in the work by Leonardo Cassuto, Der Kolloide Zustand der Materie, 221-222 (Fig. 18), and 230-231 (1913). Verlag von Theodor Steinkopff.

Graphic Representation of the Conditions for the Transition of Any Solid Substance from the "World of Crystalloids" to the "World of Colloids" and vice versa under the Influence of the Variations of the Solubility and the Concentration of the Reacting Solutions (respectively the Velocity of Solid Phase Formation).

(In accordance with the theory and the experiments of P. P. von Weimarn),



CONCENTRATION OF THE REACTING SOLUTIONS.

(respectively: velocity of solid phase formation).

Explanations:

The precipitation curves (e. g. L_A^I) have, at first, a maximum which, in the course of time, is being displaced to the left and upwards, so that, after the lapse of some time from the beginning of the precipitation, the curves will practically assume a sensibly hyperbolic (e. g. L_B^I) form (y-const./x¹¹, where, x, signifies e. g. the absolute supersaturation, being equal to the amount of the substance of which weare studying the precipitation, minus the solubility of this substance: x=Q-L). The solubility L^{I} is greater than L^{II} , L^{II} being greater than L^{III} . The values of L^{III} are already so small that

the substance is said to be under the conditions of a practically complete insolubility.

As may clearly be seen from the Scheme, with the decreasing solubility of the substance, other conditions being equal, its precipitation curves are shifting downward and extending in the left direction.

What is plotted as ordinates are the magnitudes of the individual crystals; one is to be very careful, not to confound them with the magnitudes of the aggregate-particles (aggregates built up of individual crystals) of the precipitates.

either be isolated ultramicrocrystals, or ultramicroaggregates of minute ultramicrocrystals.

- 2. Dependent on the conditions of dispersoid synthesis, all of the particles present in the dispersoid solution may represent isolated ultramicrocrystals, or all of the particles may be ultramicroaggregates of ultramicrocrystals, or finally, a mixture of both kinds of particles may be present in the dispersoid solution.
- 3. Dependent on the conditions of dispersoid synthesis, the isolated ultramicrocrystals may represent holohedral crystals, figures of growth, needles (the long needles are specifically characteristic of such substances as will crystallize in so-called negative crystals), spherites, and so on.
- 4. Dependent on the conditions of dispersoid synthesis, and also on the peculiarities of the substance with respect to its crystallization (e. g. its yielding positive or negative crystals), the ultramicroaggregates may either display the form, more or less rounded off (the contours being either somewhat regular or altogether irregular), of ultramicroflakes, or they may display the elongated form of ultramicrofibres.

b. On the chemical composition.

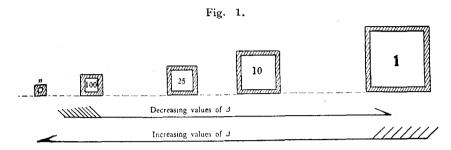
1. (See: Fig. 1.). The chemical composition of some substance X which, by the superficial layer of its crystal, is taking up some other substance² Y, is expressed by the general formula³: XY₄, where the value of Δ , being practically zero if the substance is taken in coarsely dispersed crystals (e. g. No. 1 in Fig. I), will increase with the increase of the degree of dispersity (respectively-the decrease of the crystal

¹ This is the case which is most frequently met with under the ordinary conditions of dispersoid synthesis, whenever not excessively small concentrations of the reacting solutions are used.

² This reasoning will certainly not be altered, if some additional substances: Y₁, Y₂, and so on, are taken up simultaneously.

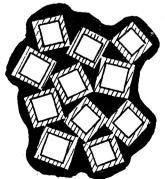
It goes without saying that this is the expression for the mean composition, for it is clear (see Fig. 1) that, while the superficial layer is of some particular chemical composition, the composition of the nucleus of the crystal is a different one (e. g. that of the pure substance X). It is the average of these two compositions that can be expressed by the formula XY△

size) and decrease with the decrease of this latter (respectively—the increase of the crystal size).



- 2. In conformity with Principle 1, if the conditions of the experiment are such that the *only* variable is the degree of dispersity (the crystal dimension), then the change in chemical composition of the disperse phase particles is simply a consequence of the magnitude of the surface bound to unit mass having changed.
- 3. The reasons (see Principle 1) to which the taking up of substance Y by the superficial layer of the crystals X was due may be extremely manifold: they may be of identical nature with those producing true solution of substances (e.g. the formation of complex compounds), but this taking up may also be due to the formation on the surface of the crystals of some insoluble reaction product (e. g. of AgJ on Ag-crystals), and so on.
- 4. When the size of the ultramicrocrystals becomes extremely small (see Fig. 1: the crystals No. 'n', and even smaller ones), so





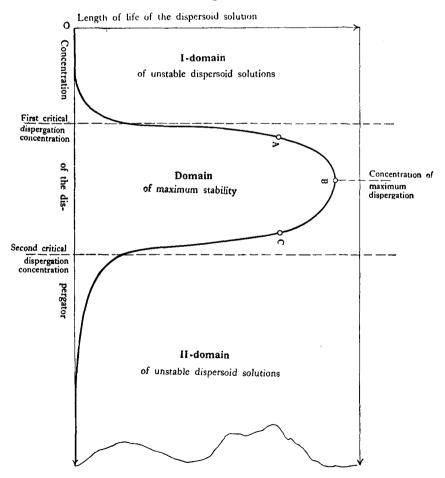
that the superficial layer is already constituting by far the larger part of the ultramicrocrystals, it will no longer be possible to draw a sharp boundary between that kind of ultramicrocrystals and the complex molecular aggregates which are of an equal size with the above ultramicrocrystals (see below: on the vectoriality of the molecules).

5, (See Fig. 2). The aggregates

of ultramicrocrystals having soaked in into their capillary interstice channels the dispersion medium with everything contained therein, their chemical composition is naturally a still more complicated one than is that of the isolated ultramicrocrystals.

- 6. With either the contraction or the internal relaxation of the aggregates, a change in chemical composition is taking place.
- 7. With the breaking down of the aggregates, and with the increase in size of the crystals they were made of, a "self-purification" takes place of disperse phase and of precipitates, while matters absorbed are, of course, given back to the dispersion medium.

Fig. 3.



- 8. (See: Fig. 3). With varying concentration of the despergator the composition of the dispersed particles (XD_A) will also vary, keeping pace with the alterations suffered by the dynamic processes which take place at the surfaces of the dispersed particles (both the isolated and the aggregate-particles). For the same length of life (points A and C in the stability curve) the composition of disperse phase in not the same.
- 9. (See: Fig. 3). It is altogether irrational, to work out theories as to the chemical composition of the disperse phase of dispersoid solutions, on the ground of the results obtained in studying these dispersoid solutions subsequent to their purification, by either dialysis or some other analogous means, for it is quite clear that, by removing the dispersator, we are producing changes in both the composition of the disperse phase and the length of life of the dispersoid solution.
- 10. (See: Figs. 1, 2 and 3). The dispersoid solutions contain generally, for each given moment, a disperse phase with particles of different magnitudes, these magnitudes (as well as the closeness of contiguity of the ultramicrocrystals within the aggregates) being subject to constant changes in the course of time.

Hence it clearly follows that it is quite out of question, to speak of a definite chemical composition of disperse phase.

11. The dispersoid precipitates, which are separated out on coagulation of a dispersoid solution, will go over, with time, into more coarsely-dispersed ones (coarse microcrystals), while acquiring a constancy of composition, for there is a "self-purification" taking place simultaneously, so that in the last item we shall practically have:

$$XY_{\Delta} = XY_{0} = X$$
.

12. The equation:

$$\lim (XY_{\triangle})_{t-T} = XY_0 = X$$

may be regarded as schematic expression for the limit to the changes in chemical composition of the disperse phase—at first in the dispersoid solution, and afterwards under the form of the precipitate given birth to by the above dispersoid solution—when, after the lapse of time t=T, this disperse phase will have reached a coarsely—disperse (coarsely—microcrystalline) condition.

¹ The letter 'D' is here to signify symbolically the chemical composition of a solvated molecule of the dispergator.

C. Principles on the Temperature-Reversible Dispersoid State.

- 1. Any substance whatever can be obtained, on cooling its solution sufficiently rapidly, in the state of a highly-disperse jelly or in that of a highly-disperse glass which, on being sufficiently rapidly heated, will, in a reversible way, go over into the original true or dispersoid solution, without separating the substance in a coarsely-disperse condition.
- 2. In the above processes, the rate of cooling, and the rate of heating can be reduced, by properly selecting the dispersion medium, to values so small, that it becomes *practically* impossible to obtain from such a dispersion medium, the substance in coarsely-disperse condition.
- 3. The most important factors which permit to obtain any substance whatever in a typical reversible dispersoid condition are: solvation, solventolysis, dispersoidal parasitism, and the ability of the dispersion medium to solidify to glass or to jelly (For instance, the alcoholic-aqueous dispersoid solutions mentioned in Section B, II, 3 are able to solidify reversibly, *under suitable conditions*, so as to form jellies or glasses).

D. The Principle of Vectoriality of Matter.

1. Matter is vectorial in all its states; and no such thing as absolute amorphy exists in Nature.

This principle is to be understood in the broadest thinkable sense; that is to say, in the sense that, not only are the various solid systems which up to the present were and still are described as "amorphous" (e.g. the amorphous and the colloidal precipitates, the glasses, and other formations of a similar kind) made up of very minute particles endowed with vectorial structure and vectorial forces (i.e. of very minute crystals), but also the particles (molecular complexes, molecules, atoms) as are present in "true" solutions as well as those

P. P. von Weimarn. Journ. Russ. Chem. Soc. 1906 and 1907; Kolloid-Zeitschrift 2, 83 (1907); 219 (1908) and so on.

constituting the liquids and the gases, are endowed with *vectorial* forces and a *vectorial* structure.

In other words, vectoriality is a property inherent in matter; and therefore, whatever the elements into which we might differentiate matter (electrons, subelectrons, and so on), these elements must equally possess vectorial forces, and be constructed vectorially.

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Note: From September 1907 the publications of the present author began to appear regularly in "Kolloid-Zeitschrift" (respectively in "Kolloidchemische Beihefte") where they may easily be found.

XXIII. A New World of Chemical Compounds. May issue 1919 of the Journal "Young Russia" published in Ekatherinburg. This paper was also published in the News of the Ural Mining Institute, Vol. 1. Part III. 35-42 (Russian); 43-49 (English); 70-77 (German) 1918-1919. See also: Koll.-Zeitschr 28. 97 (1921). In the work quoted evidence is adduced that any substance whatever may, under appropriate conditions, form a complex compound with any substance with which it has common atoms or atomic groups. Complex compounds of that kind may be called homochemical, or still better, to bestow on the term a purely empirical character,—homoatomic double compounds; e.g. for the BaSO4 these compounds will be:

BaSO₄. 'x**Ba**Cl₂; **Ba**SO₄. x**Ba**Br₂;......; **Ba**SO₄. x**Ba**(NO₃)₂;......; **Ba**SO₄. x**Ba**(CNS)₂.....; Ba**SO₄**. xMn**SO₄**; Ba**SO₄**. xCo**SO₄**;; Ba**SO₄**. xNa₂**SO₄**;.... and so on. Compare also : Koll.–Zeitschr. **32**. 145 (1923).

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