The following contribution to this section of the Discussion was received from **Professor Dr. Wolfgang Ostwald** (Leipzig) in response to an invitation :—

CONTRIBUTION TO THE DISPERSOID ANALYSIS OF NON-AQUEOUS SYSTEMS

BY

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1. *Introduction.*—Although the study of non-aqueous dispersoids is of well-recognised importance, especially in technical respect—as is proved by the selection of the subject as one of the problems for this discussion—there are only a few researches on certain dispersoid-chemical characteristics of such systems. Solutions of nitrocellulose, *e.g.*, are usually spoken of as colloidal. De Mosenthal¹ has, indeed, found that nitrocellulose solutions in acetone do not dialyse through pig's bladder and parchment paper, and that they do not exert any "osmotic" pressure. On the other hand, J. Duclaux and E. Wollman² observe distinct "osmotic" pressures and at least partial dialysis when using membranes of denitrated collodion. Still less accurate is, for instance, our knowledge of the degree of dispersions in solutions of resins, fats, oils, dyes, &c., in organic dispersion media. *Indirectly* we conclude sometimes that such systems are colloidal in nature because of the marked viscosity-concentration function, the formation of jellies or the phenomena of swelling. An exact characterisation by the classical methods of diffusion or dialysis is almost always missing, however.

The main reason for the want of such researches lies presumably in our methods. We may not, without restrictions, apply to non-aqueous systems the methods worked out for aqueous dispersoids, nor the membranes used. If we study the dialysis of acetone solutions through parchment paper, *e.g.*, we must first establish that there are, with respect to these membranes, *both* diffusing *and* non-diffusing acetone solutions. An always negative dialytic effect, as well as an always positive effect, would only show that the membrane is either too dense or too permeable for the solvent in question to admit of differentiation according to degrees of dispersity. The point is not only whether the membrane in itself possesses a gel structure; the degree of shrinkage or solvation of the membrane must have suitable mean values in the respective organic solvents.

The following is a small contribution to the methodologies of dispersoid analysis for systems, the dispersion medium of which is alcohol of 96 or 97 per cent. The selection of this alcoholic concentration is not arbitrary, but the result of practical experience with alcoholic media of various concentrations. This concentration has proved to yield much more stable and more easily reproducible relations than alcohol of higher strength; the concentration is particularly interesting also in technical respect. Experiments with other dispersion media will be published on another occasion. Many years ago the author conducted experiments, not yet published, on dialysers for organosols. The experiments described in this communication are new and were made by the author in conjunction with Dr. P. Wolski.

2. *Preparation of a Stable Alcosol for Purposes of Control.*—It is very easy, it will be seen, to prepare molecularly-dispersed, *i.e.*, dialysing and diffusing alcoholic solutions, but not easy to prepare stable alcosols. On the other hand, the possibility of preparing a tolerably stable alcosol as standard liquid is presumed for the experiments to be described. Of the various alcosols tried, (Ag, $\text{Fe}(\text{OH})_3$, As_2S_3 , &c.) the *mercury sulphide alcosol*, previously prepared by A. Lottermoser, proved most suitable. We start from a solution of any concentration, including the saturated (10 per cent.) solution, of mercury cyanide $\text{Hg}(\text{CN})_2$ in alcohol of 97 per cent. (*not stronger*). A brisk current of H_2S is passed through this solution for a considerable time, say, 10 minutes. Any flakes, occasionally noticed, will be peptised again on further treatment with H_2S . A sol of dark deep-brown colour is formed; it may be diluted with alcohol of 97 per cent. and then be stabilised by further treatment with H_2S . In a closed vessel the sol may be kept for weeks; a certain excess of H_2S seems to favour stability.

The *freshly*-prepared sol, containing H_2S , may be diluted with the same volume of ether without showing any precipitate after two days. This is important for some of the experiments.

As a typical molecularly-dispersed system in alcohol of 97 per cent. *Night Blue* may be recommended, which is known as a typical colloid in water. The following arrangements for dialysis and diffusion are best tested with the mercury sulphide alcosol on the one hand, and alcoholic night blue on the other.

3. *Dialysers for Alcosols.*—Among the membranes which admit of dialytic differentiation of dispersoids in alcohol of 97 per cent. are the following :—

(a) Common Parchment Paper.

(b) Collodion Membranes. These membranes are prepared by the same method which the author recently described for the preparation of analytical dialysers for hydrosols.³ Extraction bags of paper are impregnated with 97 per cent. alcohol. Pharmaceutical collodion solution of 4 per cent. is poured into the still wet bag; the bag is quickly dried in a warm place, so as to feel dry to the touch of the finger, until the smell of ether has disappeared. The same collodion solution is poured in for the second time and the drying is renewed; the dialysers will then be ready for use.

In making use of the dialysers care should be taken to have the liquid inside and outside at the same levels; excess pressure may render these dialysers—as well as the others to be mentioned—leaky. With long standing some collodion will dissolve in the alcohol; the bags need not lose their tightness for this reason, however.

(c) *Rubber Membranes.*—The material used is a thickish ethereal solution of unsmoked crepe as formed when an excess of caoutchouc is kept standing with ether for a long time in the dark. Diluted thinnish solutions of rubber have not given good results. Exactly as with the colloid membranes just mentioned the bags are moistened with alcohol and treated and dried for periods of from 5 to 10 minutes.

(d) *Gelatine Membranes.*—The solution used was 1 per cent., aged under thymol. The preparation is as just described, except that the two drying intervals must be prolonged to 24 hours.

4. *An Alcoholic Jelly for Diffusion Experiments.*—In demonstrations of dispersoid analysis it is customary to place a layer of the solution to be tested on a suitable jelly. Especially when the systems are

coloured, it is easy rapidly to distinguish colloidal from molecularly-dispersed systems either by the penetrations of the solution into the jelly, or by the observation that the contact surface becomes indistinct. The jelly suitable for alcoholic systems is prepared from collodion by the following method :—

(a) In the first instance we may directly place pieces of nitrated cotton, *e.g.*, the commercial *celloidin* of *Schering*, into the solution to be analysed, and then look for any penetration after rinsing the cotton and cutting it open. This gel., which is supplied in transparent blocks, is said to contain about 30 per cent. of nitrocellulose and no medium except alcohol. As a matter of fact ether is not quite absent, as the smell indicates. By repeated washing with 97 per cent alcohol the ether may, at any rate, partly be removed; only traces of nitrocellulose will be dissolved by this operation.

Into such blocks Night Blue and Magdala Red will deeply penetrate within a few hours, whilst the HgS-sol. will not enter into the gel. even in the course of days.

b) When alcoholic collodion jelly is prepared for the test-tube experiment in the usual way, the following difficulties will arise : Even solutions of collodion rich in alcohol do not gelate on cooling, nor in the course of time. The gelation takes place only with change in the concentration, and in the composition of the disperse phase. There is the further difficulty of obtaining the jellies free of ether. The following procedure has answered best : The collodion wool is disintegrated and kept standing for four or five hours with ether until it has completely dissolved. The solution is rubbed with four times its volume of alcohol and evaporated to a thick consistency at 50° or 60° C. Alcohol is again added as before, and the evaporation repeated, several times if necessary. The final solution will be a slightly turbid thickish liquid of about three times the volume of the original solution in ether (containing, therefore, 5 or 6 per cent. of nitrocellulose) faintly smelling of ether. The criterion for the "maturity" of the solution is a strong tendency to surface-skin formation. The solution is poured into test tubes and allowed to stand for 24 hours at ordinary temperature. The skin first forming will gradually thicken, but the solution underneath it may remain fluid for a long time. The formation of a skin thus imparts to the experiment the character of a dialysis, which spontaneously passes into that of a jelly-diffusion. Since the last traces of ether are retained with great persistency, the solutions to be examined should not be sensitive to ether; that is so in the case of the HgS-alcosol, as was stated above. For the demonstration of these diffusion experiments this HgS-sol and night blue in alcoholic solution may again be utilised.

5. *Some Results of Dialysis and Diffusion Experiments with Solutions in 97 per cent. Alcohol.*—It should be pointed out in the first instance that the HgS-alcosol described could neither be dialysed, nor be diffused with any of the arrangements mentioned, although it passed readily through the densest paper filters of Schleicher and Schüll, 602 e.h. The membranes and gels described were hence, without doubt, impervious to colloids. That could not be ascribed to coagulation at the membrane, although such coagulation was occasionally noticed. It was observed, on the contrary, that the sols, kept merely covered up in the collodion dialyser, or over the diffusion jelly, remained deep dark-brown for 10 days. When poured off finally the sols passed through a baryta filter without any decomposition. On the other

hand, we frequently found dialysers which were not impervious, and through which the colloid passed in a short time, yet *likewise undecomposed*. The point in question is hence actually the mechanical density of the membrane or gel, and not perhaps any chemical or colloidchemical reaction with the sol.

The dispersoid analysis of substances which are spontaneously soluble in alcohol of 97 per cent. yielded a somewhat surprising result. *So far we have not succeeded in finding any substance, spontaneously soluble in alcohol of 97 per cent., which would not dialyse and diffuse to a perceptible degree.* All the solutions so far studied are, *at least partly*, molecularly-disperse. It is presumable that, in 97 per cent. alcohol, *dispersoids of variable concentration*⁴ will frequently occur, *i.e.*, systems, the degree of dispersion of which strongly varies with the concentration, decreasing as the concentration decreases. Only in more concentrated solutions the individuals unite to coarser aggregates. We meet with similar relations in dyes, *e.g.*; at the same time these structures are also "polydisperse"; they contain both molecular aggregates and coarser aggregates, presumably in a definite equilibrium ratio.

Not all the substances enumerated below have been submitted to all the dialyser tests mentioned, although the more interesting substances were analysed by all the methods mentioned. The majority of the tests was made with the collodion and gelatin dialysers and with the collodion jellies. It should, however, be emphasised that membranes of various types gave throughout *equal* results. Substances which passed through gelatin, hardened with alcohol, passed also through collodion or rubber, &c. It should be stated also that the imperviousness of the dialyser to the HgS-sol was in most cases retested after the experiment. Whenever permeability was noticed, the experiment was repeated.

The following substances did dialyse and diffuse :—

Dyes.—Night blue, Magdala red, alkannin, cyanin, alizarine, nigrosin (faintly violet); further six different technical spirit lacquers, &c.

Iodine diffused at a strikingly rapid rate in 97 per cent. alcohol.

Of *resins* dialysed in 97 per cent. alcohol : colophony, copal, mastic, dammar, Burgundy resin, guajac, dragon's blood, &c.

The permeability test is easily made in these cases by dropping the external liquid into a beaker containing water or solution of aluminium sulphate; after dialysing for 24 hours a milky turbidity was always noticed.

Dialysis was further observed with alcoholic solutions of linseed oil, bees' wax, neutral fats (like cocoa fat), lard, &c.; further capric acid, aluminium oleate. The test is here made as first indicated with the aid of water or of a solution of aluminium sulphate. Confusion with traces of collodion, which might be dissolved by the alcohol as stated above, is easily avoided; the collodion is precipitated in films or scales, but does not give rise to a milky turbidity. It is of special interest to mention that an alcoholic albumenoid, zein, is also distinctly dialysed. This material is prepared by extracting granulated maize with alcohol of 97 per cent at 50° or 60° C., and by filtering the yellowish solution. The analytical test was, in this case, performed with the aid of the Essbach reagent (picric acid plus citric acid) after dilution with water to three or four times the volume, or with the xanthoprotein-reaction. Mere pouring into water was

not decisive since the solution might contain lipoids. Pouring of the external liquid into ether also furnishes a sensitive test. Zein diffuses, in solution in alcohol of 97 per cent., through all the following membranes: parchment paper, collodion, rubber, gelatine. In this case as well the dialysers were subsequently submitted to a test with the HgS-sol. The diffusion experiment into collodion jelly did not lead to any definite result, because zein, differing from the HgS-sol in this respect, is easily precipitated by small proportions of ether.

This dialysis of zein in 97 per cent. alcohol is of special interest because it points undoubtedly to a molecularly-dispersed condition of this albumenoid in that dispersing medium. It would be very desirable to study these solutions from the standpoint of physical chemistry with respect to true solutions, *e.g.*, by determining the boiling point at reduced pressure. So far colloid-chemists have mainly been endeavouring to transform "crystalloids" in the sense of Graham into the colloidal state. The case of zein may indicate the way conversely of transforming Graham's colloids or, more generally, substances of complex chemical composition by gentle methods into the molecularly dispersed state.

Summary

The author describes the preparation of membranes and jellies suitable for the dispersoid analysis of solutions in alcohol of 97 per cent., for both dialysis and diffusion experiments.

The mercury sulphide alcosol, the preparation of which is explained, proves to be an especially stable sol suitable for these tests.

It results that the solutions so far examined, of dyes, resins, neutral salts, fatty acids, soaps, &c., produced by the spontaneous solution of these substances in alcohol of 97 per cent., are all molecularly-dispersed or contain, at any rate, molecularly-dispersed particles in considerable proportions. Zein, the albumenoid of maize which is soluble in alcohol, is also found to be dialysable.

¹ De Mosenthal, *Journ. Chem. Soc.*, **30**, p. 782 (1911).

² J. Duclaux and E. Wollman, *Compt. Rend.*, **152**, p. 1580; *Bull. Soc. Chim.* [4], **27**, p. 414 (1920); "*Le Caoutchouc et la Guttapercha*," p. 10579 (1920).

³ *Cp.* "*Kleines Praktikum der Kolloidchemie*," Dresden, 1920, Th. Steinkopff, p. 22.

¹ Wo. Ostwald, "*Grundriss der Kolloidchemie*," 6th edition, p. 39 (1921).