

XXXIX.—*The Absorption of Gases by Colloidal Solutions.*

By ALOIS GATTERER.

ONE of the most important studies of colloid chemistry is that dealing with adsorption and absorption in colloidal solutions, for not only is it of considerable practical value, but also it may throw light on the structure of the colloids themselves. The study of gaseous absorption in particular may be expected to yield definite and valuable results because of the chemical and electrical neutrality of solvent and solute. Of the few investigations of this kind that have hitherto been made, those of Geffcken (*Z. physikal. Chem.*, 1904, **49**, 297) and Findlay and his co-workers (*J.*, 1910, **97**, 536; 1912, **101**, 1459; 1913, **103**, 636; 1914, **105**, 291) are limited in their scope, being confined to comparatively few gases and solutions, to low concentrations and, above all, to one temperature, *viz.*, 25°.

Consequently, our knowledge of the absorptive power of colloidal

solutions is meagre and does not furnish a sufficiently broad experimental foundation for a trustworthy theory. A wide investigation of absorption has therefore been undertaken, with various colloidal solutions and at temperatures ranging from 5° to 25°. The colloidal solutions have been characterised by determinations not only of density and concentration but also of electrical conductivity, viscosity, the Tyndall effect, and absorption of light, for only in this way is it possible to define these complex systems so precisely that they can be exactly reproduced.

The observations here recorded refer only to two gases, carbon dioxide and acetylene, and to two colloidal solutions, ferriferrocyanide and ferric hydroxide; the former were chosen because of their acidic and neutral character respectively, and the latter because they are, respectively, positive and negative colloids.

#### EXPERIMENTAL.

*Preparation of Solutions.—Ferriferrocyanide.* The solution was prepared according to Zsigmondy ("Kolloid Chemie," 1920, 3rd ed., p. 300) by mixing 2*N*-solutions of sodium ferrocyanide and ferric chloride. The precipitate was carefully washed, redissolved in a small quantity of the ferrocyanide, and the solution was concentrated by heating in a vacuum. The maximum concentration obtained was about 3%.

*Ferric hydroxide.* A solution of pure ferric hydroxide in acetic acid was diluted and, after the method of Péan de St. Gilles, boiled until the ratio of acetic acid to ferric hydroxide became 1 : 30—1 : 60. The solution was then evaporated, not under atmospheric pressure, but under reduced pressure, whereby a much higher degree of dispersion, as shown by the Tyndall effect (compare Figs. 1 and 2), was obtained. This more highly dispersed solution appears to be intermediate between the solution of Graham and that of P. de St. Gilles.

*Preparation of Gases.*—The carbon dioxide was carefully washed and its purity was confirmed by the value obtained for its solubility in distilled water. Acetylene was generated from calcium carbide and freed from impurities by treatment with chromic acid and potassium hydroxide and by absorption in acetone. Analyses of the purified product by means of ammoniacal cuprous chloride showed residues of 0, 2, and 3 c.c. in 100 c.c.

*Apparatus and Outline of Method.*—The method of Ostwald was employed to measure absorption (Ostwald-Luther, "Handbuch der Physicochemischen Messungen," 1910, 3rd ed., p. 246). The solutions were freed from air by boiling in a vacuum and, without contact with air, transferred to the vacuum mixing vessel at 25°.

The gases were saturated with water vapour at the same temperature. Five measurements were made with a given solution at five different temperatures, the process being repeated after an interval of several hours to check the former results. The calculation of the solubility is based on the formula (see Ostwald-Luther, *op. cit.*)

$$l = \left[ V_{b_1} \frac{T_a(b_1 - h_{b_1})}{T_{b_1} T_a (b_1 - h_a)} - V_{b_2} \frac{T_a(b_2 - h_{b_2})}{T_{b_2} T_a (b_2 - h_a)} - V_a \right] \frac{1}{V_f},$$

where  $l$  = Ostwald's solubility;  $V_{b_1}$  = initial volume of gas in the burette at temperature  $T$  (abs.) and pressure  $b_1$ ;  $V_{b_2}$  = final volume of gas in the burette;  $T_a$  = absolute temperature of the thermostat;  $T_{b_1}$  and  $T_{b_2}$  = initial and final temperature, respectively, of gas in burette;  $b_1$  and  $b_2$  = pressure of the atmosphere at commencement and end of experiment;  $h_a$ ,  $h_{b_2}$ , and  $h_{b_1}$  = tension of water vapour at  $T_a$ ,  $T_{b_2}$ , and  $T_{b_1}$ , respectively;  $V_a$  = volume of liquid withdrawn, measured at  $T_a$ ;  $V_f = V - V_a$  = volume of liquid contained in the absorption vessel; and  $V$  = volume of the absorption vessel at temperature  $T_a$ .

The changes in volume of the solutions and of the mixing vessel at various temperatures were taken into consideration. The probable error was  $\pm 0.4\%$ . In certain cases, owing to an exceedingly slow rate of absorption, the completion of this was not reached, and this may be the explanation of the lack of smoothness in some of the curves. The values of  $l$  are given either in percentages, *i.e.*, number of grams in 100 c.c. of solution, or in gram-equivalents. All values of volume are calculated for  $20^\circ$ . Although it is uncertain whether the colloids in question have definite chemical formulæ, yet for the sake of clearness the gram-equivalent of Prussian blue was taken as  $1/12 \text{ Fe}_4[\text{Fe}(\text{CN})_6]_3 = 71.603$ , and that of ferric hydroxide as  $1/3 \text{ Fe}(\text{OH})_3 = 35.621$ .\*

#### *Solubility of Carbon Dioxide in Solutions of Prussian Blue.*

The values in Table I have been obtained by different workers for the solubility of carbon dioxide in water.

Findlay (*loc. cit.*) gives a somewhat lower value, *viz.*, 0.817 at  $25^\circ$ .

The solubility values ( $l$ ) of carbon dioxide in solutions of Prussian blue are in Table II and Fig. 3 (unbroken lines).

\* According to Hofmann ("Lehrbuch der Anorganischen Experimental-chemie," 1918, p. 641) soluble Prussian blue has the formula  $\text{Fe}(\text{CN})_6\text{NaFe}$ . This, of course, would change the above equivalent weight. Hofmann's formula, however, is not generally accepted, and, moreover, does not agree with the author's results. Further, if Hofmann's formula is assumed, the results obtained by the gravimetric and the volumetric methods do not agree.

TABLE I.

| T.  | Bohr and | Geffcken.† | Gatterer.‡ |       |       | Mean. |
|-----|----------|------------|------------|-------|-------|-------|
|     | Bock.*   |            | l.         |       |       |       |
|     | l.       | l.         |            |       |       |       |
| 25° | 0.829    | 0.8255     | 0.826      | 0.823 | 0.830 | 0.826 |
| 20  | 0.942    | —          | 0.933      | 0.936 | 0.940 | 0.936 |
| 15  | 1.072    | 1.070      | 1.066      | 1.072 | 1.073 | 1.070 |
| 10  | 1.238    | —          | 1.233      | 1.244 | 1.242 | 1.240 |
| 5   | 1.449    | —          | 1.440      | 1.453 | 1.445 | 1.446 |

\* *Wied. Ann.*, 1891, 44, 318. † *Loc. cit.* ‡ In this and the following tables the exact temperatures are : 25.00°, 19.98°, 14.96°, 9.95°, and 4.97° instead of 25°, 20°, 15°, 10°, and 5°, respectively. In the solubility diagrams, the mean values in the tables are represented. For economy in space, the curves of different temperature intervals are moved closer together.

TABLE II.

|                           | 25°.          | 20°.          | 15°.         | 10°.         | 5°.          |
|---------------------------|---------------|---------------|--------------|--------------|--------------|
| Soln. 1.                  | 0.8424        | 0.9510        | 1.086        | 1.254        | 1.451        |
| <i>c</i> = 0.896 <i>N</i> | 0.8418        | 0.9515        | 1.087        | 1.255        | 1.454        |
|                           | <i>0.8421</i> | <i>0.9512</i> | <i>1.087</i> | <i>1.255</i> | <i>1.453</i> |
| Soln. 2.                  | 0.8516        | 0.9617        | 1.095        | 1.262        | 1.463        |
| <i>c</i> = 0.51 <i>N</i>  | 0.8494        | 0.9610        | 1.092        | 1.265        | 1.466        |
|                           | <i>0.8505</i> | <i>0.9613</i> | <i>1.093</i> | <i>1.264</i> | <i>1.464</i> |
| Soln. 3.                  | 0.8566        | 0.9696        | 1.105        | 1.276        | 1.477        |
| <i>c</i> = 0.37 <i>N</i>  | 0.8588        | 0.9672        | 1.106        | 1.279        | 1.479        |
|                           | <i>0.8577</i> | <i>0.9684</i> | <i>1.106</i> | <i>1.277</i> | <i>1.478</i> |
| Soln. 5.                  | 0.8544        | 0.9653        | 1.100        | 1.270        | 1.472        |
| <i>c</i> = 0.178 <i>N</i> | 0.8517        | 0.9613        | 1.096        | 1.267        | 1.472        |
|                           | <i>0.8530</i> | <i>0.9633</i> | <i>1.098</i> | <i>1.268</i> | <i>1.472</i> |
| Soln. 4.                  | 0.8430        | 0.9510        | 1.0850       | 1.254        | 1.463        |
| <i>c</i> = 0.126 <i>N</i> | 0.8456        | 0.9568        | 1.092        | 1.263        | 1.469        |
|                           | <i>0.8443</i> | <i>0.9549</i> | <i>1.089</i> | <i>1.258</i> | <i>1.465</i> |

Mean values are printed in italics in all the tables.

The temperature coefficients of absorption of carbon dioxide in solutions of Prussian blue ( $\Delta l/\Delta t$ ) are in Table III, and have been calculated from the results in Table II.

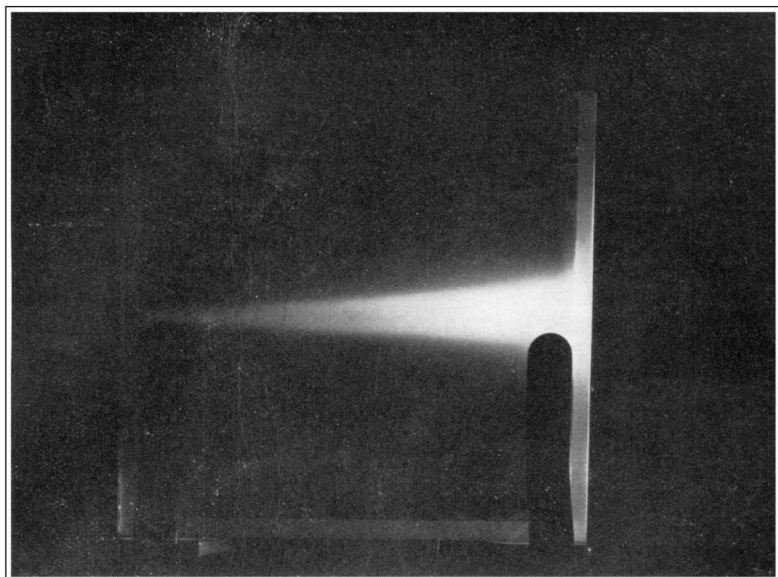
TABLE III.

| Soln.            | 25—20°. | 20—15°. | 15—10°. | 10—5°. |
|------------------|---------|---------|---------|--------|
| 1                | 0.0218  | 0.0271  | 0.0336  | 0.0396 |
| 2                | 0.0221  | 0.0264  | 0.0342  | 0.0400 |
| 3                | 0.0221  | 0.0274  | 0.0342  | 0.0402 |
| 5                | 0.0221  | 0.0268  | 0.0340  | 0.0408 |
| 4                | 0.0219  | 0.0268  | 0.0338  | 0.0414 |
| H <sub>2</sub> O | 0.0220  | 0.0268  | 0.0340  | 0.0412 |

#### *Solubility of Carbon Dioxide in Solutions of Ferric Hydroxide.*

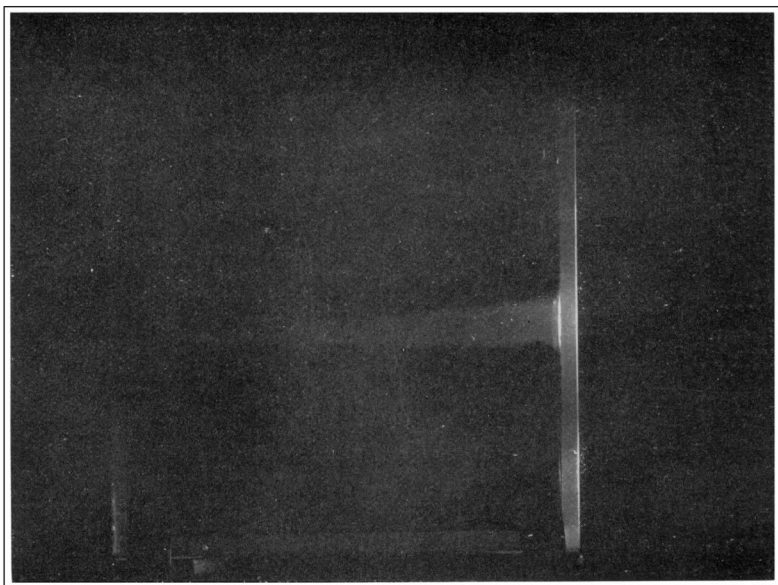
In Table IV and Fig. 3 (broken lines) are the solubilities of carbon dioxide in solutions of ferric hydroxide at temperatures ranging from 5° to 25° in intervals of 5°, whilst in Table V are the temperature coefficients ( $\Delta l/\Delta t$ ).

FIG. 1.



*Tyndall effect for solution evaporated under atmospheric pressure.*

FIG. 2.



*Tyndall effect for solution evaporated in a vacuum.*

[To face p. 302.]

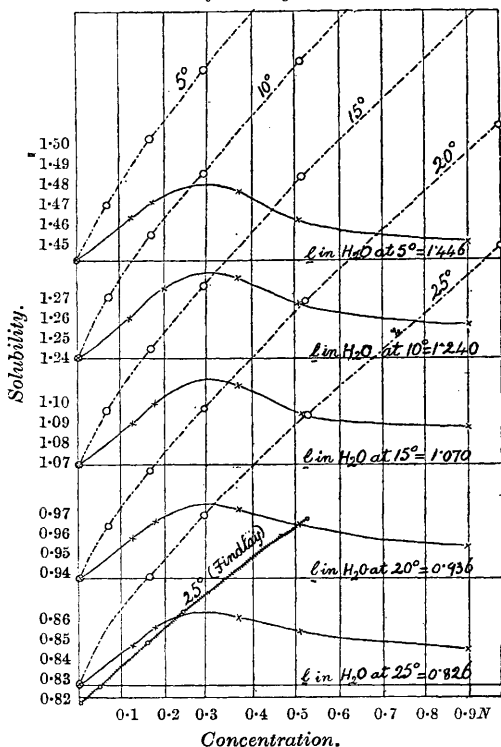
TABLE IV.

|                             | 25°.   | 20°.   | 15°.  | 10°.  | 5°.   |
|-----------------------------|--------|--------|-------|-------|-------|
| Soln. 2.                    | 0.8518 | 0.9601 | 1.093 | 1.264 | 1.467 |
| <i>c</i> = 0.071 <i>N</i>   | 0.8547 | 0.9619 | 1.098 | 1.271 | 1.476 |
|                             | 0.8533 | 0.9610 | 1.095 | 1.267 | 1.471 |
| Soln. 1.                    | 0.8788 | 0.9906 | 1.127 | 1.300 | 1.509 |
| <i>c</i> = 0.144 <i>N</i>   | 0.8740 | 0.9834 | 1.119 | 1.297 | 1.498 |
|                             | 0.8764 | 0.9870 | 1.123 | 1.297 | 1.503 |
| Soln. 4.                    | 0.9073 | 1.017  | 1.155 | 1.326 | 1.536 |
| <i>c</i> = 0.293 <i>N</i>   | 0.9053 | 1.016  | 1.153 | 1.326 | 1.533 |
|                             | 0.9063 | 1.016  | 1.154 | 1.326 | 1.534 |
| Soln. 3.                    | 0.9531 | 1.067  | 1.203 | 1.379 | 1.583 |
| <i>c</i> = 0.513 <i>N</i> * | 0.9521 | 1.066  | 1.205 | 1.380 | 1.585 |
|                             | 0.9526 | 1.066  | 1.204 | 1.379 | 1.584 |
| Soln. 5.                    | 1.030  | 1.146  | 1.287 | 1.467 | —     |
| <i>c</i> = 0.967 <i>N</i>   | 1.035  | 1.152  | 1.295 | 1.473 | 1.684 |
|                             | 1.032  | 1.149  | 1.291 | 1.470 | 1.680 |

\* This value was obtained from a density determination.

FIG. 3.

Solubility of carbon dioxide in solutions of Prussian blue and ferric hydroxide.



--- CO<sub>2</sub> in Fe(OH)<sub>3</sub>. — CO<sub>2</sub> in Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>.

TABLE V.

| Soln.            | 25—20°. | 20—15°. | 15—10°. | 10—5°. |
|------------------|---------|---------|---------|--------|
| 2                | 0.0215  | 0.0268  | 0.0344  | 0.0408 |
| 1                | 0.0221  | 0.0272  | 0.0348  | 0.0412 |
| 4                | 0.0220  | 0.0276  | 0.0344  | 0.0416 |
| 3                | 0.0227  | 0.0276  | 0.0350  | 0.0410 |
| 5                | 0.0234  | 0.0284  | 0.0358  | 0.0420 |
| H <sub>2</sub> O | 0.0220  | 0.0268  | 0.0340  | 0.0412 |

*Solubility of Acetylene in Solutions of Prussian Blue.*

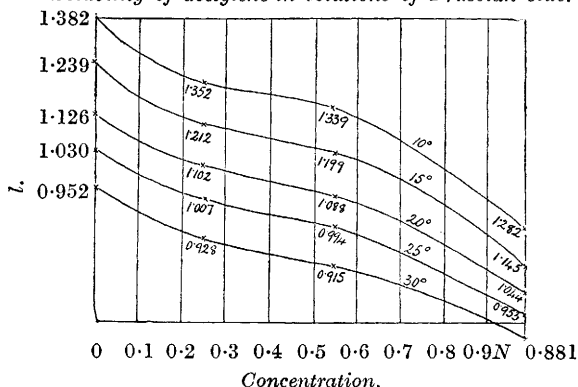
The following solubility values of purified acetylene in distilled water were obtained (Table VI).

TABLE VI.

| T.  | l.    |       |       | Mean. |
|-----|-------|-------|-------|-------|
| 30° | 0.951 | 0.950 | 0.954 | 0.952 |
| 25  | 1.030 | 1.028 | 1.031 | 1.030 |
| 20  | 1.126 | 1.125 | 1.127 | 1.126 |
| 15  | 1.239 | 1.239 | 1.241 | 1.239 |
| 10  | 1.381 | 1.383 | 1.383 | 1.382 |

FIG. 4.

*Solubility of acetylene in solutions of Prussian blue.*



The values of Winkler, according to unpublished communications (Landolt-Börnstein-Roth, "Physikalisch-Chemie Tabellen," 1912, p. 600), are calculated only to the second decimal place and, on the average, are smaller by 1.5—2% than those of the author, as the following figures show :—

|                                                 | 30°.  | 25°.  | 20°.  | 15°.  | 10°.  |
|-------------------------------------------------|-------|-------|-------|-------|-------|
| Abs. coeff. (Winkler) .....                     | 0.84  | 0.93  | 1.03  | 1.15  | 1.31  |
| Abs. coeff. from Table VI,<br>mean values ..... | 0.858 | 0.944 | 1.049 | 1.175 | 1.330 |
| Diff. % .....                                   | 2.1   | 1.5   | 1.8   | 2.1   | 1.5   |

Only a more accurate study of Winkler's experiments could determine whether or not this difference is due to impurities in the gas.

Table VII and Fig. 4 show the solubility of acetylene in solutions of Prussian blue, and Table VIII the temperature-coefficients per degree.

TABLE VII.

|               | 30°.             | 25°.             | 20°.           | 15°.           | 10°.           |
|---------------|------------------|------------------|----------------|----------------|----------------|
| Soln. II.     | 0.9286           | 1.007            | 1.100          | 1.210          | 1.351          |
| $c = 0.250N$  | 0.9292<br>0.9289 | 1.007<br>1.007   | 1.103<br>1.102 | 1.214<br>1.212 | 1.365<br>1.358 |
| Soln. I.      | 0.9186           | 0.9966           | 1.089          | 1.199          | 1.335          |
| $c = 0.548N$  | 0.9113<br>0.9149 | 0.9908<br>0.9937 | 1.086<br>1.088 | 1.199<br>1.199 | 1.343<br>1.339 |
| Soln. III.    | 0.8808           | 0.9543           | 1.042          | 1.147          | 1.276          |
| $c = 1.028N$  | 0.8825<br>0.8816 | 0.9512<br>0.9527 | 1.046<br>1.044 | 1.142<br>1.145 | 1.289<br>1.282 |
| Soln. IV.     |                  |                  |                |                |                |
| $c = 0.75N^*$ | 0.901            | 0.976            | 1.071          | 1.179          | 1.317          |

\* This value was obtained from a density determination, and the corresponding values of  $l$  from the graph (Fig. 4).

FIG. 5.

Solubility of acetylene in solutions of ferric hydroxide.

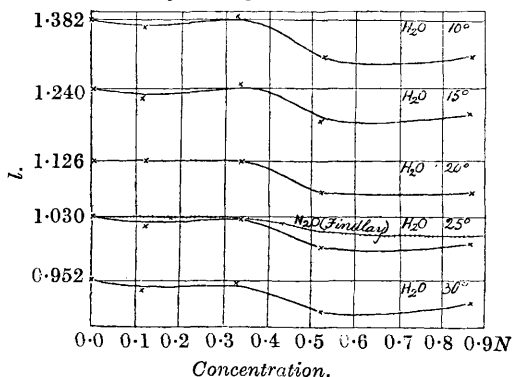


TABLE VIII.

| Soln.            | 30—25°. | 25—20°. | 20—15°. | 15—10°. |
|------------------|---------|---------|---------|---------|
| II               | 0.0156  | 0.0190  | 0.0220  | 0.0282  |
| I                | 0.0158  | 0.0188  | 0.0222  | 0.0280  |
| IV               | 0.0150  | 0.0190  | 0.0216  | 0.0276  |
| III              | 0.0142  | 0.0182  | 0.0202  | 0.0274  |
| H <sub>2</sub> O | 0.0156  | 0.0192  | 0.0226  | 0.0286  |

*Solubility of Acetylene in Solutions of Ferric Hydroxide.*

The data are in Table IX and are shown by the curves in Fig. 5: the temperature coefficients are in Table X.



TABLE IX.

|              | 30°.   | 25°.  | 20°.  | 15°.   | 10°.  |
|--------------|--------|-------|-------|--------|-------|
| Soln. III.   | 0.9405 | 1.020 | 1.109 | 1.229  | 1.372 |
| $c = 0.871N$ | 0.9394 | 1.016 | 1.112 | 1.225  | 1.366 |
|              | 0.9400 | 1.018 | 1.111 | 1.227  | 1.364 |
| Soln. II.    | 0.9360 | 1.015 | 1.111 | 1.226  | 1.368 |
| $c = 0.521N$ | 0.9360 | 1.016 | 1.111 | 1.223  | 1.361 |
|              | 0.9360 | 1.016 | 1.111 | 1.224  | 1.364 |
| Soln. I.     | 0.9499 | 1.030 | 1.126 | 1.240  | 1.381 |
| $c = 0.336N$ | 0.9492 | 1.028 | 1.126 | 1.243  | 1.386 |
|              | 0.9495 | 1.029 | 1.126 | 1.241  | 1.383 |
| Soln. IV.    | 0.9446 | 1.025 | 1.125 | 1.230  | 1.380 |
| $c = 0.12N$  | 0.9426 | 1.024 | 1.129 | 1.233  | 1.378 |
|              | 0.9479 | 1.027 | 1.123 | 1.236  | 1.378 |
|              | 0.9450 | 1.026 | 1.126 | 1.236* | 1.379 |

\* More probable value.

TABLE X.

| Soln.            | 30—25°. | 25—20°. | 20—15°. | 15—10°. |
|------------------|---------|---------|---------|---------|
| III              | 0.0156  | 0.0186  | 0.0232  | 0.0274  |
| II               | 0.0160  | 0.0190  | 0.0226  | 0.0280  |
| I                | 0.0158  | 0.0194  | 0.0230  | 0.0284  |
| IV               | 0.0162  | 0.0200  | 0.0220  | 0.0292  |
| H <sub>2</sub> O | 0.0156  | 0.0192  | 0.0226  | 0.0286  |

*Examination of the Colloidal Solutions.*

In order to define the colloid systems employed and to facilitate re-examination, detailed investigations have been made into the chemical and physical properties of the colloidal solutions used, in the hope that from a consideration of the solubility phenomena and other properties, the intrinsic structures may perhaps be determined. The systems were investigated, therefore, from the point of view of (1) concentration, (2) density, (3) electrical conductivity, (4) depression of the freezing point, and (5) viscosity.

1. *Concentration.*—(a) *Prussian blue.* Gravimetric and volumetric analyses were made. The evaluation of the effective concentration met with some difficulty, owing to a certain quantity of peptising agent which was present in solution. This was avoided in the following way. A certain quantity of solution (5—10 g.) was heated and sodium hydroxide added until all the Prussian blue was converted into ferric hydroxide, which was filtered off. The filtrate was acidified with dilute sulphuric acid, and the sodium ferrocyanide titrated with  $N/10$ -potassium permanganate until the pink colour was permanent. From the quantity of permanganate used, the amount of  $\text{Fe}(\text{CN})_6'''$  ions which remained after the reaction with sodium hydroxide was easily calculated. There were also  $\text{Fe}(\text{CN})_6'''$  ions present from the beginning in the peptised solution, and for this reason the total  $\text{Fe}(\text{CN})_6'''$  found would give too large a

value for the Prussian blue content. To establish the exact quantity of the latter volumetrically, the ratio ( $\varphi$ ) of  $\text{Fe}(\text{CN})_6'''$  formed from the Prussian blue to the total  $\text{Fe}(\text{CN})_6'''$  present was determined by gravimetric analysis of the precipitated ferric hydroxide. This was dissolved in dilute hydrochloric acid, re-precipitated with ammonia, and estimated as ferric oxide. The sodium ferrocyanide equivalent to the ferric oxide found was the amount of ferrocyanide obtained from the Prussian blue, which was thus directly determined. The value of  $\varphi$  could now be found—using the results with permanganate—and was calculated to be 0.9430. Since  $\varphi$  was constant (all solutions being of one preparation), all measurements of the concentration of Prussian blue could then be made by the permanganate method, which was therefore used. Both methods show a satisfactory agreement to within 0.1%, *e.g.*, solution I gave 3.91% volumetrically and 4.02% by the gravimetric method, and solution III, 7.368 and 7.362%, respectively.

(b) *Ferric hydroxide.* The concentration of this solution was determined from the amount of ferric oxide obtained on evaporating a definite quantity of the solution and heating the residue to redness. Considerable difficulty was experienced in determining the quantity of the peptising agent (acetic acid). In the first place, the ratio  $\text{Fe}(\text{OH})_3$  : peptising agent was not constant, because the latter changed whenever the solution was boiled; and secondly, the quantity of acetic acid present was so small that direct titration could afford no exact results. Finally, about 30–40 g. of the solution were acidified with dilute sulphuric acid and about one litre of the resulting solution was distilled. The acetic acid in the distillate was neutralised with baryta, and the excess of this precipitated with carbon dioxide. The whole was concentrated to a small volume, the barium carbonate filtered off, and the barium acetate in the filtrate precipitated with sulphuric acid. The amount of acetic acid was calculated from the weight of barium sulphate found. The greater solubility of barium carbonate over barium sulphate was taken into consideration in the results, which are in Table XII.

2. *Density.*—Densities were determined with a large pycnometer, and the results compared with the density of water at 4° and reduced to vacuum values. Only the results actually obtained are in Tables XI and XII. The results show that, over the whole temperature range studied, density is a linear function of concentration.

3. *Electrical Conductivity.*—The object of these measurements was to determine to what degree the colloid was free from contamination by electrolytes; for an increase in conductivity might have been due to such contamination and eventually to colloidal

TABLE XI.  
Concentration and Density,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

| No.                          | Concentration. |       | Peptis., $\text{Na}_4[\text{Fe}(\text{CN})_6]$ . |      | Density. |         |         |         |         |        |
|------------------------------|----------------|-------|--------------------------------------------------|------|----------|---------|---------|---------|---------|--------|
|                              | Equiv. N.      | %.    | Equiv. N.                                        | %.   | 30°.     | 25°.    | 20°.    | 15°.    | 10°.    | 5°.    |
| $\text{H}_2\text{O}^\dagger$ | —              | —     | —                                                | —    | 0.9957   | 0.9971  | 0.9982  | 0.9991  | 0.9997  | 1.0000 |
| 4                            | 0.126          | 0.94  | 0.008                                            | 0.06 | —        | 1.0029* | 1.0040  | 1.0049  | 1.0054* | 1.0059 |
| 5                            | 0.178          | 1.27  | 0.011                                            | 0.08 | —        | 1.0055* | 1.0066  | 1.0075  | 1.0081* | 1.0086 |
| II                           | 0.250          | 1.788 | 0.016                                            | 0.12 | 1.0671   | 1.0085  | 1.0096* | 1.0105  | 1.0111  | —      |
| 3                            | 0.37           | 2.64  | 0.022                                            | 0.17 | —        | 1.0142* | 1.0153  | 1.0162  | 1.0168* | 1.0172 |
| 2                            | 0.51           | 3.65  | 0.030                                            | 0.23 | —        | 1.0213* | 1.0224  | 1.0233* | 1.0239  | 1.0242 |
| I                            | 0.546          | 3.91  | 0.033                                            | 0.25 | 1.0205*  | 1.0219  | 1.0230* | 1.0238  | 1.0244* | —      |
| I                            | 0.896          | 6.41  | 0.053                                            | 0.40 | —        | 1.0374* | 1.0385  | 1.0394  | 1.0401* | 1.0404 |
| III                          | 1.028          | 7.36  | 0.062                                            | 0.47 | —        | 1.0427* | 1.0442  | 1.0454* | 1.0467* | —      |

† Compare Landolt-Börnstein-Röth, *op. cit.*, p. 42.

TABLE XII.  
Concentration and Density,  $\text{Fe}(\text{OH})_3$ .

| No.                          | Concentration. |       | Peptisation, $\text{CH}_3\text{-COOH}$ . |       | Density. |         |         |         |         |        |
|------------------------------|----------------|-------|------------------------------------------|-------|----------|---------|---------|---------|---------|--------|
|                              | Equiv. N.      | %.    | Equiv. N.                                | %.    | 30°.     | 25°.    | 20°.    | 15°.    | 10°.    | 5°.    |
| $\text{H}_2\text{O}^\dagger$ | —              | —     | —                                        | —     | 0.9957   | 0.9971  | 0.9982  | 0.9991  | 0.9997  | 1.0000 |
| 2                            | 0.071          | 0.252 | 0.002                                    | 0.01  | —        | 0.9982  | 0.9993  | 1.0002* | 1.0008  | 1.0011 |
| IV                           | 0.12           | 0.425 | —                                        | —     | 0.9984   | 0.9998  | 1.0009  | 1.0018* | 1.0024  | —      |
| I                            | 0.144          | 0.514 | 0.0036                                   | 0.021 | —        | 1.0002* | 1.0014  | 1.0023* | 1.0027* | 1.0030 |
| 4                            | 0.293          | 1.042 | 0.003                                    | 0.017 | —        | 1.0037* | 1.0048  | 1.0057  | 1.0063* | 1.0066 |
| I                            | 0.336          | 1.196 | —                                        | —     | 1.0031*  | 1.0046  | 1.0057* | 1.0066  | 1.0072* | —      |
| 3                            | 0.513†         | 1.825 | 0.0096                                   | 0.057 | —        | 1.0087* | 1.0098  | 1.0106  | 1.0112* | 1.0115 |
| II                           | 0.521          | 1.875 | —                                        | —     | 1.0075*  | 1.0089  | 1.0100* | 1.0109  | 1.0114* | —      |
| III                          | 0.871          | 3.103 | —                                        | —     | 1.0157   | 1.0171  | 1.0182  | 1.0191* | 1.0197  | —      |
| 5                            | 0.967          | 3.446 | 0.011                                    | 0.064 | —        | 1.0191* | 1.0202  | 1.0211  | 1.0218* | 1.0221 |

† Compare Landolt-Börnstein-Röth, *op. cit.*, p. 42.

‡ This number is obtained from a density determination.

The values marked \* in Tables XI and XII were obtained experimentally, the others by interpolation.

ions. Moreover, the questions arise (1) to what extent is peptisation changed by the action of the colloidal solution, and (2) are ionisation and ionic mobility much the same, at similar concentrations, as in a pure solvent?

The Kohlrausch method, with inductor and telephone, was employed and the results are in the following tables and diagrams.

(a) *Prussian Blue* (see Table XIII and Fig. 6). All measurements were made at 18°. For purposes of comparison the conductivity of pure sodium ferrocyanide is given in Table XIV and shown graphically in Fig. 7.

FIG. 6.  
*Prussian blue.*

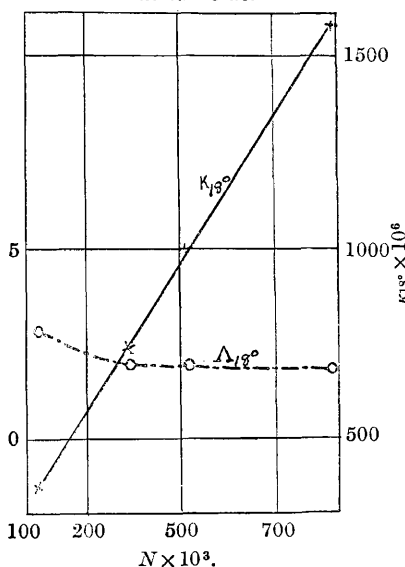


TABLE XIII.  
*Prussian blue.*

| Soln. | $N \times 10^3$ . | $\kappa_{18^\circ} \times 10^6$ . | $\Delta_{18^\circ}$ . |
|-------|-------------------|-----------------------------------|-----------------------|
| 1     | 896               | 1575.0                            | 1.75                  |
| 2     | 510               | 992.6                             | 1.94                  |
| 3     | 370               | 750.0                             | 2.03                  |
| 4     | 126               | 359.4                             | 2.85                  |

$$\Delta = \kappa \times 10^6 / N \times 10^3.$$

FIG. 7.  
*Sodium ferrocyanide.*

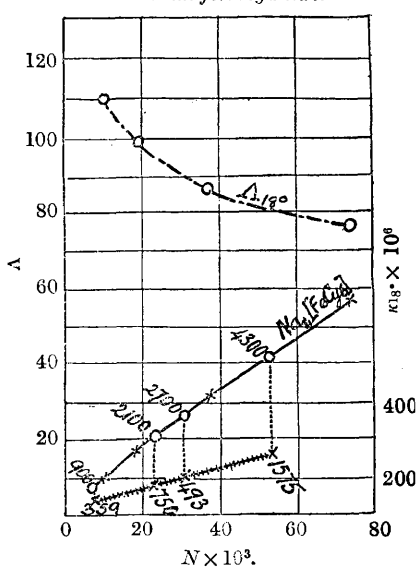


TABLE XIV.  
 $\text{Na}_4\text{Fe}(\text{CN})_6$ .

| $N \times 10^3$ . | $\kappa_{18^\circ} \times 10^6$ . | $\Delta_{18^\circ}$ . |
|-------------------|-----------------------------------|-----------------------|
| 74                | 5664                              | 76.6                  |
| 37                | 3205                              | 86.8                  |
| 18.5              | 1803                              | 97.5                  |
| 9.3               | 1000                              | 110.0                 |

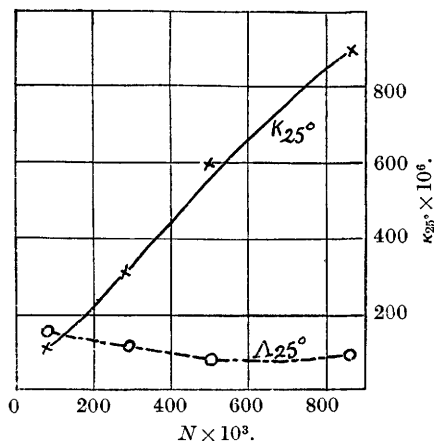
A remarkable feature of Fig. 7 is that the curve for the peptising agent in the solution lies below that of the ferrocyanide in water. Hence it was assumed that the conductivity of the colloid was wholly due to the amount of peptising agent present, and therefore the

abscissæ of the lowest curve in the figure are those of the peptising agent in Prussian blue solution: the ordinates are corresponding values of equivalent conductivity of Prussian blue. The values are taken from Table XIII. The continuations of these ordinates cut the curve for sodium ferrocyanide in water, and the data at these points of intersection show the conductivities of a pure solution of sodium ferrocyanide of the same concentration as in the colloid. The conductivity curve for sodium ferrocyanide with peptisation

TABLE XV.

| Soln. | $N \times 10^3$ . | $\kappa_{25^\circ} \times 10^6$ . | $\Delta_{25^\circ}$ . |
|-------|-------------------|-----------------------------------|-----------------------|
| 2     | 71                | 104.6                             | 1.511                 |
| 1     | 144               | 238.0                             | 1.641                 |
| 4     | 293               | 314.3                             | 1.073                 |
| 3     | 513               | 508.5                             | 1.741                 |
| 5     | 967               | 903.0                             | 0.934                 |

FIG. 8.

*Ferric hydroxide.*

is a straight line, and the gradient of this line with respect to the curve for sodium ferrocyanide in water is about 0.368. Hence the ordinates,  $y_1$ , of the one curve are constant multiples of the ordinates,  $y_2$ , of the other, *i.e.*,  $y_1 = \text{constant} \times y_2$ . It would be of interest to investigate the behaviour of other colloids in a similar way.

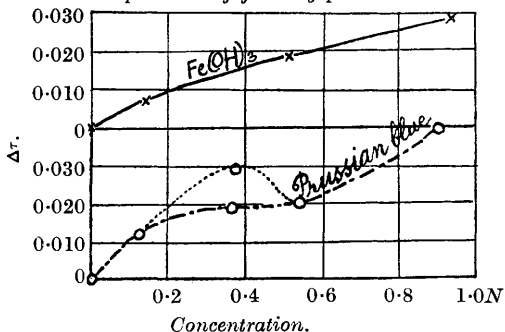
(b) *Ferric hydroxide* (see Table XV and Fig. 8). All the measurements were made at  $25^\circ$ . The curve for equivalent conductivity seems to pass through a minimum at a normality of about 0.5. The equation,  $y_1 = y_2 \times \text{constant}$ , found for Prussian blue, unfortunately, cannot be examined in this case, for the conductivity of

this colloid is far superior to that of the peptising agent—if this alone is considered—as the following data show :

| Acetic acid.      |                                   | Coll. Fe(OH) <sub>3</sub> . |                                     |                                   |
|-------------------|-----------------------------------|-----------------------------|-------------------------------------|-----------------------------------|
| $N \times 10^3$ . | $\kappa_{25^\circ} \times 10^6$ . | No.                         | Peptisation<br>( $N \times 10^3$ ). | $\kappa_{25^\circ} \times 10^6$ . |
| 2                 | 67                                | 2                           | 2                                   | 105                               |
| 5                 | 110                               | 4                           | 3                                   | 314                               |
| 10                | 158                               | 3                           | 9.6                                 | 509                               |
| 20                | 229                               | 5                           | 11.0                                | 903                               |

The figures in this table show that ions of acetic acid—and it may be others as well—transport electric charges. These others, especially chlorine ions, may arise from impurities adsorbed by the ferric hydroxide when it was first precipitated and irremovable by washing. The discussion which follows later shows that the

FIG. 9.  
*Depression of freezing-point.*



greater conductivity of these solutions of ferric hydroxide may possibly be due to "colloidal ions."

4. *Depression of Freezing-point.*—These determinations, which were carried out in a Beckmann apparatus, were made in order to estimate, as far as possible, the relative numbers of particles in the solutions and also to determine whether these numbers vary proportionally to the concentration. The results are in Table XVI (see also Fig. 9).

TABLE XVI.  
*Freezing-point Depression, Δτ.*

| Prussian blue. |            |                      | Ferric hydroxide. |            |        |
|----------------|------------|----------------------|-------------------|------------|--------|
| Soln.          | Conc. (N). | Δτ.                  | Soln.             | Conc. (N). | Δτ.    |
| 1              | 0.896      | 0.040°               | 5                 | 0.967      | 0.029° |
| 2              | 0.51       | 0.020                | 3                 | 0.513      | 0.018  |
| 3              | 0.37       | { 0.030**<br>0.019** | 1                 | 0.144      | 0.008  |
| 4              | 0.126      |                      | 0.012             |            |        |

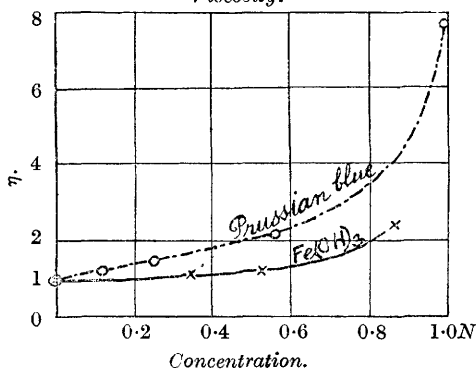
A small freezing-point depression is an indication of the comparative purity of a colloidal system. The values marked \*\* in the table were obtained at different times and the value 0.030 was constant. The curve may possibly rise to a maximum for a concentration of 0.3*N*, or there may here be a point of inflexion if the lower and more probable value, 0.019, be plotted.

TABLE XVII.  
*Viscosities at 25°.*

| Ferric hydroxide. |           |                   |          | Prussian blue.   |           |                   |          |
|-------------------|-----------|-------------------|----------|------------------|-----------|-------------------|----------|
| Soln.             | <i>s.</i> | <i>t</i> (secs.). | $\eta$ . | Soln.            | <i>s.</i> | <i>t</i> (secs.). | $\eta$ . |
| H <sub>2</sub> O  | 0.9960    | 62.8              | 1.000    | H <sub>2</sub> O | 0.9960    | 62.8              | 1.000    |
| 2                 | 0.9982    | 63.7              | 1.017    | 4                | 1.0029    | 73.0              | 1.170    |
| I                 | 1.0046    | 67.8              | 1.089    | II               | 1.0085    | 84.4              | 1.361    |
| II                | 1.0089    | 72.0              | 1.161    | I                | 1.0219    | 128.8             | 2.104    |
| III               | 1.0171    | 150.6             | 2.448    | III              | 1.0442    | 446.7             | 7.452    |

FIG. 10.

*Viscosity.*



The molecular weights of ferric hydroxide calculated from the results are 2240, 2000, and 1090 for solutions 5, 3, and 1, respectively. These values, of course, carry little weight, but they seem to indicate that with increasing concentration the particles in the solution coalesce to form larger aggregates.

5. *Viscosity.*—These measurements were made because there may be an intimate relation between the viscosity of a colloidal solution and its absorptive power. The apparatus, an Ostwald viscosimeter, was in a large thermostat at 25° and, as usual, two series of experiments were made. The viscosities were calculated by means of the equation  $\eta = \eta_w \cdot st / s_w t_w$ , where  $\eta$  and  $\eta_w$  are the relative viscosities of the solution and water, respectively, *s* is the density of the solution and *t* is the time of flow. The results are in Table XVII and are shown graphically in Fig. 10.

*Discussion of Results.*

An examination of the solubility tables reveals the very different behaviour of the two colloidal solutions towards carbon dioxide and acetylene.

The solubility of carbon dioxide in the more concentrated solutions of ferric hydroxide exceeds its solubility in water by as much as 20%. Moreover, it is almost directly proportional to the concentration—a relation found by Findlay also (*loc. cit.*), although his absolute values of  $l$  were considerably smaller than those now recorded.

Carbon dioxide is also more soluble in solutions of Prussian blue than in water, but only moderately so (at the most, 3—4%). A well-defined maximum occurs in the values of  $l$  at all the temperatures used, in every case at a concentration of 0.3-normal.

Towards acetylene, however, both colloidal solutions display an essentially different behaviour, the solubility of the gas being always less than its solubility in water. The diminution is 1% for ferric hydroxide and 7—8% for Prussian blue (compare Findlay's curves, reproduced in Fig. 5, for nitrous oxide in ferric hydroxide at 25°).

For these colloidal systems the relation between the solubility of gases and the temperature is in accord with the ordinary laws governing the solution of gases, *viz.*, the temperature coefficient is negative and its numerical value increases rapidly with diminishing temperature (see Table VIII). This magnitude appears to be a function of concentration (at constant temperature). The following rule, therefore, may be deduced. At a given temperature, the numerical value of the temperature coefficient varies, with increasing concentration, as the absorptive power of the colloidal solution for the dissolving gas. For instance, in the system carbon dioxide-ferric hydroxide,  $l$  increases rapidly with  $c$  and consequently the quotient  $\Delta l/\Delta t$  increases as  $c$  increases: or, in the system acetylene-ferriferrocyanide,  $l$  diminishes greatly as  $c$  increases, and consequently  $\Delta l/\Delta t$  decreases as  $c$  increases. Such behaviour, however, is not so well defined in the systems carbon dioxide-ferriferrocyanide and acetylene-ferric hydroxide, since  $l$  varies but little. In the latter case, a diminution even of the temperature coefficient might be assumed owing to the small diminution of  $l$ .

The factors which may account for the observed phenomena are (1) the chemical nature of the colloid and of the gas absorbed (chemical combination), (2) the influence of the specific surface (adsorption), (3) the nature of the electric change, and (4) temperature.

1. *Chemical nature.* This is, presumably, the most important factor in all absorption phenomena, but, unfortunately, it is still



very obscure. Clearly, the more inert the gas and the colloidal solution are chemically, the smaller will be the effect of this factor. An obvious conclusion from this is that  $l$  for the systems carbon dioxide-Prussian blue and acetylene-ferric hydroxide will differ but little from the value of  $l$  for water, since fairly inert substances meet each other. On the other hand, a chemical reaction may be expected to take place between the basic ferric hydroxide and the acidic carbon dioxide. It is true that there is as yet no evidence of the existence of a compound  $\text{Fe}_2(\text{CO}_3)_3$ . Since, however, electro-positive ferric hydroxide, according to Pauli and Mattula (*Kolloid-Z.*, 1917, **21**, 49), has the constitution  $[x\text{Fe}(\text{OH})_3]_y\text{Fe}^{+++}$ , and there is formed by the dissociation of the dissolved carbon dioxide a small amount of  $\text{CO}_3''$ , a combination of this with the trivalent iron to give complex colloidal  $\{[x\text{Fe}(\text{OH})_3]_y\text{Fe}\}_2(y\text{CO}_3)_3$  may reasonably be assumed. This assumption seems to be justified by the strikingly high conductivity of the colloidal solution, which far exceeds that due to the peptising agent present.

2. *Specific surface.* The present results, as well as those of Geffcken and Findlay, clearly show that some factor is operating in addition to adsorption. The extent of the latter is determined by the degree of dispersion, and to account for the different behaviour of the two colloids by adsorption alone the specific surface of the ferric hydroxide would have to be 8—10 times larger than that of the Prussian blue—an assumption that cannot be justified.

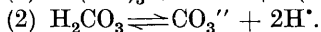
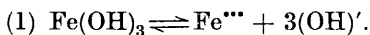
Dispersion, however, has an effect, and to determine it the absorption of carbon dioxide for different dispersions of ferric hydroxide at the same concentration (0.066*N*) was measured.

*Values of  $l$ .*

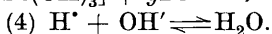
|                       | 25°.  | 20°.  | 15°.  | 10°.  |
|-----------------------|-------|-------|-------|-------|
| High dispersion ..... | 0.854 | 0.961 | 1.095 | 1.268 |
| Low dispersion .....  | 0.817 | 0.930 | 1.068 | 1.239 |
| Water .....           | 0.826 | 0.936 | 1.070 | 1.240 |

At the higher temperatures the absorptive power of the less highly dispersed system is markedly depressed, even below that of water. This diminution, however, depends not only on the specific surface of the colloid, but also on the quantity of peptising agent present. In the less highly dispersed system this was 0.3% and the basic character of the ferric hydroxide was greatly diminished and its electrical nature correspondingly changed.

3. *Electric change.* The changes that take place when carbon dioxide is in contact with a colloidal solution of ferric hydroxide may be represented by the following scheme; for a given temperature and pressure a definite equilibrium will be set up :



(3) The colloidal particles become associated with  $\text{Fe}^{+++}$ :  
 $[\text{xFe(OH)}_3] + \text{yFe}^{+++} \rightarrow [\text{xFe(OH)}_3]\text{yFe}^{+++}$ .



(5)  $2[\text{xFe(OH)}_3]\text{yFe}^{+++} + 3\text{yCO}_3'' \rightleftharpoons \{[\text{xFe(OH)}_3]\text{yFe}\}_2 (\text{yCO}_3)_3$   
 (compare Pauli and Mattula, *loc. cit.*).

The remarkably high solubility of carbon dioxide in ferric hydroxide and the readiness with which the gas is expelled by heating may thus be explained.

The preceding explanation involves the basic character of ferric hydroxide, the positive charge on the colloidal particles, and the acid nature of the gas. The last factor may for all practical purposes be neglected in the case of acetylene and nitrous oxide. Geffcken (*loc. cit.*, p. 301) has shown the indifferent nature of nitrous oxide by conductivity determinations with saturated aqueous solutions. The following measurements, made by the author, reveal the slight increase in conductivity that occurs when water is saturated with acetylene: water 2.18, 2.81,  $2.94 \times 10^{-6}$ ; mean  $2.63 \times 10^{-6}$ . Water saturated with acetylene 5.64, 4.98,  $4.03 \times 10^{-6}$ ; mean  $4.88 \times 10^{-6}$ . This result is in agreement with the investigations of Billitzer (*Z. physikal. Chem.*, 1902, **40**, 535), who pointed out a very slight dissociation of acetylene, represented by the following scheme,



and found that the gas in saturated aqueous solution at atmospheric pressure corresponds to an acid about 400 times weaker than carbonic acid. Acetylene, therefore, and nitrous oxide may be regarded as inert gases, and their similar behaviour towards ferric hydroxide is thus satisfactorily explained. It is chiefly absorption that takes place, and this accounts, to some extent at least, for the diminution of solubility which occurs with increasing concentration. The large decrease of  $l$  for the system acetylene-Prussian blue is attributable to the high concentration of the colloid (above 7%), in comparison with that of the ferric hydroxide (3%), and to its negative charge.

4. *Temperature.* The rule stated on p. 313 may be explained on the basis of the kinetic theory. If the solubility increases with the concentration, the content both of colloid and of gas particles in the solution also increases and the conditions for the presence of gas particles become less favourable; so the rate of diminution of solubility per  $1^\circ$  rise in temperature becomes greater. A decrease in solubility with increasing concentration favours the retention of the gas particles in the solution: hence the diminished quantity

of gas corresponding with  $1^\circ$  may be expected to remain constant or even to fall.

*Summary.*

1. Two typical, highly concentrated colloidal solutions have been prepared, and a very highly dispersed system of ferric hydroxide has been obtained by a modification of P. de St. Gilles's method.

2. Measurements of the solubility of carbon dioxide and acetylene in these systems have been made at five temperatures and different concentrations, and the temperature coefficients determined.

3. The colloids have been characterised by determinations of density, concentration, conductivity, viscosity, and depression of freezing-point.

4. Certain regularities in solubility have been found and an attempt has been made to analyse the factors that produce them.

The author wishes to express his thanks to Dr. Charles Brunner, and to acknowledge his indebtedness to the late Dr. Chas. Hopfgartner, at whose suggestion the work was undertaken.

INNSBRUCK,  
SILLGASSE, 2.

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