

*Citation:*

H.R. Kruyt & Spek, J. van der, The connection between the limit value and the concentration of arsenic trisulphide sols, in:

KNAW, Proceedings, 17 III, 1914-1915, Amsterdam, 1915, pp. 1158-1163

departures from the average in the strength of the North-East trade, it seems possible to us, to make a forecast about the sign of the departure from the normal of some phenomena in the Northern European seas.

Whether the correlation will prove to be greater or smaller if longer series are at our disposition, cannot be said with any certainty beforehand.

**Chemistry.** — *“The connexion between the limit value and the concentration of Arsenic Trisulphide sols”*. By Dr. H. R. KRUYT and JAC. VAN DER SPEK. (Communicated by Prof. E. COHEN).

(Communicated in the meeting of February 27, 1915).

1. When one of us<sup>1)</sup> carried out experiments with the  $As_2S_3$  sol conjointly with C. F. VAN DUIN, it once struck us that a sol, which we had diluted to half its concentration, had retained nearly the same limit value. The object of the investigation communicated here was to endeavour to get some more knowledge as to the connexion between the  $As_2S_3$  concentration and the limit value of the sol.

2. One may preconceive an idea as to this connexion. We assume for the moment that the sols differ only in concentration but not in the size of their particles. Now the limit value  $\gamma$  is the concentration at which so much of the coagulating cation is withdrawn by adsorption that the charge of the particles is diminished to a definite value differing but little from 0. Hence, the adsorbed quantity of cation ( $a$ ) per particle is characteristic of the limit value. This again is connected with the concentration  $\chi$  in cation in the solution after the congulation<sup>2)</sup> according to this equation:

$$a = k\chi^{\frac{1}{n}}$$

so that  $\chi$  is, therefore, also characteristic of the limit value *but independent of the concentration of the sol*. As for the limit value  $\gamma$  we simply take into account the bruto-added electrolyte quantity,  $\gamma$  is as a rule not independent of the concentration.

In the Fig. 1 and 2 are represented schematically two sols in which the second has the double concentration of the first. When properly choosing the units we have in Fig. 1:  $\gamma_1 = \chi + a$ , in Fig. 2:  $\gamma_2 = \chi + 2a$ .

<sup>1)</sup> KRUYT and VAN DUIN, Koll. Beih. 5, 269 (1914).

<sup>2)</sup> For fuller details compare KRUYT, Proc. 17, 623 (1914).

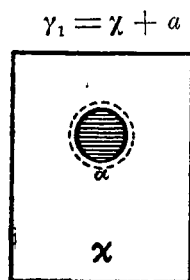


Fig. 1.

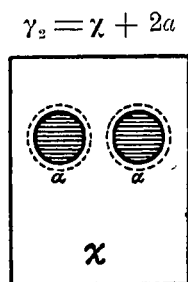


Fig. 2.

It will now be evident without any further comment that the limit value is not (or but very faintly so) a function of the concentration when  $a$  is small in regard to  $\gamma$  and when consequently  $\gamma = \chi$ . In the case of monovalent cations with their relatively high limit value this will have to be the case. In the di-, and still in a higher degree in the trivalent cations, the limit value will have to increase with the concentration.

3. Concentrated sols of  $\text{As}_2\text{S}_3$ -were made according to a method devised by SCHULZE<sup>1)</sup>. After in a nearly saturated solution of  $\text{As}_2\text{O}_3$  this had been converted into  $\text{As}_2\text{S}_3$ , a fresh quantity of  $\text{As}_2\text{O}_3$  was dissolved and  $\text{H}_2\text{S}$  again passed through. This treatment was then repeated a few times<sup>2)</sup>. The determination of the limit value for such concentrated sols must be modified somewhat. A mere shaking of the glasses is not sufficient as after the congulation, they may be placed upside down without anything running out. Hence, before and after the two hours required, stirring rods were used. In the case of monovalent cations the precipitate obstinately adheres to the glass walls thus rendering the observation much more difficult.

In the first five columns of the subjoined table 1 are communicated the results of a series of measurements. The determinations have been carried out with the same measuring instruments, standard solutions, working arrangements, in fact as much as possible under the same conditions. For each concentration a separate sol was prepared.

The concentration was determined by precipitating the  $\text{As}_2\text{S}_3$  with  $\text{HCl}$ , drying on a GOOCH filter at  $80^\circ$  and weighing.

In Table 1 all concentrations are *end* concentrations, that is they relate to the volume after addition of the electrolyte solution.

In Fig. 3 these results are represented in such a manner that the limit value of experiment 1 is put for each electrolyte each time as

<sup>1)</sup> Journ. f. prakt. Chem. N. F. 25, 431 (1882).

<sup>2)</sup> Full experimental details will be published elsewhere.

TABLE I.

No.	gr. $As_2S_3$ per K.G. Sol	Limit value			Number of particles		
		KCl	BaCl <sub>2</sub>	AlK[SO <sub>4</sub> ] <sub>2</sub>	Dilution used	20 times the number	Number calcul- ated for 1:2000
1 <sup>1)</sup>	5	56	0.99	0.183	—	—	—
2	18.0	69	1.20	0.291	2.10 <sup>4</sup>	38	19
3	42.8	50	1.92	0.540	1.10 <sup>5</sup>	22	55
4	74.7	59	2.87	0.649	2.10 <sup>5</sup>	37	185

<sup>1)</sup> No. 1 is borrowed from the investigation of KRUYT and VAN DUIN, loc.cit. Table X.

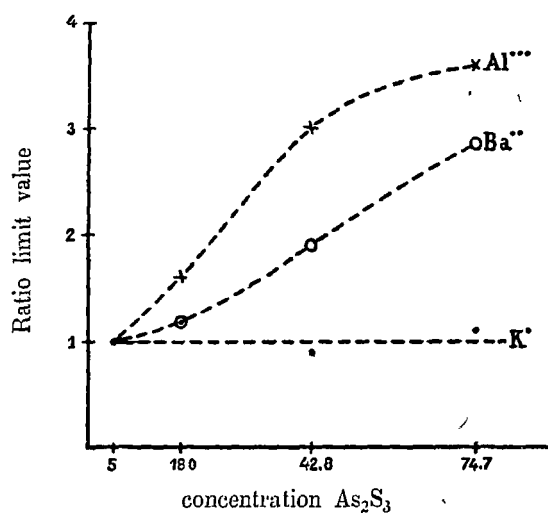


Fig. 3.

1.00. From this we notice how the *results completely confirm the correctness of the train of thoughts of the previous paragraph*. To the less regular course with the monovalent cation we will refer presently.

4. We desired to get some insight whether our premise that the dispersity degree of our sols was still the same, had proved satisfactory. Direct determinations of the dispersity degree have been carried out by ZSIGMONDY <sup>1)</sup> with gold sols, by WIEGNER <sup>2)</sup> with oil

<sup>1)</sup> Ann. de Phys. [4] **10** 16 (1903).

<sup>2)</sup> Koll. Beih. **2** 213 (1911).

emulsions. For that purpose are counted in the ultramicroscope the number of particles in a definite volume-element. We have also done this with the ultra microscope (source of light self-regulating arc lamp according to WEULE, width of aperture 5, objective ZEISS D<sup>6</sup>, compensation ocular 18, length of cylinder 16, EHRLICH'S screen 17). Dilutions were made in such a manner that never more than five particles were simultaneously present in the field of vision. In consequence of the BROWNIAN movement the mean from a number of observations had to be taken. Generally a series of 20 observations was made four times. Below in Table 2 the list of the observations of one sol (N<sup>o</sup>. 2) is given; for the other sols the end results are given in Table 1.

TABLE 2.

2 1 1 2	2 2 2 1	1 1 2 3	1 2 3 1
2 2 2 1	2 1 3 2	3 2 2 3	2 1 2 2
2 2 2 2	2 2 1 2	2 2 3 3	1 1 3 4
3 3 3 1	1 2 1 3	3 1 2 0	1 2 2 2
2 1 2 2	1 1 2 2	1 2 1 2	2 3 3 1
total 38	total 35	total 39	total 39
general average of 20 measurements 38			

These results cannot be interpreted in the same manner as those relating to gold sols. For there we see the luminous particles against a completely dark background. Here on the other hand we notice besides the particles an undistinguishable pale blue illumination of the field. We therefore have particles of unequal size in the sol and we *only count the large particles*. If now at the different concentrations all was equal, we ought, on recalculating our results to one standard solution, to find figures which increase proportionally with the concentration. Such figures are found in the last column of Table 1; they are so chosen that the concentration and standard figure in experiment 2 are about equal. We now see at once that the number of large particles increases more rapidly than the concentration, therefore, the concentrated sols possess probably a smaller average dispersity degree than the diluted ones. This can be readily understood because the repeated boiling, in order to dissolve fresh  $As_2O_3$ , probably leads to enlargement of the particles.

Nevertheless this result does not diminish the value of our con-

firmatory experiment. Just the reverse; with a *lesser* dispersity corresponds a *lower* limit value. Hence, if the dispersity had been the same in all these experiments the difference between the  $K^+$ ,  $Ba^{++}$  and  $Al^{+++}$  ion would have been still more pronounced.

5. In order to completely exclude meanwhile the complication of the difference in dispersity degree we have still made another series of experiments. We have prepared a large quantity of a concentrated sol and from this made by dilution with water three sols of different concentration. Of these four sols which thus were derived from the same original liquid and exhibit undoubtedly<sup>1)</sup> the same average size of particles, we have again determined the value limits with  $KCl$ ,  $BaCl_2$  and  $AlK(SO_4)_2$ . To eliminate all differences which might occur owing to the duration of the experiment all determinations have been made within 38 hours. Table 3 shows the result:

TABLE 3.

No.	gr. $As_2S_3$ per K.G. sol	Limit value		
		$KCl$	$BaCl_2$	$AlK(SO_4)_2$
1	5	81'	1.35	0.106
2	25	61	1.79	0.266
3	36	56	2.11	0.350
4	50	53	2.53	0.442

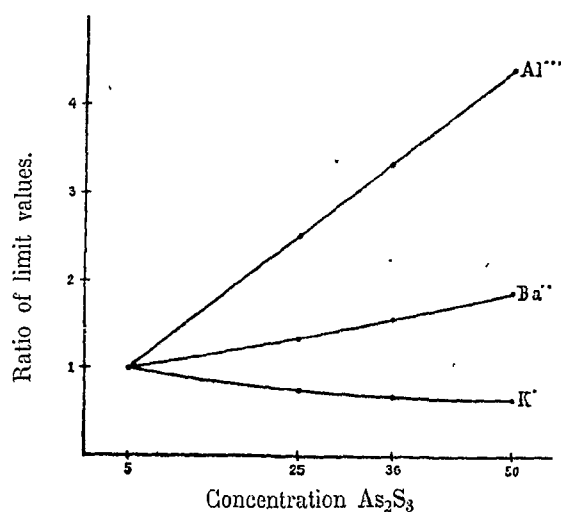


Fig. 4.

<sup>1)</sup> It cannot be denied with absolute certainty that the dilution may exert an influence on the size of the particles, but even if such an influence does exist it is certainly of a lower order.

In Fig. 4 the results are again represented graphically with the limit value of the sol N<sup>o</sup>. 1 as unit. The result agrees well with what was expected, only the limit values for K. exhibit an unmistakable depression with increasing sulphide concentration. We must for the present refrain from trying to explain this remarkable anomaly.

6. The experience gained during the above described research has given rise to a number of questions; fresh experimental series started with the intention of answering those had to be postponed on account of the present circumstances. Hence, we can only point to some provisional results.

We feel convinced that on boiling an As<sub>2</sub>S<sub>3</sub> sol an enlargement of the particles really takes place (light absorption, ultramicroscopic image, depression of the limit value of the Al<sup>+++</sup>-ion). At the same time it appeared that, on boiling, the particles do not become enlarged equally, but that the boiled sol contains particles of all sizes and that a *fractional precipitation seems possible*. This fact has, up to the present, only been recorded in the case of colloidal sulphur<sup>1)</sup>, but does not seem to be a specific property of that colloid.

The frequently recorded dependence of the value limit on the previous history becomes more comprehensible by these experiences. Further researches concerning all the above cited questions, as to the density of the sols (on which we already carried out a few series of measurements) and other correlated problems must be postponed till more peaceful times.

Utrecht.

VAN 'T HOFF-Laboratory.

**Chemistry.** — “*Action of sodium hypochlorite on amides of  $\alpha$ -oxyacids. A new method for the degradation of sugars.* By R. A. WIERMAN. (Communicated by Prof. FRANCHIMONT).

(Communicated in the meeting of February 27, 1915).

In a previous communication<sup>2)</sup> a method was described by me for the degradation of amides of  $\alpha$ - $\beta$  unsaturated acids to the aldehydes containing one atom of carbon less.

It now seemed possible to degrade in the same manner the amides of  $\alpha$ -oxyacids. The experiment has confirmed this supposition.

<sup>1)</sup> SVEN ODEN, *Der kolloide Schwefel*, Upsala 1913.

<sup>2)</sup> *Proc.* 1909; more fully in *LIEBIG'S Annalen* **401**, 1 [1913].