

On the Influence of Colloids on the Stability of Supersaturated Solutions of Carbon Dioxide. With Special Reference to Wild Beer

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Moderately supersaturated, homogeneous systems are apparently stable, metastable.

In supersaturated solutions of carbon dioxide in water small quantities of colloid ferric oxide or aluminium hydroxide can cause spontaneous release of the carbon dioxide. The colloid particles participate in the formation of the nuclei on which the supersaturation is released. Knowledge of the processes leading to nuclei formation may be of importance to the understanding of the causes of the phenomena of over-foaming sometimes occurring in beer and other carbonated beverages.

This paper presents the results of some experiments which show that the boundary surface between the liquid and gaseous phases seems to play a rôle in the processes leading to the formation of nuclei.

In experiments with ultrafiltration and diffusion through a collodion membrane it is demonstrated that the bicarbonate ions displace the Gegen-ions of the colloid particles. The consequences which the latter process may have for the stability of the colloid system and the possibilities of nuclei formation hereby arising are finally discussed.

In 1897 Ostwald¹ introduced the expression metastability as a designation for the apparent stability, which may exist in homogeneous systems which are not too strongly supersaturated. The supersaturation may be released by seeding, but Ostwald showed that this requires a certain amount of seeding material; smaller amounts have no effect.

The theoretical explanation for these facts has been given by Gibbs² and Volmer³.

For solutions of gases in liquids, an equilibrium bubble of definite radius corresponds to every degree of supersaturation. The stronger the supersatura-

tion, the smaller the equilibrium bubble. Supersaturation can only be released when, for some reason, a bubble is formed, the radius of which is equal to, or larger than, the radius of the equilibrium bubble. All bubbles of smaller radius will be forced into solution again.

This is true for homogeneous systems without phase boundaries. Such systems do not in fact occur, since there will always be a phase boundary. Gibbs, however, has also investigated the conditions for stability in such cases. It is possible to conclude from his results that supersaturation will be released earlier at the phase boundary than in the liquid, if the surface tension of the foreign phase against the dissolved gas is equal to or less than the surface tension of the liquid.

In a paper, *On the stability of supersaturated carbon dioxide solutions — with special reference to beer*, Krause ⁴ has given a more detailed account of the conditions described above, and on the basis of this has put forward a hypothesis on the causes of the phenomenon of over-foaming in beer.

Knowledge of the factors which influence the stability of supersaturated carbon dioxide solutions is of great importance to all industries which prepare carbonated beverages.

In the brewing industry, the phenomenon of over-foaming in bottled beer is well known. Over-foaming appears as a spontaneous release of part of the carbon dioxide dissolved in the beer immediately the bottle is opened. This results in such strong foaming that some of the beer is spilled from the bottle.

Over-foaming does not usually occur or appears only to a very slight extent just after bottling. Only when the beer has been subjected to shaking, *e. g.* during transport to the consumers, does over-foaming appear.

The tendency of the beer to over-foaming is usually investigated in the brewery in the following way. A suitable number of bottles, 10—20, is placed in an apparatus in which they are subjected to shaking, hopping or rocking movements in order to give an exaggerated imitation of the movements during transport, to which the beer is subjected on the way to the consumers. When the bottles have remained here for a certain number of days, they are taken out and placed at rest for temperature adjustment for a definite number of hours. They are then opened carefully and the amount of beer which runs out is determined. Over-foaming often occurs in periods, and the cause or causes of the phenomenon are not known. Many experiments have been carried out and many hypotheses put forward, but a satisfactory explanation, based on experimental facts, has not so far been obtained.

Krause's hypothesis, however, is one of the most important contributions which have been given in recent years to the understanding of the causes for this phenomenon. It is based on generally valid considerations, but has no

experimental support. As so many others, Krause imagines that over-foaming is due to nuclei which are formed in the beer during shaking, and he explains the formation of the nuclei thus:

“Their formation is best explained by assuming that the beer during bottling or during transport has foamed and splashed, causing large or small bubbles to be whipped down into the beer. In this case the large bubbles will rise rapidly, small bubbles, rather slowly and very small bubbles, very slowly. In this connection it must be remembered that no supersaturation is found in the closed bottle, hence there is no possibility for the formation of a bubble which is in equilibrium with the surrounding liquid — the equilibrium bubble would have radius ∞ . This means that all bubbles which are shaken down into the solution will decrease in size so long as they remain there, and in the case of the smallest and most slowly rising bubbles, this means that they are forced into solution before they reach the surface.

The substances adsorbed onto the surface of the bubbles will be “compressed” during the shrinkage of the bubble surface and the least surface-active will be forced away from the surface by the more surface-active.

As a result of the decrease in size of the bubble, the compression of the adsorbed substances causes, in some cases, a change in the nature of the surface from gaseous-liquid to gaseous-solid. Due to this change, the pressure in the bubble must become less and less as the motility of the surface gradually decreases, the carbon dioxide coming into equilibrium with the carbon dioxide concentration in the beer by diffusion through the adsorbed layer. This will normally be drawn by capillary action into the small cavity in the interior of the aggregate, so that the final result will be the same as before, but if the adsorbed layer has a smaller surface tension to carbon dioxide than to beer, capillary action will not occur and in this case we have a bubble in equilibrium with the beer. Since this bubble will always be very small, its buoyancy will be reduced or completely counteracted by the weight of the adsorbed substances; when the bottle is opened, the fall in pressure will cause expansion, hence a bubble of above equilibrium size may be formed.

If the explanation given here is feasible, then the beer must contain certain colloid particles with surface activities higher than those of the other components of the beer, and in addition, their surface tension to beer — in any case when they occur in compact form — must be relatively high.”

Quite apart from whether this hypothesis is correct, it is worth emphasizing the importance for nuclei formation which Krause ascribes to the surface between the liquid and gaseous phase. In the absence of this boundary, as in completely filled bottles, there is no possibility for nuclei formation.

In 1942 the author of this paper began some experiments in order to investigate which substances reduce the stability of supersaturated carbon dioxide solutions. The first experiments were quite simple, but since their results were decisive for the direction in which the later experiments proceeded, they will be discussed briefly here. Similar experiments will be described later in greater detail.

0.1 Molar acetate buffer with pH 4.4, *i. e.* with the same pH as normal beer, was saturated with carbon dioxide at 0° and a counter-pressure of about 200 mm Hg. Under these conditions the concentration of saturation is about 0.42 per cent. In normal bottled beer the concentration of carbon dioxide is of the same magnitude. The carbonated buffer solution was then filled into ordinary beer bottles and examined for "over-foaming" in the usual way. Contrary to expectation considerable "over-foaming" occurred. As soon as a bottle was opened, so much carbon dioxide was released spontaneously that the solution shot out of the bottle in a 10–20 cm high spray. The "over-foaming" did not occur when water, redistilled in a glass apparatus, was used for the preparation of the buffer solution. A further investigation of the cause for this phenomenon showed that the distilled water used contained very small amounts of colloidal aluminium hydroxide. "Over-foaming" could also be produced by the use of redistilled water to which 1–2 mg of colloidal aluminium hydroxide per l were added.

At the pH in question this colloid is positively charged. Colloidal ferric oxide, which also has positively charged particles, was found to behave in exactly the same way. Colloidal silicic acid, which has negatively charged particles, had no effect as will be shown later.

Findlay and co-workers^{5,6} have published comprehensive and accurate investigations on the influence of various compounds on the solubility of carbon dioxide in water and on the stability of supersaturated solutions. The stability of the supersaturated solutions was determined by measuring the velocity with which the carbon dioxide escaped when the pressure above the solution was reduced to atmospheric pressure. Findlay showed that water which contains colloidal ferric oxide dissolves larger amounts of carbon dioxide than pure water, and that the solubility does not follow Henry's law. Findlay considers that this is due to the adsorption of the carbon dioxide on the colloid.

The observations made by Findlay on the effect of this compound on the stability of supersaturated solutions are, however, especially interesting in this connection. Immediately the pressure was reduced to atmospheric pressure, the solutions spontaneously released part of the carbon dioxide. The velocity with which this occurred was so high that it was not possible to

measure it with the apparatus used. Findlay has not investigated this phenomenon further. He concludes thus: "It would therefore appear that in the case of solutions of ferric hydroxide there exists no essential difference as compared with other colloids, but that the metastable region with regard to gaseous supersaturation is much less."

This spontaneous release of carbon dioxide, however, can only be due to the presence of a large number of particles, which act as nuclei for bubble formation.

As previously mentioned, Findlay is of the opinion that the carbon dioxide is adsorbed on the colloid. Gatterer⁷ thinks that the dissolved carbon dioxide reacts chemically with the colloid, and Luther and Krsnjavi⁸, that it is a question of formation of complexes, but this alone is not sufficient to explain the formation of nuclei. As will appear from some experiments to be described later, the formation of the nuclei, which cause the spontaneous release of carbon dioxide, also seems to be conditioned in this case by the presence of a boundary between the liquid and gaseous phases.

EXPERIMENTAL

The following preparations were used in the experiments:

I. Hydrosol of aluminium hydroxide, prepared according to Crum⁹, concentration 0.46 per cent, calculated as $\text{Al}(\text{OH})_3$.

II. Hydrosol of hydrated ferric oxide, commercial preparation Merck, "Liquor ferri oxydati dialysati", concentration 10.1 per cent, calculated as Fe_2O_3 .

The effect exerted by these colloids on the stability of supersaturated carbon dioxide solutions can be demonstrated very simply. The method used and the results of a few typical experiments will be described in detail here.

The bottles which were used were Danish beer bottles of the old standard type. When normally filled, *i. e.* half way up the neck, they contain about 335 ml, with an air space of about 20 ml. The crown corks used were of the normal type with plastic discs.

The carbon dioxide solution was prepared by leading carbon dioxide through distilled water at 0° C and at a counter-pressure of about 200 mm Hg. When the water is saturated with carbon dioxide it contains about 0.42 per cent CO_2 . At 20° C and atmospheric pressure, the supersaturation is hence about 150 per cent. The filling of the bottles was also carried out at 0° C and without counter-pressure. When the bottles were closed immediately after filling, there was no appreciable loss of carbon dioxide.

The apparatus used for shaking was constructed by Krause in 1930; it was built as a cupboard into which the bottles can be placed horizontally, separated from each other and fastened by rubber rollers. The apparatus performs rapid ascending and descending movements, about 180 times a minute. The designation "hopping-cupboard" is usually used for apparatus of this type, and the process to which the bottles are subjected is by analogy called "hopping". These designations will be used in the present paper. The hopping-cupboard is placed in a room with a constant temperature of 10° C.

[The effect of colloidal aluminium hydroxide and
ferric oxide

The aluminium hydroxide sol was diluted 1 : 10. Hence 5.0 ml of the diluted sol contained 2.3 mg $\text{Al}(\text{OH})_3$.

30 bottles were used for the experiment. 5.0 ml of the diluted sol was measured into each bottle, the bottles were then filled up with carbon dioxide solution and closed. 10 bottles were kept for 4 days in the hopping-cupboard.

10 » » » » 4 » » » » and
then for 4 days at rest at room temperature.

10 bottles were kept for 8 days at rest at room temperature.

Before the bottles were opened their temperature was adjusted by standing for 2 hours in a thermostat at 20° C.

The experiments with colloidal ferric oxide were carried out in the same way. A sol, containing 3.3 mg Fe_2O_3 per 5.0 ml was prepared by dilution of the ferric oxide sol.

The results are given in Table 1. The individual figures in the table show the number of g of the solution, which ran out of the bottle in question on opening.

In the bottles which were kept in the hopping-cupboard for 4 days, some of the dissolved carbon dioxide was released spontaneously immediately the bottles were opened, causing about 1/5 of the solution to be spilled.

The same result was obtained even when the bottles were kept at rest at room temperature for 4 days after shaking in the hopping-cupboard. The added colloids had no effect in the control bottles which stood at rest at room temperature.

Table 1. The effect of colloidal aluminium hydroxide and ferric oxide.

Bottle no.	4 days in hopping-cupboard		4 days in hopping-cupboard + 4 days at rest at room temperature		8 days at rest at room temperature	
	$\text{Al}(\text{OH})_3$	Fe_2O_3	$\text{Al}(\text{OH})_3$	Fe_2O_3	$\text{Al}(\text{OH})_3$	Fe_2O_3
1	83	72	94	72	0	0
2	71	67	72	66	0	0
3	72	72	69	74	0	0
4	74	62	84	61	0	0
5	70	63	69	76	0	0
6	79	69	74	71	0	0
7	36	71	82	63	0	0
8	81	63	65	65	0	0
9	64	69	60	68	0	0
10	32	57	61	65	0	0
Mean	66	67	73	68	0	0

When small amounts of these colloids are present in the supersaturated carbon dioxide solution, shaking in the hopping-cupboard causes changes in the system which influence the stability, and which can be recognized clearly by the spontaneous evolution of carbon dioxide. These changes are apparently permanent. In this respect the system behaves in a similar way to beer which has a tendency to over-foaming.

The effect of colloidal silicic acid

As mentioned in the introduction, colloidal silicic acid is without effect. A sol, containing 3.0 mg per ml calculated as SiO_2 , was prepared according to a method given by Schwarz¹⁰. The results of an experiment with this sol are given in Table 2. Each bottle contained about 4.0 mg colloidal silicic acid, calculated as SiO_2 . The bottles were kept in the hopping-cupboard for 7 days. When the bottles were opened only slight foaming was observed, in some cases this caused a few grams to spill from the bottle.

The influence of the surface

Some experiments performed similarly to those just described were carried out in order to determine whether the liquid surface plays any part in the processes which lead to the formation of nuclei.

As previously mentioned, the existence of a boundary between the liquid and gaseous phases is, according to Krause's hypothesis, an essential condition for the formation of the nuclei, which cause over-foaming in beer.

Since ordinary beer bottles which are closed with crown corks were unsuited to the experiments, they were replaced by 1/4 l mineral water bottles with patent closures. These bottles could be filled practically completely.

In normally filled bottles the bubbles will be continually whipped down into the liquid during hopping and hence will cause circulation. If, however, the bottles are completely filled, the circulation in the liquid will be considerably reduced. For this reason, a rotation apparatus was used for these experiments in place of the hopping-

Table 2. The effect of colloidal silicic acid.

Bottle no.	g "over-foaming"	
	7 days in hopping-cupboard	
1		4
2		0
3		2
4		0
5		4
6		3
7		0
8		2

Mean 2

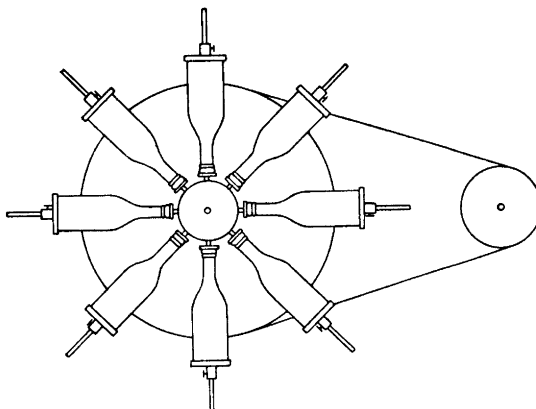


Fig. 1. Rotation apparatus.

cupboard; this is illustrated in Fig. 1. The bottles are placed radially around the axis of rotation, with their mouths pointing towards it. The apparatus, which is placed in a room at constant temperature, 10° C, rotates at 56 revolutions per minute and can contain 8 bottles. 10 5 mm glass balls were placed in each bottle. Satisfactory liquid circulation was thus obtained in the completely filled bottles during rotation.

The aluminium hydroxide sol was diluted 1 : 10. 3.0 ml of the diluted sol thus contained 1.4 mg $\text{Al}(\text{OH})_3$. 8 bottles were used for the experiment with this sol. 3.0 ml of the diluted sol were measured into each bottle, and the bottle was then filled with carbon dioxide solution. 4 bottles were normally filled and 4 bottles were completely filled. The bottles were then placed in the rotation apparatus and rotated for 4 days. Before opening their temperature was adjusted for 2 hours at 20° C.

The experiment with colloidal ferric oxide was performed in exactly the same way. A sol, containing 1.5 mg Fe_2O_3 per 3.0 ml, was prepared by dilution of the ferric oxide sol. The results are presented in Table 3.

Table 3. Influence of the surface
g "over-foaming"

Bottle no.	Normally filled		Completely filled	
	$\text{Al}(\text{OH})_3$	Fe_2O_3	$\text{Al}(\text{OH})_3$	Fe_2O_3
1	55	63	0	0
2	57	57	0	0
3	49	60	0	0
4	58	56	0	0
Mean	55	59	0	0

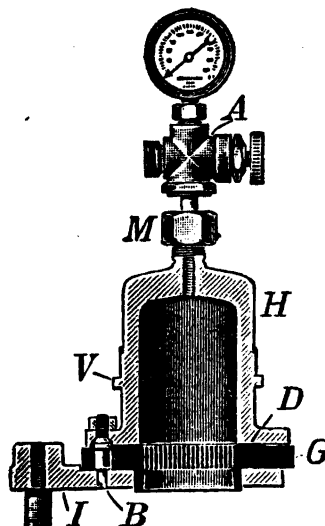


Fig. 2. Ultrafiltration apparatus. For explanation of letters see text.

In the bottles which were filled normally, the release of carbon dioxide on opening was so violent that the liquid shot out of the bottle in a 30–40 cm high spray; about 1/5 of the content was thus spilled. In the bottles which were completely filled, on the other hand, it was not possible to demonstrate any effect of the added colloid.

Hence the experiment appears to confirm the assumption that the liquid surface plays a part in the processes which lead to the formation of nuclei.

The addition of these colloids to a supersaturated solution of carbon dioxide thus gives a system which behaves essentially in the same way as beer which has a tendency to over-foaming.

The adsorption on colloidal ferric oxide

If the carbon dioxide is bound to the colloid, it must be assumed that complex compounds are formed in the surface of the particles by reaction between the bicarbonate ions and the positive ions in the surface of the particles. Hence this reaction is presumably the first step in the processes which lead to the formation of nuclei.

The experiments described here are designed for the purpose of confirming the assumption that the particles bind carbon dioxide.

The experiments were performed with the same ferric oxide sol used in the experiments described previously.

When the particles bind negative ions, in this case bicarbonate ions, some of the Gegen-ions already present will be displaced. An analysis of the ferric oxide sol showed that it contained 0.90 per cent Cl, which is present as

1. Chlorine ions, bound *in* the particles.
2. Chlorine ions, bound *to* the particles as associated ions (Gegen-ions).
3. Intermicellary ions, *i. e.* free chlorine ions.

The concentration of the chlorine ions, which are present as intermicellary ions, can be determined by ultrafiltration. Since the ions are not bound to the particles, they pass

Table 4. Filtration under oxygen pressure.

Fraction no.	ml	c_{Cl^-} $n \times 10^3$	c_{Fe} $m \times 10^3$
I	23	3.1	0.05
II	24	3.7	0.08
III	30	3.7	0.16
IV	25	3.7	0.15
V	25	3.9	0.16

freely through the filter and the concentration can be determined by analysis of the ultrafiltrate.

When bicarbonate ions are bound to the particles, some of the Gegen-ions will be released, resulting in a rise in the concentration of intermicellary chlorine ions. In order to demonstrate this, an ultrafiltration apparatus was used; this is illustrated in Fig. 2.

The liquid to be filtered is poured into the bell-jar H. The filter is placed between the flange D of the bell-jar and the perforated plate G. The liquid is forced through the filter by means of compressed gas which is led into the bell-jar at M. The apparatus is designed for pressures of up to 125 atmospheres and the bell-jar has a volume of about 250 ml.

Zsigmondy's ultrafilters from the firm Membranfilter Gesellschaft, Göttingen, were used for the experiments, and the procedure was as follows:

The ferric oxide sol was diluted 1 : 20. Hence the diluted sol contained:

Fe_2O_3 : 0.505 per cent
Cl, (total): 0.045 per cent \sim 12.7 millinormal.

1. Filtration under oxygen pressure

200 ml of the diluted sol were forced through the filter by means of compressed oxygen at about 50 atmospheres. As the filtration gradually proceeded, the ultrafiltrate was removed in fractions of 25–30 ml. The chlorine ion concentration in the first 5 fractions was determined by titration according to Mohr's method. The filtration lasted about two hours.

2. Filtration under carbon dioxide pressure

The filtration experiment was repeated in exactly the same way, except that carbon dioxide at about 50 atmospheres replaced the oxygen.

The results of the filtration experiments are presented in Tables 4 and 5.

Table 4 shows that the concentration of chlorine ions remains rather constant during the whole filtration. Assuming that the oxygen which dissolves in the sol during filtra-

Table 5. Filtration under carbon dioxide pressure.

Fraction no.	ml	c_{Cl^-} $n \times 10^3$	c_{Fe} $m \times 10^3$
I	23	3.9	0.02
II	24	5.4	0.04
III	28	6.2	0.11
IV	31	7.1	0.20
V	16	6.8	0.21

tion does not cause any change in the sphere of ions of the particles, the concentration of the intermicellary chlorine ions is thus determined. In the diluted sol the total chlorine content is 0.045 per cent, corresponding to 12.7 millinormal, of which about 29 per cent is present as intermicellary ions. On the other hand, when carbon dioxide is used for the filtration, it is dissolved in the sol during filtration and the bicarbonate ions thus formed will displace some of the associated ions. Hence the concentration of chlorine ions in the ultrafiltrate rises during filtration and gradually reaches about 56 per cent of the total chlorine content.

The concentration of ferric ions was also determined in the different fractions with *o*-phenanthroline. The figures are given in the last column of the tables. It can be seen that the concentration in the last fractions is slightly higher when carbon dioxide is used for filtration instead of oxygen, but the difference is relatively small and without significance for the conclusions which can be drawn from the experiment.

It can thus be shown in this way that the particles bind carbon dioxide. It must, however, be pointed out that shortly after the beginning of filtration complete coagulation occurs in the sol, and that a continuously increasing layer of precipitated ferric oxide deposits on the filter as the filtration proceeds. The possibility of further investigation of the process by means of ultrafiltration is thus very limited.

If it is possible to determine the concentration of the intermicellary chlorine ions in the sol itself by electrometric methods, *e. g.* by means of a silver chloride electrode, it should be possible to follow the reaction without simultaneously causing changes in the system. This is only possible if the electrode potential is determined by the intermicellary ions alone.

Lamb and Jacques¹¹ have used the silver chloride electrode in some investigations on the slow hydrolysis which occurs in diluted solutions of ferric chloride. The electrode potential was measured at suitable intervals during the hydrolysis, and a silver chloride electrode dipping into a hydrogen chloride solution of known concentration was used as a reference electrode. The two half cells were connected by a salt bridge of saturated ammonium nitrate. It appeared that it was not possible to determine changes in the activity of the chlorine ion during hydrolysis in a 0.001 *N* solution, and measurements in a 0.004 *N* solution showed only a very slight, but nevertheless definite decrease in activity.

Thus by this method Lamb and Jacques did not obtain results which could serve as a basis for calculations on the course of hydrolysis. The author, using the same method, has tried to determine the concentration of free chlorine ions in the ferric oxide sol. The results in this case also indicate that it is not possible to be certain that the electrode potential is determined by the free chlorine ions alone. The use of a salt bridge must also be considered as rather unfortunate, especially when the potential measurements are repeated over a long period in the same sol. It will not be possible to avoid gradual leakage of the ammonium nitrate into the sol, where it may be able to influence the chlorine ion activity or even produce coagulation in the sol.

As a result of these experiments and considerations, an apparatus, shown in Fig. 3, was used for the further experiments.

The triple-necked flask A contains about 1 l. The collodion sack B is prepared according to the method given by Sørensen¹² and mounted on the glass tube C. A hydrogen electrode D and a silver chloride electrode E are placed inside the sack. The two glass tubes F and G serve as delivery tubes for carbon dioxide and hydrogen respectively. The silver chloride electrode was prepared according to a method given by Brown¹³. These electrodes are very simple to prepare and many measurements in dilute hydrogen chloride

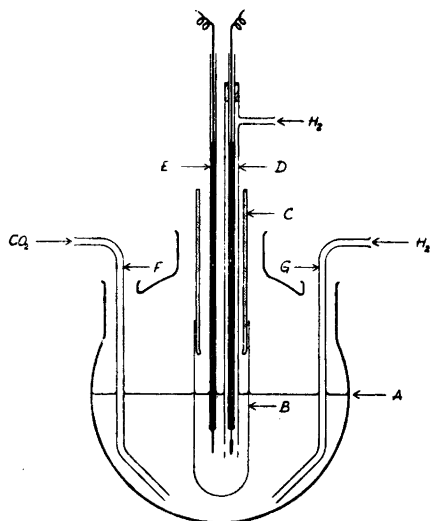


Fig. 3. Apparatus for measuring the activity of intermicellary ions. A triple-necked flask. B collodion sack. C glass tube. D hydrogen electrode. E silver chloride electrode. F and G delivery tubes for carbon dioxide and hydrogen respectively.

solutions have shown that the setting of potential occurs rapidly and that the accuracy is adequate for the present purpose.

The flask was placed in a water thermostat at 25.0° C. The separate parts of the apparatus were supported by means of clamp stands.

The carbon dioxide used for the experiments was taken from a steel cylinder and washed by passing through a solution of sodium bicarbonate and then through water. The hydrogen, which was also used to supply the hydrogen electrode, was similarly taken from a steel cylinder and cleaned by passing through five spiral wash bottles which contained, 1. alkaline pyrogallol solution, 2. ditto, 3. saturated potassium permanganate, 4. 0.1 *N* silver nitrate solution, 5. water.

500 ml of the solution to be examined were measured into the flask and 25 ml of water were measured into the sack. Hence the intermicellary ions will be free to wander through the collodion membrane and the concentration of these ions within the sack will thus rise until, at equilibrium, the same concentration is present on both sides of the membrane.

The use of a cell consisting of a hydrogen electrode and a silver chloride electrode has the great advantage that the salt bridge can be omitted. The potential is determined by the activity of the hydrogen ions and of the chlorine ions.

In pure hydrochloric acid solutions the potential E of the cell is determined by the expression:

$$E = E_0 - 2 \cdot 2.303 \frac{RT}{NF} \log a_{\text{HCl}}$$

where a_{HCl} is the activity of the hydrochloric acid and E_0 the normal potential of the silver chloride electrode. At 25.0° C $E_0 = 0.2224$ Volt (Harned and Ehlers¹⁴). If the potential of the cell at this temperature is E_{25} , we obtain:

$$\log a_{\text{HCl}} = \frac{0.2224 - E_{25}}{0.1182}$$

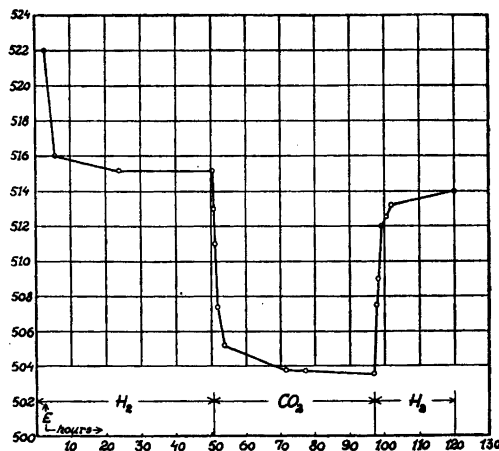


Fig. 4. Results of an experiment with the ferric oxide sol. Ordinate: Potentials in millivolt. Abscissa: Time in hours.

The procedure in experiments with this apparatus is as follows:

During the first period a weak current of hydrogen is led through the sol in order to obtain circulation in it, and hence promote diffusion of ions through the collodion membrane. When the measurements show that the potential has become constant, equilibrium has been reached and the chlorine ion concentration is the same on both sides of the membrane. The stream of hydrogen is then stopped, and a stream of carbon dioxide led through the sol. The concentration of chlorine ions rises again and after an interval the potential is again constant. If the dissolved carbon dioxide is now driven out by leading hydrogen through the sol, the process is reversed until the state present in the system before the carbon dioxide was introduced, is reached. On the basis of the potential measured after the introduction of hydrogen, the concentration of free chlorine ions in the sol can be calculated.

The first experiments were carried out with the ferric oxide sol. These showed that the measurements could not be reproduced with the necessary accuracy. Further investigation showed that the difficulties arose from the fact that the electrodes were placed side by side inside the sack. Measurements in hydrochloric acid solutions of known concentrations thus gave values that were too low, when the electrodes were placed side by side in the electrode vessel. On the other hand, good agreement between the measured and the theoretically calculated potentials was obtained when a U-tube was used, in which the electrodes were placed in the two arms. It must therefore be assumed that when the electrodes are placed side by side, the hydrogen affects the potential of the silver chloride electrode. For this reason all measurements in the following experiments were carried out in a U-tube. The solution in the sack was transferred to the U-tube and poured back into the sack again after completion of each measurement.

The electrodes were controlled during each experiment at suitable intervals by measuring in two hydrochloric acid solutions with c_{HCl} , 0.1006 *N* and 0.0101 *N* respectively. Hydrochloric acid "pro analysi" was used for the preparation of these solutions; it was first evaporated to about half the volume, small amounts of potassium permanganate being added, and then distilled twice in a quartz distillation apparatus. A U-tube was used as electrode vessel and the electrodes were placed in the two arms of the U-tube.

The potentials of the two elements:

I. H_2 (1 atm.) / HCl 0.1006 *N* / AgCl / Ag

II. H_2 (1 atm.) / HCl 0.0101 *N* / AgCl / Ag

at 25.0° C are 0.3519 Volt and 0.4639 Volt respectively.

The control measurements showed that in no case there were deviations, which exceeded the accuracy of measurement, $\pm 0.2-0.3$ mV.

The results of an experiment with the ferric oxide sol are presented graphically in Fig. 4. The ferric oxide sol was used in the same dilution as in the ultrafiltration experiment. Fig. 4 shows that constant potential was reached after leading hydrogen through for 24 hours, as the measured value of 0.5152 Volt did not change demonstrably after passing hydrogen through for further 26 hours.

0.5152 Volt corresponds to $a_{\text{HCl}} = 0.00335$ *N*. c_{HCl} can be calculated from the equations:

$$c_{\text{HCl}} \gamma = 0.00335$$

$$\log \gamma = -0.5 \sqrt{c_{\text{HCl}}}$$

and hence $c_{\text{HCl}} = c_{\text{Cl}^-} = 0.0036$ *N*. After correction for the 25 ml of water in the sack, $c_{\text{Cl}^-} = 0.0038$ *N*, is obtained for the diluted sol, which is in good agreement with the value found in the ultrafiltration experiment, $c_{\text{Cl}^-} = 0.0037$ *N* for the concentration of free chlorine ions in the sol.

The effect of the stream of carbon dioxide soon shows itself by a sudden fall in the potential; after about 21 hours it is 0.5038 Volt and it does not change in the next 24 hours.

0.5038 Volt corresponds to $a_{\text{HCl}} = 0.0042$ *N* and $c_{\text{Cl}^-} = 0.0045$ *N*. About 0.9 milliequivalents of chlorine ion per l. of the diluted sol is thus displaced by the bicarbonate ions.

When the carbon dioxide is finally driven out of the sol by the hydrogen, the potential rises rapidly indicating that the process is now reversed.

In order to calculate $c_{\text{HCO}_3^-}$ in the intermicellary liquid, it must be presupposed that the solubility and dissociation of the carbon dioxide in this liquid is the same as it is in water, and that the hydrogen ion activity is the same on both sides of the collodion membrane.

Inside the sack $a_{\text{H}^+} = a_{\text{HCl}} = 4.2 \cdot 10^{-3}$ *N*. In a saturated solution of carbon dioxide in water, $a_{\text{HCO}_3^-}$ can be calculated from the equilibrium expression:

$$a_{\text{HCO}_3^-} = K \frac{a_{\text{CO}_2}}{a_{\text{H}^+}}$$

At 25° C *K* is about $3.6 \cdot 10^{-7}$ (Faurholt¹⁵). If the solubility of carbon dioxide in water at 25° C and atmospheric pressure, which is about $3.3 \cdot 10^{-2}$, is substituted for a_{CO_2} , then

$$a_{\text{HCO}_3^-} = 2.8 \cdot 10^{-6}$$
 N

If the concentration of the bicarbonate ions in the intermicellary liquid is of this order of magnitude, it can be seen from the figures that these ions are rather strongly bound by the particles.

DISCUSSION

Krause's hypothesis presupposes, besides the existence of a surface between liquid and gaseous phase, that the substances which form the nuclei are present in higher concentration in the surface than in the liquid. When used as an explanation for the observations made in the previously described experiments, it indicates that the colloid particles must occur in the highest concentration in the surface and that an association (coagulation) of the particles occurs here during shaking. Among earlier investigations on coagulation in surfaces, a paper by Freundlich and Kroch¹⁶ must be mentioned in this connection. These authors investigated ferric oxide sols, prepared by hydrolysis of ferric carbonyl and found that coagulation occurs in the surface when the sol is subjected to mechanical stirring, while this is not the case in the more stable sols prepared by hydrolysis of ferric chloride.

Hence from these results it can not be expected that the ferric oxide sol used for the experiments described here has a tendency to coagulate directly in the surface. The fact that the particles bind bicarbonate ions, possibly during formation of complex compounds, however, causes a decrease in the net charge of the particles. Decreasing charge of the particles in a sol usually indicates an increased tendency to coagulation. Hence the possibility can not be excluded that the reaction with the bicarbonate ions causes a change in the properties of the sol, and that the tendency on the part of the particles to adsorption and coagulation in the surface is thus increased.

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