

Chemistry. — “*Colloïds and the phase rule.*” By Dr. E. H. BÜCHNER.
(Communicated by Prof. A. F. HOLLEMAN).

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The question, whether the phase rule can be applied to systems, in which a colloïd occurs, and if so, in what way, has been discussed more than once. Some investigators have concluded, that it is not allowed; the greater part, however, think, that — under certain restrictions — it can be done; systems, in which irreversible reactions occur, must, for instance, be excluded¹⁾. The question has been examined most closely by PAVLOV²⁾ and JONKER³⁾. Both consider a colloïd a system of two phases, but, whilst JONKER applies the usual rule, PAVLOV introduces a new independent variable, namely the specific surface of a phase, i.e. the ratio of its surface to its quantity. He gives the phase rule then naturally the form

$$F = n + 3 - r,$$

without applying it practically or giving any experimental proof of its exactness. It is certainly easy to see, that such a proof will be impossible, since the number of degrees of freedom is found to be just as great if one applies the ordinary phase rule, provided that the colloïd is taken as one phase. If we take e.g. a solution of gelatine in equilibrium with its vapour at a certain temperature, $n = 2$, and according to PAVLOV $r = 3$; the system has therefore one degree of freedom. If, on the other hand, we consider the solution one phase, and apply the familiar rule, then it follows from $F = n + 1 - r$ (1, because the temperature is fixed), that in like manner $F = 1$, because now r is taken = 2. Thus it will never be possible to decide by experimental evidence, which of the two formulae has to be applied; this must be deduced from considerations a priori: we should ask ourselves whether really a new independent variable must be introduced, and whether a colloïd actually consists of two phases. As to these questions, JONKER has adopted the view, that neither the surface-tension, nor any other quantity must be taken into consideration, and that therefore the ordinary rule may be maintained. Taking a colloïdal solution as composed of two phases, one will find — ceteris paribus — one degree of freedom less than in an ordinary solution, and JONKER thinks this to be confirmed by the absence of the depression of the freezing point and the other quantities connected therewith in typical colloïdal

¹⁾ HENRI, Z. phys. Chem. 51, 31.

²⁾ Z. phys. Chem. 75, 48.

³⁾ Kolloid-Zeitschrift 8, 15.

solutions. From the formula $F = n + 3 - r$ it would indeed follow, that the freezing point depends on the concentration, whereas $F = n + 2 - r$ would lead to the conclusion, that the freezing point does not vary with the concentration, which is in agreement with the observations.

It seems to me that new light is thrown upon these questions, if we take a view, which was brought forward, a few years ago, by EINSTEIN and PERRIN. Our starting-point then will be EINSTEIN'S declaration ¹⁾ that the only difference between a dissolved molecule and a suspended body lies in their size, and that one cannot see, why a number of suspended bodies should not exert an osmotic pressure just as well as a number of dissolved molecules. It will be superfluous to point out, how rich in results this conception has become in PERRIN'S hands. I only wish to mention that PERRIN ²⁾, with the help of considerations on that very osmotic pressure, deduced a formula for the distribution of a suspension under the influence of gravity, which was fully confirmed by the experiments. Should objections be raised against his reasoning, LORENTZ ³⁾ has shown, that the formula can be obtained with perfect strictness. Moreover we find it developed by VAN DER WAALS—KOHNSTAMM ⁴⁾ in a third way; in fact these authors apply to PERRIN'S suspensions a formula, deduced rigorously for ordinary diluted solutions, only making those alterations that are necessary and permissible because of the enormous molecular weight of one of the components. It is quite evident from all this, that suspended granules may really be treated as enormous molecules.

Now it is only a short step to the conception, which I propose, namely, that a colloidal substance must be considered one phase, as well as a solution of sugar in water is one phase. Let us confine ourselves for the present to the sols, cases, that are usually treated as suspensions or emulsions. For these the given conception leads to the conclusion, that they really exhibit a diminution of the vapour pressure, that, therefore, the freezing point changes with the concentration, but at the same time it shows this depression to be exceedingly small, because the molecular weight or the quantity, which we may in this case regard as such, the weight of the particles floating in the liquid — is so considerable. The proposed assumption is therefore in agreement with the experimental results,

¹⁾ Ann. d. Phys. [4] 17, 549.

²⁾ Ann. d. Chim. et de Phys. 8e Sér. T. 18.

³⁾ Chem. Weekbl. 7, 827.

⁴⁾ Lehrb. der Thermodyn. II, p. 567.

as was that of JONKER; perhaps very exact observations on colloïds, the molecular weight of which is not too great, as for instance tannin, may assist in clearing up this point. SVEN ODÉN's¹⁾ solutions of sulphur also, which melt sharply and reversibly, seem to be a favourable subject for the determination of the depression of the freezing point, or, perhaps still better, of the osmotic pressure.

If this idea is accepted, one must evidently reject PLANCK's opinion²⁾; that the alteration of the vapour pressure would afford a means of distinguishing between emulsion and real solution. Emulsions too will show diminution of the vapour pressure, but in such a slight degree, that it escapes observation.

It is curious to note, that the workers in this field have made their experiments as if the colloid consisted of one phase, although they were, of late at least, theoretically convinced, that it was composed of two phases. A striking example is found in JONKER's second paper³⁾. This investigator takes a solution of tannin in water as having two phases; when adding a definite amount of ether, he observes a division into three liquid layers, the composition of which is determined to 0,5 %, 3,1 % and 44,3 % tannin respectively. Now he calls the system, at fixed pressure and temperature, an invariant one, because it is composed of three components and three phases. That is quite correct in my opinion; but, if one conceives tannin in water two phases, why then does tannin in water with some percentage of ether added suddenly become one phase?⁴⁾

Everyone who is acquainted with, for instance, OSTWALD's Kolloïd-chemie, will see, that my conception is absolutely contrary to the current views of the present time. I think this to be caused by the fact, that one has gradually been led to confuse the notions "heterogeneous" and "composed of several phases." OSTWALD⁵⁾ for instance, says: colloidal systems, especially colloidal solutions, belong to the systems, which are called in physical chemistry heterogeneous or plural phase systems, and FREUNDLICH⁶⁾ joins him by remarking, that it is appropriate to consider generally systems of two components to be two-phase systems: real solutions, especially the dilute ones, form extreme

¹⁾ Z. phys. Chem. 80, 709.

²⁾ Thermodynamik, § 223, 3rd ed., p. 205.

³⁾ Kolloid-Zeitschr. 10, 126.

⁴⁾ It will be evident, that I certainly think JONKER's determination of the critical solution temperature of the two phases with a slight percentage of ether to be conclusive.

⁵⁾ Grundriss der Kolloidchemie, 3rd ed., p. 23.

⁶⁾ Kapillarchemie, p. 308.

cases, to be regarded as one-phase systems. This view, the consequence of which would be, that an ordinary solution of salt would consist of two phases, and that even one phase would be composed of separate molecules, is the fundamental difference between OSTWALD and FREUNDLICH on one side, and myself on the other. As to this point I wish to refer to BAKHUIS ROOZEBOOM's clear representation ¹⁾ of the fact, that the notion "homogeneous" is only a relative one, and that, what is called by us a homogeneous system, deserves this name only, because the molecules are so small and our observations not delicate enough. When defining later the "phase" ideal he speaks of homogeneous states (it is clear now, what is meant by this), and further of internally uniform forms of appearance of a substance, differing in state of aggregation, composition or energy. Of course, one cannot speak of a state of aggregation, when treating of molecules; further, the energy content of different molecules will differ, so that one will have to consider each molecule as a phase and there should be as many phases as molecules. Those, who desire a more thermodynamical treatment of the idea phase, will find it in VAN DER WAALS-KOHNSTAMM's text-book ²⁾. When giving a definition of phase, these authors claim that there must exist a relation between the different thermodynamical factors, potentials, pressure and temperature. How can there be any question of that, so long as we have not a complex, composed of numerous molecules, whose number permits us to apply statistical methods? To carry the idea phase so far seems to me to be in complete contradiction to the notion itself, as we are used to apply it. An other question is connected herewith. The defenders of the two-phase conception add, that the systems are complicated by this fact, that the surface of contact between the phases is very great, and that consequently surface forces must play an important role. But this, too, only holds good within certain limits; for, once more I put the question, what, if one of the so-called phases is composed of separate molecules — not an impossible state of affairs, when we think of the size of albumen-molecules? Do the laws of surface action, which are known to us, hold good in that case? It requires no argument to show that the special forces, which certainly come into action in sharply curved surfaces, are always calculated and measured in cases, in which we still have a great many molecules,

¹⁾ Heterogene Gleichgewichte I, 9.

²⁾ Vol II, p. 11. Professor KOHNSTAMM was kind enough to direct my attention to the fact, that in the same book, vol. I, p. 123 the condition, that a phase must consist of a great number of particles, is plainly stated.

and that, when we pass on to the molecules themselves, the ordinary attractive forces — the a_{12} in VAN DER WAALS'-equation — must be able to explain the phenomena in first approximation.

Of course, in this conception we are breaking to a certain extent with homogeneity as a necessary element of the notion "phase". But, as I pointed out above, homogeneous is only relative, and so it is only the limits, which are removed. An emulsion too may after all be homogeneous, as long as we do not divide it in parts of too small a size. It depends on the circumstances, how far one may go on with that. As long as we have in the separated part so many molecules — either "really" dissolved, or suspended granules or droplets of liquid — that statistical methods are applicable, that therefore mean values of velocity, energy etc. may be calculated, so long are we allowed to speak of homogeneity. If we go further — so that finally one granule in a quantity of liquid is left, then we must call this heterogeneous. A system, for instance, consisting of one drop of oil, floating in a mixture of water and alcohol, is decidedly heterogeneous. For the rest, the remarks just made turn out to be the same in principle as the question, how to consider a gas in such extreme dilution, that there is only one molecule in the unity of volume.

To summarize, my opinion is, that when we desire to treat the questions, usually dealt with by means of the phase rule, for the case, that any one of the phases is a colloidal solution, we have to apply the rule in its ordinary form; only when making quantitative determinations, we have to pay attention to the size of the molecules. When, however, we wish to investigate as to whether the so-called suspended granules exclusively consist of one component or — as probably the ions do — condense a mantle of liquid-molecules around themselves, we are not likely to succeed with the phase rule, and we shall be obliged to have recourse to other methods, as for instance those in use for the electrolytic or gaseous ions just mentioned.

Although I have restricted myself to sols, I see no objection at present — in connexion with the results of a previous investigation ¹⁾ — to extending the given considerations to gels.

After the above paper had been written, the April number of the Journal of the American Chemical Society came into my hands, in which TOLMAN treats the same question in an analogous manner as PAVLOV did, though he obtains different results. I shall return to this point shortly in another periodical.

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¹⁾ WOLFF and BÜCHNER, These Proc. 15, 1078.