

*Citation:*

Reinders, W., The distribution of a colloiddally dissolved substance over two layers, in:  
KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 379-385

Benzenesulphonamide when cooled in ice and salt gives with absolute nitric acid but little gas but this increases on elevation of temperature.

The sulphonisobutyric diamide of MOLL VAN CHARANTE dissolves slowly in absolute nitric acid without evolution of gas even after two days and is reprecipitated unchanged by addition of water particularly on neutralising the acid.

Hence also in regard to absolute nitric acid this substance behaves quite differently than was to be expected from the diamide.

Finally, it may be mentioned here that just as HINSBERG prepared benzenesulphonnitramide from benzenesulphamide by means of nitric and sulphuric acid at low temperatures, ethylsulphonnitramide is to be obtained also from ethanesulphonamide in this manner, though with a poor yield, as a substance crystallizing beautifully from benzene in which it is fairly soluble and melting at  $\pm 70^\circ$ .

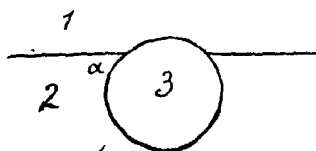
**Chemistry.** — “*The distribution of a colloiddally dissolved substance over two layers*”. By Prof. W. REINDERS. (Communicated by Prof. SCHREINEMAKERS).

(Communicated in the meeting of September 27, 1913).

1. When three non-miscible liquids meet, three things may happen depending on the values of the contact surface tensions  $\sigma_{1,2}$ ,  $\sigma_{2,3}$  and  $\sigma_{3,1}$ , apart from the action of the gravitation; either the three phases meet in one common side or one of them expands between the other two and prevents these from coming into contact.

The first will happen if none of the three contact surface tensions is greater than the sum of the other two; the second if this should be the case. If, for instance  $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$ , 3 will expand between 1 and 2<sup>1)</sup>.

2. If one of the phases (3 for instance) is solid and the other two liquid we can again distinguish the same two cases with this difference, however, that when  $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$ , the expansion of 3 between 1 and 2 is not possible. Phase 3 will then arrive at the contact surface of 1 and 2.



Let us now suppose the phase 3 to be in the form of a small globule. There will then be an equilibrium if  $\sigma_{1,3} = \sigma_{2,3} + \sigma_{1,2} \cos \alpha$ . If  $\sigma_{1,3} > \sigma_{2,3} + \sigma_{1,2} \cos \alpha$ ,  $\cos \alpha$  will be positive and  $\alpha < 90^\circ$ . The greater part

<sup>1)</sup> QUINCKE. Consult the test-books, for instance BOSSCHA-KUENEN II, 658.

of 3 is then enveloped by the liquid 2. If  $\sigma_{1,3} < \sigma_{2,3}$ ,  $\cos \alpha$  will be negative, hence,  $\alpha > 90^\circ$  and the greater part of 3 is drawn into the liquid 1.

3. If now the phase 3 is suspended in the liquid 1 in the form of a fine powder and this suspension shaken with the liquid 2, three things may occur.

a. If  $\sigma_{2,3} > \sigma_{1,2} + \sigma_{1,3}$ , 3 will be completely enveloped by 1 and thus the suspension remains unchanged in 1.

b. If  $\sigma_{1,3} > \sigma_{1,2} + \sigma_{2,3}$ , the stable condition will be such that 3 is completely enveloped by 2. The suspension will then disappear from 2 and pass entirely into the liquid 2.

c. If  $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$ , or none of the three contact surface tensions greater than the sum of the other two, the powder is deposited entirely on the surface of contact <sup>1)</sup>.

4. Let us now apply these considerations to colloidal solutions, which according to modern views may be looked upon as transition stages between suspensions, or emulsions, and true solutions.

Let us first consider a suspenoid in which solid, floating particles are supposed to be present.

If these particles are fairly large and practically of uniform dimension we may assume that the surface tension in regard to the surrounding medium will be but little dependent on this dimension and therefore, the same for all particles. The same three possibilities which could be distinguished in the case of the coarse suspensions will consequently apply here also. The colloidal substance remains entirely in the first medium, passes entirely into the second or is deposited quantitatively at the surface of contact. In the first case the division coefficient = 0, in the second case it becomes  $\infty$ .

If the size of the particles becomes smaller, the resultant of the molecular attractions which appears as surface tension will be very much dependent on the number of molecules which together form the particle. Hence, the behaviour in regard to a second liquid phase will become dependent on this size. For instance, it will then be possible for particles below a certain size, to pass into the second liquid, for particles of greater dimension to arrive at the contact surface or to remain in the first liquid. According to the degree of

<sup>1)</sup> Instances of these different cases, a principle of separation for a mixture of solid, insoluble substances which is based on the different behaviour in regard to a liquidum couple, and the practical application thereof, are cited in a publication in the *Chemisch Weekblad*. Vol 10, 700 (1913). Also compare J. B. HOFMANN, *Zeitschr. f. physik. Chem.* 83, 385 (1913).

dispersion, colloidal solutions of a same substance will behave in a different manner.

If finally the colloidal particles exist of a few molecules only the idea of surface and surface tension loses its significance. The solution is then an ordinary molecular one and the dissolved substance will distribute itself over both liquids according to the "dividing rule". Other factors than surface tension, then dominate the distribution over the two-phases.

5. Some complications may still occur owing to the fact that the particles deposited at the surface of contact do not keep apart but unite to larger coagulum. This may happen very readily with very instable solutions.

In the case of emulsoids or solutions in which floating droplets of liquid must be assumed, these, if deposited at the contact surface may unite to form a separate liquid layer when  $\sigma_{1,2} < \sigma_{2,3} + \sigma_{3,1}$ . If however the separation has taken place at the contact surface, because none of the three surface tensions was greater than the sum of the other two, the expansion of liquid 3 between 1 and 2 becomes impossible and the isolated droplets of 3 will unite with greater difficulty.

6. In order to prove these considerations experimentally, I have investigated the behaviour of a few different colloidal solutions towards a second liquid. A few provisional results are communicated here.

In the first place, colloidal *gold*.

A red gold solution was obtained by passing CO into a dilute solution of  $\text{AuCl}_3$ . If into this solution was dropped cautiously isobutylalcohol or an aqueous solution of the same, the colloidal solution remained unchanged. Not a trace of coagulation which would show itself by a change of colour to bluish-violet was observed. Hence in homogeneous solution isobutylalcohol has no influence on the stability of the colloidal gold solution.

As soon, however, as the limit of solubility of the isobutylalcohol had been exceeded and this begun to form a separate layer, the gold, on shaking, gradually disappeared from the water and collected at the surface of contact. This then assumes a splendid colour, blue in transmitted, and a golden lustre in incident light<sup>1)</sup>.

<sup>1)</sup> As the alcohol layer does not moisten the glass owing to a thin layer of water collecting between the alcohol and the glass, the whole of the alcohol phase (upper layer) is surrounded at the nether side and the glass walls by a water-alcohol demarcation in which the gold is distributed very homogeneously. At first we thus get the impression that the alcohol-phase itself was coloured. If,

7 Similar to isobutylalcohol is the behaviour of various other solvents such as amylalcohol, benzene, lightpetroleum, carbon tetrachloride, carbon disulphide and ether<sup>2)</sup>.

8. Goldsolutions prepared in another way (for instance by electric dispersion of gold wire, or by reduction of  $\text{AuCl}_3$  with a solution of phosphorus in ether) and having a red or reddish-violet colour behaved in the same manner; the gold was deposited with a blue colour at the surface of contact. Somewhat different was the behaviour of a brownish coloured solution recently prepared from  $\text{AuCl}_3$  and solution of phosphorus in ether, for this was quite indifferent to ether and no gold was deposited at the contact surface.

9. In order to attain the equilibrium from the other side also, it was endeavoured to prepare a colloidal solution of gold in another dispersion medium. This succeeded in butyl or amylalcohol and in ether, both by electric dispersion of gold wire at a low temperature and by reduction of  $\text{AuCl}_3$  in these solvents by a solution of phosphorus in the same medium. By electric dispersion could also be obtained reddish solutions; those prepared by reduction with phosphorus had a yellowish-brown colour.

On shaking with water the gold in the first solutions passed into the surface of contact. The yellowish-brown amylalcohol solution was quite unaffected by shaking with water; not a trace of gold found its way into the water or collected at the surface of contact. This solution was also very stable in other respects and could be boiled without undergoing any change.

It thus appears that the gold of the yellowish-brown amylalcohol solutions is stable with regard to the aqueous phase. On the other hand, the gold from the red and reddish-violet solutions is stable in the contact layer. When, as is very probable in the case of colloidal silver, the differences in colour must be attributed to a difference in the size of the gold particles present we should have here a case of the possibility suggested in 4.

The yellowish-brown solution of gold in ether is very unstable.

---

however, the tube containing the liquids is placed in an inclined position the gold will somewhat lag behind the liquid and it appears that the phase is colourless.

<sup>2)</sup> Carbon disulphide in presence of water forms the bottom layer; this is entirely surrounded by a splendid blue coloured golden skin, which has collected at the place of contact of the carbon disulphide and the water; a very beautiful demonstration of the fact that water penetrates between the glass and the carbon disulphide. When shaking, every drop of carbon disulphide is coloured blue by gold adhering to the surface and thus it looks as if the liquid itself possessed that colour, by removing some with a pipette it will be seen that such is not the case.

At first clear, it after a while becomes opaque and after an hour a portion of the gold is already so strongly coagulated that it is left behind on filtration. When shaken with water immediately after being prepared, the gold passes with a yellowish-red colour into the water; a small portion only deposited at the surface of contact in the form of brown flakes; the ethereal layer, however, was quite decolorised. From the solution which had stood for a while, all the gold disappeared also on shaking with water. The greater part thereof arrived, however, at the layer of contact, whilst the aqueous layer was coloured yellowish-brown and looked turbid with incident light.

An aqueous solution of  $\text{AuCl}_3$ , when shaken with ether to which had been added a few drops of the solution of phosphorus was coloured yellowish-brown whilst the ethereal layer remained colourless.

Hence, in regard to ether, the yellowish-brown modification of gold is stable in the aqueous phase (also see 8) whereas the reddish-violet and blue gold is stable at the surface of contact.

10. Addition of an impeding colloid such as gum arabic to the gold exerts a twofold influence. First of all it may retard, or even entirely prevent, the separation at the surface of contact. Even 0.001 % of the gum caused the separation from a red solution (prepared from  $\text{AuCl}_3$  and CO) to take place with great difficulty and then only imperfectly; with 0.005 % of the gum, a trace of deposit could be observed only after prolonged shaking. The colour of the gold in the contact layer was, however, blue as in the solution free from gum. The separation at the surface of contact with ether was entirely prevented by as little as 0.001 % of gum arabic; all the gold was retained in the aqueous solution with a red colour.

Secondly, without retarding the separation at the contact surface, it may prevent the colour from changing from red to violet and blue. This was observed in the case of  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$  and  $\text{CCl}_4$ , a very small quantity of gum arabic (0.001—0.005 %) being sufficient.

11. Besides colloidal gold, the colloidal solutions of the following substances were also investigated.

*Silver.* (Collargolum. Fabrik VON HEYDEN). With amylalcohol, isobutylalcohol and carbon tetrachloride a portion passed with a brown colour into the surface of contact, another portion remained unchanged in the water. With benzene and with ether, nothing was deposited at the contact surface and all was retained in the water.

*Ferric hydroxide* (1½ years old). This was retained in the water with every liquid used.

*Arsenic trisulphide* (1½ year old). With paraffin oil, carbon tetrachloride, benzene and ether the liquid remained unchanged; with amylalcohol and with isobutylalcohol, the sulphide was deposited quantitatively at the surface of contact<sup>1)</sup>.

*Selenium* (prepared from  $H_2SeO_3 + SO_2$ ). With amylalcohol a portion is deposited at the contact surface and another portion in the alcohol layer. With butylalcohol, carbon tetrachloride, benzene and ether all the sulphide collects at the surface of contact.

12. From the above it appears that case *b* — separation at the surface of contact — is a very common one. A few instances, however, could also be found in the other two cases.

In fact, case *b* is so common that it will often be possible to determine the colloidal nature of a solution by exhibiting the separation at the contact surface on shaking with a second liquid.

The above cases relate to non — or only partially — reversible colloids.

With typically reversible colloids such as gelatin, the separation at the contact surface has, however, also been observed and this reaction has even been utilised for demonstrating the presence of these substances in a solution<sup>2)</sup>. In most cases, however, the total quantity that deposits at the contact surface appears to be small. JONKER<sup>3)</sup> found for tannin and alcohol a distribution over the two layers; these solutions so far as the size of the colloidal particles is concerned will have to be classed very closely with the molecular solutions and be considered as homogeneous phases.

The adhesion to the surface of contact of a second liquid is, moreover, quite comparable to the surface adhesion of an added solid substance, a phenomenon that has been observed with different colloidal solutions.

Colloidal gold, for instance, is taken up by carbon powder, barium-sulphate and various fibrous substances; colloidal arsenic trisulphide by carbon and by barium sulphate; carbon by paper; selenium,

<sup>1)</sup> In this case also it was very evident that the separation is due to the action of the surface of contact. An aqueous solution of butylalcohol left the solution entirely unchanged; the instant, however, that an excess of the alcohol was added, thus forming a separate layer, all the  $As_2S_3$  soon deposited at the contact surface.

<sup>2)</sup> K. WINKELBLECH, *Zeitschr. f. angew. Chem.* **19**, 1953 (1906). The phenomenon is, however, somewhat different as the gelatin arrives at the contact surface as a thin, white lather. Hence, besides the liquid phases the air-phase also cooperates.

<sup>3)</sup> *Zeitschr. f. Kolloidchemie* **10**, 126.

tellurium, tungsten-blue and many other inorganic colloids by fibrous substances<sup>1)</sup>. These phenomena have been usually described as adsorptions, although the name adhesion would be the more correct one. If, however there exists a continuity between colloidal and molecular solutions, this will then also exist between adhesion and adsorption.

Delft, July 1913.

**Chemistry.** — “*Equilibria in ternary systems*”. IX. By Prof. F. A. H. SCHREINEMAKERS.

We will now consider the four-phase equilibrium  $F + F' + L + G$  in connection with the saturation- and vapour saturation-curves of  $F$  and of  $F'$  under their own vapour pressures.

These saturation-curves under their own vapour pressures may be situated with respect to one another in different ways. 1. they may intersect one another; 2. they may touch one another; 3. the one may be situated outside the other; 4. the one may surround the other.

Let us, in the first instance, consider fig. 2, in which the continuously drawn curves represent the saturation curves, the dotted curves the vapour saturation curves of  $F$  and of  $F'$  under their own vapour pressures.

At the given temperature, therefore, every liquid of the curve  $fxyg$  is saturated with the solid  $F$  and in equilibrium with a vapour of the corresponding curve  $f_1g_1$ ; every liquid of the curve  $f'x'y'g$  is saturated with the solid  $F'$  and in equilibrium with a vapour of the corresponding curve  $f'_1g'_1$ .

Because all these liquids are under their own vapour pressures, the pressure changes will, as we have seen before, move along these curves.

If we now consider  $f$  as a point on the saturation curve of  $F$ , it is under a pressure  $P$ ; if, on the other hand, we consider  $f$  as a point on the saturation curve of  $F'$ , it is under a pressure  $P'$ . The question now arises: Is  $P$  the same as  $P'$  or are they different?

Under the pressure  $P$ , therefore, the system  $F + L_f + G$  exists, and under the pressure  $P'$  the system  $F' + L_{f'} + G$ . At a definite

<sup>1)</sup> R. ZSIGMONDY, Verh. d. Ges. D. Naturf. u. Aerzte, 73 Vers. Hamburg 1901, p. 168. L. VANINO, Ber. d. D. Chem. Ges. **35**, 662 (1902).

W. SPRING, Beobachtungen über die Waschwirkung von Seifen, Zeitschr. f. Kolloidchemie **4**, 161 (1909).

W. BILTZ, Ber. d. D. Chem. Ges. **37**, 1766 (1904).