

X. *Liquid Diffusion applied to Analysis.*By THOMAS GRAHAM, F.R.S., *Master of the Mint.*

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THE property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the Diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapour tensions. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol, and sulphate of magnesia. But the substances named belong all, as regards diffusion, to the more “volatile” class. The comparatively “fixed” class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina, and other metallic peroxides of the aluminous class, when they exist in the soluble form; with starch, dextrin and the gums, caramel, tannin, albumen, gelatine, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to, appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatine appears to be its type, it is proposed to designate substances of the class as *colloids*, and to speak of their peculiar form of aggregation as the *colloidal condition of matter*. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as *crystalloids*. The distinction is no doubt one of intimate molecular constitution.

Although chemically inert in the ordinary sense, colloids possess a compensating activity of their own arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in

such colloids as can exist at a high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids, is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a *pectous** modification; and they often pass under the slightest influences from the first into the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid, deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition (H. ROSE). The colloidal is, in fact, a dynamical state of matter; the crystalloidal being the statical condition. The colloid possesses *ENERGIA*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element), may the characteristic protraction of chemicorganic changes also be referred.

A simple and easily applicable mode of effecting a diffusive separation is to place the mixed substance under a column of water, contained in a cylindrical glass jar of 5 or 6 inches in depth. The mixed solution may be conducted to the bottom of the jar by the use of a fine pipette, without the occurrence of any sensible intermixture. The spontaneous diffusion, which immediately commences, is allowed to go on for a period of several days. It is then interrupted by siphoning off the water from the surface in successive strata, from the top to the bottom of the column. A species of cohobation has been the consequence of unequal diffusion, the most rapidly diffusive substance being isolated more and more as it ascended. The higher the water column, sufficient time being always given to enable the most diffusive substance to appear at the summit, the more completely does a portion of that substance free itself from such other less diffusive substances as were originally associated with it. A marked effect is produced even where the difference in diffusibility is by no means considerable, such as the separation of chloride of potassium from chloride of sodium, of which the relative diffusibilities are as 1 to 0.841. Supposing a third metal of the potassium group to exist, standing above potassium in diffusibility as potassium stands above sodium, it may be safely predicated that the new metal would admit of being separated from the other two metals by an application of the jar-diffusion above described.

A certain property of colloid substances comes into play most opportunely in assisting diffusive separations. The jelly of starch, that of animal mucus, of pectin, of the vege-

* *Πηκρός*, *curdled*. As fibrin, casein, albumen. But certain liquid colloid substances are capable of forming a jelly and yet still remain liquefiable by heat and soluble in water. Such is gelatine itself, which is not pectous in the condition of animal jelly; but may be so as it exists in the gelatiferous tissues.

table gelose of PAYEN, and other solid colloidal hydrates, all of which are, strictly speaking, insoluble in cold water, are themselves permeable when in mass, as water is, by the more highly diffusive class of substances. But such jellies greatly resist the passage of the less diffusive substances, and cut off entirely other colloid substances like themselves that may be in solution. They resemble animal membrane in this respect. A mere film of the jelly has the separating effect. Take for illustration the following simple experiment.

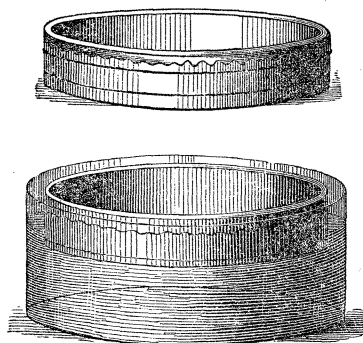
A sheet of very thin and well-sized letter paper, of French manufacture, having no porosity, was first thoroughly wetted and then laid upon the surface of water contained in a small basin of less diameter than the width of the paper, and the latter depressed in the centre so as to form a tray or cavity capable of holding a liquid. The liquid placed upon the paper was a mixed solution of cane-sugar and gum-arabic, containing 5 per cent. of each substance. The pure water below and the mixed solution above were therefore separated only by the thickness of the wet sized paper. After twenty-four hours the upper liquid appeared to have increased sensibly in volume, through the agency of osmose. The water below was found now to contain three-fourths of the whole sugar, in a condition so pure as to crystallize when the liquid was evaporated on a water-bath. Indeed the liquid of the basin was only in the slightest degree disturbed by subacetate of lead, showing the absence of all but a trace of gum. Paper of the description used is sized by means of starch. The film of gelatinous starch in the wetted paper has presented no obstacle to the passage of the crystalloid sugar, but has resisted the passage of the colloid gum. I may state at once what I believe to be the mode in which this takes place.

The sized paper has no power to act as a filter. It is mechanically impenetrable, and denies a passage to the mixed fluid as a whole. Molecules only permeate this septum, and not masses. The molecules also are moved by the force of diffusion. But the water of the gelatinous starch is not directly available as a medium for the diffusion of either the sugar or gum, being in a state of true chemical combination, feeble although the union of water with starch may be. The hydrated compound itself is solid, and also insoluble. Sugar, however, with all other crystalloids, can separate water, molecule after molecule, from any hydrated colloid, such as starch. The sugar thus obtains the liquid medium required for diffusion, and makes its way through the gelatinous septum. Gum, on the other hand, possessing as a colloid an affinity for water of the most feeble description, is unable to separate that liquid from the gelatinous starch, and so fails to open the door for its own passage outwards by diffusion.

The separation described is somewhat analogous to that observed in a soap-bubble inflated with a gaseous mixture composed of carbonic acid and hydrogen. Neither gas, as such, can penetrate the water-film. But the carbonic acid, being soluble in water, is condensed and dissolved by the water-film, and so is enabled to pass outwards and reach the atmosphere; while hydrogen, being insoluble in water, or nearly so, is retained behind within the vesicle.

It may perhaps be allowed to me to apply the convenient term *dialysis* to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable parchment or parchment-paper, which was first produced by M. GAINE, and is now successfully manufactured by Messrs. DE LA RUE. This is unsized paper, altered by a short immersion in sulphuric acid, or in chloride of zinc, as proposed by Mr. T. TAYLOR. Paper so metamorphosed acquires considerable tenacity, as is well known; and when wetted it expands and becomes translucent, evidently admitting of hydration. A slip of 25 inches in length was elongated 1 inch in pure water, and 1·2 inch in water containing one per cent. of carbonate of potash. In the wetted state parchment-paper can easily be applied to a light hoop of wood, or better, to a hoop made of sheet gutta percha, 2 inches in depth and 8 or 10 inches in diameter, so as to form a vessel like a sieve in form (fig. 1). The disc of parchment-paper used should exceed in diameter the hoop to be covered by 3 or 4 inches, so as to rise well round the hoop. It may be bound to the hoop by string, or by an elastic band, but should not be firmly secured. The parchment-paper must not be porous. Its soundness will be ascertained by sponging the upper surface with pure water, and then observing that no wet spots show themselves on the opposite side. Such defects may be remedied by applying liquid albumen, and then coagulating the same by heat. Mr. DE LA RUE recommends the use of albumen in cementing parchment-paper, which thus may be formed into cells and bags very useful in dialytic experiments. The mixed fluid to be dialysed is poured into the hoop upon the surface of the parchment-paper to a small depth only, such as half an inch. The vessel described (*dialyser*) is then floated in a basin containing a considerable volume of water, in order to induce the egress of the diffusive constituents of the mixture. Half a litre of urine, dialysed for twenty-four hours, gave its crystalloidal constituents to the external water. The latter, evaporated by a water-bath, yielded a white saline mass. From this mass urea was extracted by alcohol in so pure a condition as to appear in crystalline tufts upon the evaporation of the alcohol.

Fig. 1.—Hoop Dialyser.



1. *Jar-diffusion.*

The mode of diffusing more lately followed, which I have already alluded to as jar-diffusion, is extremely simple, and gives results of more precision than could possibly be anticipated. The salt is allowed to rise from below into a cylindrical column of water, and after a fixed time, the proportion of salt which has risen to various heights in the column is observed. The water was contained in a plain cylindrical glass jar, of about 152 millimetres (6 inches) in height and 87 millimetres (3·45 inches) in width. In operating, seven-tenths of a litre of water were first placed in the jar, and then one-tenth

of a litre of the liquid to be diffused was carefully conveyed to the bottom of the jar by means of a fine pipette. The whole fluid column then measured 127 millimetres (5 inches) in height. So much as five or six minutes of time were occupied in emptying the pipette at the bottom of the jar, and extremely little disturbance was occasioned in the superincumbent water, as could be distinctly seen when the liquid introduced by the pipette was coloured. The jar was then left undisturbed, to allow diffusion to proceed; the experiments being always conducted in an apartment of constant, or nearly constant temperature. When a certain time had elapsed, the diffusion was interrupted by drawing off the liquid from the top, by means of a small siphon, slowly and deliberately as the liquid had been first introduced, in portions of 50 cubic centimetres, or one-sixteenth of the whole volume. The open end of the short limb of the siphon was kept in contact with the surface of the liquid in the jar, and the portion of liquid drawn off was received in a graduated measure. By evaporating each fraction separately, the quantity of salt which had risen into equal sections of the liquid column was ascertained. From the bottom of two jars, A and B for instance, a 10 per cent. solution of chloride of sodium was diffused for a period of fourteen days. The whole quantity of salt present in each jar was 10 grammes, which was found at the end to be distributed as follows in the different sectional strata of fluid, numbering them from the top downwards:—

In the first or highest stratum, 0·103 and 0·105 gramme of salt in A and B respectively; in the second stratum, 0·133 and 0·125; in the third stratum, 0·165 and 0·158; in the fourth stratum, 0·204 and 0·193; in the fifth stratum, 0·273 and 0·260; in the sixth stratum, 0·348 and 0·332; in the seventh stratum, 0·440 and 0·418; in the eighth stratum, 0·545 and 0·525; in the ninth stratum, 0·657 and 0·652; in the tenth stratum, 0·786 and 0·747; in the eleventh stratum, 0·887 and 0·875; in the twelfth stratum, 0·994 and 0·984; in the thirteenth stratum, 1·080 and 1·100; in the fourteenth stratum, 1·176 and 1·198; in the fifteenth and sixteenth strata together, 2·209 and 2·324 grammes. With differences so moderate in amount between corresponding strata in the two experiments, this method of observing diffusion may claim a considerable degree of precision.

In similar experiments made at the same time and temperature with sugar, gum-arabic and tannin of nut-galls, the final distribution of each substance was different in each case, and the results may be placed together in illustration of unequal diffusibility, as exhibited by this method of observation. Two experiments were made on each substance, as with chloride of sodium, but the mean result only need be stated.

TABLE I.—Diffusion of 10 per cent. solutions (10 grammes of substance in 100 cub. cent. of fluid) into pure water, after fourteen days, at 10° (50° FAHR.).

| Number of stratum (from above downwards). | Chloride of sodium. | Sugar. | Gum. | Tannin. |
|--|---------------------|--------|-------|---------|
| 1 | ·104 | ·003 | ·003 | ·003 |
| 2 | ·129 | ·008 | ·003 | ·003 |
| 3 | ·162 | ·012 | ·003 | ·004 |
| 4 | ·198 | ·016 | ·004 | ·003 |
| 5 | ·267 | ·030 | ·003 | ·005 |
| 6 | ·340 | ·059 | ·004 | ·007 |
| 7 | ·429 | ·102 | ·006 | ·017 |
| 8 | ·535 | ·180 | ·031 | ·031 |
| 9 | ·654 | ·305 | ·097 | ·069 |
| 10 | ·766 | ·495 | ·215 | ·145 |
| 11 | ·881 | ·740 | ·407 | ·288 |
| 12 | ·991 | 1·075 | ·734 | ·556 |
| 13 | 1·090 | 1·435 | 1·157 | 1·050 |
| 14 | 1·187 | 1·758 | 1·731 | 1·719 |
| 15 and 16 | 2·266 | 3·783 | 5·601 | 6·097 |
| | 9·999 | 10·003 | 9·999 | 9·997 |

The superimposed column of water being 111 millimetres (4·38 inches) in height, the chloride of sodium, it will be observed, has diffused in sensible quantity to the top, and could have risen higher; the upper layer being found to contain 0·104 gramme of salt, or 1 per cent. of the whole quantity present. The apex of the diffusion column of sugar appears to have just reached the top of the liquid in the fourteen days of the experiment, for ·005 gramme only of that substance is found in the first stratum, followed by ·008, ·012, ·016, and ·030 in the following strata. Again, no gum appears to be carried by diffusion higher than the seventh stratum (2·2 inches), which stratum contains ·006 gramme, followed by ·031 gramme in the eighth stratum. The minute quantities of substance shown in the first to the sixth stratum, and which do not altogether exceed ·020 gramme, are no doubt the result of accidental dispersion, arising probably from a movement of the upper fluid occasioned by slight inequalities of temperature. The diffusion of tannin is even less advanced than that of gum; but the former numbers are apparently influenced by a partial decomposition, to which tannin is known to be liable, and which gives rise to new and more highly diffusible substances.

Experiments continued, like those last described, for a constant time, do not exhibit the exact relative diffusibilities, although these could be obtained by proceeding to ascertain, by repeated trial, the various times required to bring about a similar distribution and equal amount of diffusion in all the salts. The numbers observed, however, may afford data for the deduction of the relative diffusibilities by calculation.

A particular advantage of the new method is the means which it affords of ascertaining the absolute rate or velocity of diffusion. It becomes possible to state the distance which a salt travels per second in terms of the metre. It is easy to see that such a constant must enter into all the chronic phenomena of physiology, and that it holds a place in vital science not unlike the time of the falling of heavy bodies in the physics of

gravitation. It may therefore be not amiss to place here in a short tabular form the results observed of the diffusion of a few more substances, conducted in the same manner as the preceding.

TABLE II.—Diffusion of 10 per cent. solutions for fourteen days.

| Number of stratum (from above downwards). | Sulphate of magnesia, at 10°. | Albumen, at 13° to 13°·5. | Caramel, at 10° to 11°. |
|--|----------------------------------|------------------------------|----------------------------|
| 1 | ·007 | | |
| 2 | ·011 | | |
| 3 | ·018 | | |
| 4 | ·027 | | |
| 5 | ·049 | | |
| 6 | ·085 | | ·003 |
| 7 | ·133 | | ·005 |
| 8 | ·218 | ·010 | ·010 |
| 9 | ·331 | ·015 | ·023 |
| 10 | ·499 | ·047 | ·033 |
| 11 | ·730 | ·113 | ·075 |
| 12 | 1·022 | ·343 | ·215 |
| 13 | 1·383 | ·855 | ·705 |
| 14 | 1·803 | 1·892 | 1·725 |
| 15 and 16 | 3·684 | 6·725 | 7·206 |
| | 10·000 | 10·000 | 10·000 |

The sulphate of magnesia was anhydrous. The albumen was purified by WURTZ's method. The caramel was partly purified by precipitation by alcohol, as recommended by FRÉMY, and further by other means which will again be referred to. It will be remarked that the diffusion of sulphate of magnesia exhibited above is very similar to that of sugar in a former Table, but is slightly less advanced. The similarity in diffusibility of these two substances had already been observed in the experiments of former papers. The fall in rate on passing from these crystalloids to the colloids tannin, albumen, and caramel is very striking. The elevation in the liquid column attained by albumen or by caramel is moderate indeed compared with that of crystalline substances. Of albumen, which will be looked upon with most interest, no portion whatever was found in the seven higher strata. It appeared to the extent of 0·010 gramme in the eighth stratum, 0·015 in the ninth stratum, 0·047 in the tenth stratum, 0·113 in the eleventh stratum, 0·343 in the twelfth stratum; while the great mass of this substance remained in the four lower strata. The diffused albumen did not appear to lose its coagulability, or to be otherwise altered. It will be seen immediately that the diffusion of sugar advances as much in two days as the albumen above in fourteen days (Table IV.).

The diffusion of caramel is the slowest of all, and does not much exceed in fourteen days the diffusion of sugar in a single day.

It was considered useful to possess examples of the progress of diffusion, in one or two selected substances, for successive periods of time, so as to exemplify the continuous progress of diffusion in these substances. Such a chronological progress of diffusion in

a particular substance becomes a standard of comparison for single experiments on the diffusion of other substances. The substances selected were chloride of sodium and cane-sugar.

TABLE III.—Diffusion of a 10 per cent. solution of Chloride of Sodium in different times.

| Number of stratum. | In four days, at 9° to 10°. | In five days, at 11°-75. | In seven days, at 9°. | In fourteen days, at 10°. |
|--------------------|--------------------------------|-----------------------------|--------------------------|------------------------------|
| 1 | ·004 | ·004 | ·013 | ·104 |
| 2 | ·004 | ·006 | ·017 | ·129 |
| 3 | ·005 | ·011 | ·028 | ·162 |
| 4 | ·011 | ·020 | ·051 | ·198 |
| 5 | ·023 | ·040 | ·081 | ·267 |
| 6 | ·040 | ·075 | ·134 | ·340 |
| 7 | ·080 | ·134 | ·211 | ·429 |
| 8 | ·145 | ·233 | ·318 | ·535 |
| 9 | ·261 | ·368 | ·460 | ·654 |
| 10 | ·436 | ·589 | ·640 | ·766 |
| 11 | ·706 | ·762 | ·850 | ·881 |
| 12 | 1·031 | 1·090 | 1·057 | ·991 |
| 13 | 1·416 | 1·357 | 1·317 | 1·090 |
| 14 | 1·815 | 1·697 | 1·527 | 1·187 |
| 15 and 16 | 4·023 | 3·613 | 3·294 | 2·266 |
| | 10·000 | 9·999 | 9·998 | 9·999 |

TABLE IV.—Diffusion of a 10 per cent. solution of Cane-sugar in different times.

| Number of stratum. | In one day, at 10°-75. | In two days, at 10°. | In six days, at 9°. | In seven days, at 9°. | In eight days, at 9°. | In fourteen days, at 10°. |
|--------------------|---------------------------|-------------------------|------------------------|--------------------------|--------------------------|------------------------------|
| 1 | | | ·001 | ·002 | ·002 | ·005 |
| 2 | | | ·002 | ·002 | ·003 | ·008 |
| 3 | | | ·002 | ·003 | ·003 | ·012 |
| 4 | | | ·002 | ·004 | ·004 | ·016 |
| 5 | | | ·003 | ·004 | ·007 | ·030 |
| 6 | | | ·005 | ·007 | ·012 | ·059 |
| 7 | | | ·011 | ·020 | ·031 | ·102 |
| 8 | ·002 | ·002 | ·024 | ·051 | ·072 | ·180 |
| 9 | ·002 | ·008 | ·071 | ·121 | ·154 | ·305 |
| 10 | ·005 | ·027 | ·170 | ·260 | ·304 | ·495 |
| 11 | ·024 | ·107 | ·376 | ·507 | ·555 | ·740 |
| 12 | ·133 | ·344 | ·727 | ·897 | ·858 | 1·075 |
| 13 | ·597 | ·930 | 1·282 | 1·410 | 1·365 | 1·435 |
| 14 | 1·850 | 1·940 | 1·930 | 1·950 | 1·955 | 1·758 |
| 15 and 16 | 7·386 | 6·641 | 5·392 | 4·760 | 4·674 | 3·783 |
| | 9·999 | 9·999 | 9·998 | 9·998 | 9·999 | 10·003 |

The scheme of the diffusion of the chloride of sodium may afford terms of comparison for the metallic salts, acids and other highly diffusible substances, while the scheme of sugar will be found more useful in appreciating the diffusion of organic and other less diffusible substances. In comparing the two Tables together, it appears that a fourteen days' diffusion of sugar is greater in amount than a four days' diffusion of chloride of sodium, but less than a five days' diffusion of the same substance. The diffusion of

chloride of sodium appears to be pretty nearly three times greater (or more rapid) than that of sugar.

The following experiments were made upon hydrochloric acid and chloride of sodium at a somewhat lower temperature and for times which are different, but which give a nearly equal diffusion for each substance.

TABLE IV. *bis.*—10 per cent. solutions.

| Number of stratum. | Hydrochloric acid, in grammes. Three days at 5°. | Chloride of sodium, in grammes. Seven days at 5°. |
|--------------------|--|---|
| 1 | •003 | •003 |
| 2 | •006 | •009 |
| 3 | •012 | •010 |
| 4 | •022 | •026 |
| 5 | •043 | •055 |
| 6 | •086 | •082 |
| 7 | •162 | •165 |
| 8 | •308 | •270 |
| 9 | •406 | •403 |
| 10 | •595 | •595 |
| 11 | •837 | •823 |
| 12 | 1•080 | 1•085 |
| 13 | 1•163 | 1•270 |
| 14 | 1•578 | 1•615 |
| 15 and 16 | 3•699 | 3•589 |
| | 10•000 | 10•000 |

The diffusion of hydrochloric acid in three days corresponds closely with the diffusion of chloride of sodium in seven days. The times of equal diffusion for these two substances, at the temperature of the experiment, appear accordingly to be 1 (hydrochloric acid) and 2•33 (chloride of sodium). Hydrochloric acid and the allied hydracids, with other monobasic acids, are the most diffusive substances known. The general results of several series of experiments may be expressed approximately by the following numbers:—

Approximate times of equal diffusion.

| | |
|--------------------------------|------|
| Hydrochloric acid | 1 |
| Chloride of sodium | 2•33 |
| Sugar | 7 |
| Sulphate of magnesia | 7 |
| Albumen | 49 |
| Caramel | 98 |

It is curious to observe the effect of changing the liquid atmosphere in which diffusion takes place, which is water in all these experiments, and replacing it by another fluid, namely alcohol. Two substances were diffused in the usual manner, but with this difference, that the substances were dissolved in alcohol, and the solutions placed under a column of the same liquid in the jar. The alcohol was of sp. gr. 0•822 (90 per cent.).

TABLE V.—Diffusion in Alcohol of 10 per cent. solutions of Iodine and of Acetate of Potash in seven days.

| Number of stratum. | Iodine at 14°. | Acetate of potash, at 14° to 15°. |
|--------------------|----------------|--------------------------------------|
| 1 | ·028 | ·055 |
| 2 | ·033 | ·057 |
| 3 | ·046 | ·061 |
| 4 | ·038 | ·063 |
| 5 | ·037 | ·064 |
| 6 | ·039 | ·066 |
| 7 | ·081 | ·070 |
| 8 | ·143 | ·071 |
| 9 | ·263 | ·072 |
| 10 | ·417 | ·095 |
| 11 | ·637 | ·285 |
| 12 | ·936 | ·619 |
| 13 | 1·235 | 1·157 |
| 14 | 1·506 | 1·907 |
| 15 and 16 | 4·561 | 5·358 |
| | 10·000 | 10·000 |

TABLE V. *bis*.—Diffusion in Alcohol of a 10 per cent. solution of Resin, for seven days, at 14°·5.

| Number in stratum. | Diffusate, in grammes. |
|--------------------|------------------------|
| 1 | ·017 |
| 2 | ·017 |
| 3 | ·018 |
| 4 | ·017 |
| 5 | ·019 |
| 6 | ·020 |
| 7 | ·022 |
| 8 | ·024 |
| 9 | ·025 |
| 10 | ·080 |
| 11 | ·210 |
| 12 | ·498 |
| 13 | ·992 |
| 14 | 1·700 |
| 15 and 16 | 6·341 |
| | 10·000 |

The experiments were conducted in the absence of light, and there is no reason to believe that the iodine acted chemically upon the alcohol. The diffusion is more advanced in the iodine than in the acetate of potash, but in both is moderate in amount, confirming the early experiments with phials, which appeared to show that the diffusion process was several times slower in alcohol than in water. The small quantities of iodine found in each of the six superior strata are nearly equal, and were no doubt accidentally elevated by the mobility of this fluid, arising from its high dilatibility by heat compared with that of water at the same low temperature. The diffusion may be

considered then as confined to the nine lower strata, and considerably resembles that of sugar in water for eight days.

The diffusion of acetate of potash is still less advanced than that of iodine, and is probably confined to the six lower strata, the salt found in the higher strata presenting in its distribution the appearance of having been carried there by a movement of the fluid consequent upon heat-dilatation, and not by diffusion. The diffusion of acetate of potash in alcohol observed during seven days approximates to that of sugar in water during six days (Table IV.).

I now proceed to observations of the simultaneous diffusion of two substances in the same fluid. The great object of this class of experiments was to separate salts of unequal diffusibility, and to test the application of diffusion as an analytical process. A mixture of two salts being placed at the bottom of the jar, it may be expected that the salts will diffuse pretty much as they do when they are diffused separately; the more diffusive salt travelling most rapidly, and showing itself first and always most largely in the upper strata. The early experiments of diffusion from phials had shown indeed that inequality of diffusion is increased by mixture, and the actual separation is consequently greater than that calculated from the relative diffusibilities of the mixed substances. Chlorides of potassium and sodium diffuse nearly in the proportion of 1 to 0·841, according to the earlier experiments. They may afford, therefore, the means of observing the amount of separation that may be produced by a very moderate difference in diffusibility. A mixture of 5 grammes of each salt in the usual 100 cub. cent. of water was diffused.

TABLE VI.—Diffusion of a mixture of 5 per cent. of Chloride of Potassium and 5 per cent. of Chloride of Sodium, for seven days, at 12° to 13°.

| Number of stratum. | Chloride of potassium. | Chloride of sodium. | Total diffusate. |
|--------------------|------------------------|---------------------|------------------|
| 1 | ·018 | ·014 | ·032 |
| 2 | ·025 | ·015 | ·040 |
| 3 | ·044 | ·014 | ·058 |
| 4 | ·075 | ·017 | ·092 |
| 5 | ·101 | ·034 | ·135 |
| 6 | ·141 | ·063 | ·204 |
| 7 | ·185 | ·104 | ·289 |
| 8 | ·252 | ·151 | ·403 |
| 9 | ·330 | ·212 | ·542 |
| 10 | ·349 | ·351 | ·700 |
| 11 | ·418 | ·458 | ·876 |
| 12 | ·511 | ·559 | 1·070 |
| 13 | ·552 | ·684 | 1·236 |
| 14 | ·615 | ·772 | 1·387 |
| 15 and 16 | 1·385 | 1·551 | 2·936 |
| | 5·001 | 4·999 | 10·000 |

In the upper part of the Table chloride of potassium always appears in excess, but not in so large a proportion in the first three strata as in the fourth. This inequality

may be partly owing to mechanical dispersion of the mixed solution, but is to be referred chiefly, I believe, to errors of analysis from a loss of the chloride of potassium difficult to avoid in the determination of minute proportions of that salt by means of chloride of platinum. Of 92 milligrammes of salt found in the fourth stratum, 75 milligrammes, or 81·5 per cent., are chloride of potassium. The first six strata contain together 561 milligrammes, of which 404 milligrammes, or 72 per cent., that is nearly three-fourths, are chloride of potassium. We have to descend to the tenth stratum before the salts are found in equal proportions. The progression is then inverted, and chloride of sodium comes to preponderate in the lower strata.

It is evident that the preceding experiment might be so conducted as to diffuse away the chloride of potassium and leave below a mixture containing chloride of sodium in relative excess, to as great an extent as the chloride of potassium is found above, in the last experiment.

Further, the mixture in which chloride of potassium was concentrated in the experiment described, so as to form 72 per cent. of the whole mixture, might be subjected again to diffusion in the same manner. In an experiment upon a mixture of 7·5 grammes of chloride of potassium and 2·5 grammes of chloride of sodium, the six upper strata gave 640 milligrammes of salt, of which 610 milligrammes, or 95·3 per cent., were chloride of potassium. It is obvious that by repeating this diffusive rectification a sufficient number of times, a portion of the more diffusive salt might be obtained at last in a state of sensible purity.

The preceding example illustrates the separation of unequally diffusive metals or bases; the following example, on the other hand, the separation of unequally diffusive acids united with a common base. Chloride of sodium and sulphate of soda diffuse separately in the phial experiments in the proportion of 1 to 0·707.

TABLE VII.—Diffusion of 5 per cent. of Chloride of Sodium and 5 per cent. of anhydrous Sulphate of Soda, for seven days, at 10° to 10°·75.

| Number of stratum. | Chloride of sodium, in grammes. | Sulphate of soda, in grammes. | Total diffusate, in grammes. |
|--------------------|------------------------------------|----------------------------------|---------------------------------|
| 1 | ·009 | | ·009 |
| 2 | ·013 | ·001 | ·014 |
| 3 | ·024 | ·002 | ·026 |
| 4 | ·038 | ·003 | ·041 |
| 5 | ·060 | ·006 | ·066 |
| 6 | ·095 | ·012 | ·107 |
| 7 | ·141 | ·029 | ·170 |
| 8 | ·203 | ·059 | ·262 |
| 9 | ·278 | ·115 | ·393 |
| 10 | ·360 | ·205 | ·565 |
| 11 | ·473 | ·317 | ·790 |
| 12 | ·560 | ·507 | 1·067 |
| 13 | ·637 | ·694 | 1·331 |
| 14 | ·718 | ·909 | 1·627 |
| 15 and 16 | 1·390 | 2·141 | 3·531 |
| | 4·999 | 5·000 | 9·999 |

Here the separation is still more sensible than before with the bases. The six upper strata contain 263 milligrammes of salt, of which 239 milligrammes, that is 90·8 per cent., are chloride of sodium. The salt of the upper eight strata amounts to 695 milligrammes, of which 583 milligrammes, or 83·9 per cent., are chloride of sodium.

How long the diffusion should be continued in a liquid column of limited height, such as in these experiments, so as to produce the greatest separation, is a question of some interest, which can only be answered by experiment. The last diffusion was accordingly repeated, with the difference that it was continued for double the former time.

TABLE VIII.—Diffusion of 5 per cent. of Chloride of Sodium and 5 per cent. of Sulphate of Soda, for fourteen days, at 10° to 11°.

| Number of stratum. | Chloride of sodium, in grammes. | Sulphate of soda, in grammes. | Total diffusate, in grammes. |
|--------------------|------------------------------------|----------------------------------|---------------------------------|
| 1 | ·077 | ·005 | ·082 |
| 2 | ·089 | ·009 | ·098 |
| 3 | ·105 | ·014 | ·119 |
| 4 | ·130 | ·026 | ·156 |
| 5 | ·161 | ·044 | ·205 |
| 6 | ·199 | ·072 | ·271 |
| 7 | ·240 | ·111 | ·351 |
| 8 | ·289 | ·173 | ·462 |
| 9 | ·337 | ·241 | ·578 |
| 10 | ·392 | ·334 | ·726 |
| 11 | ·433 | ·433 | ·866 |
| 12 | ·487 | ·539 | 1·026 |
| 13 | ·525 | ·646 | 1·171 |
| 14 | ·555 | ·745 | 1·300 |
| 15 and 16 | ·979 | 1·609 | 2·588 |
| | 4·998 | 5·001 | 9·999 |

The salt contained in the three upper strata amounts to 299 milligrammes, of which 271, or 90·6 per cent. of the whole, are chloride of sodium. The upper five strata yield 660 milligrammes of salt, of which 562 milligrammes, or 85·1 per cent., are chloride of sodium. These proportions are not dissimilar to those deduced from the former Table, and show that little is gained in the way of separation by extending the diffusion period from seven to fourteen days; unless indeed the column of fluid be increased in height at the same time.

It might be worth observing whether the separation of two unequally diffusive metals can be favoured by varying the acid, or form of combination; whether, for instance, the hydrates of potash and soda would not separate to a greater extent than has been observed of the chlorides of potassium and sodium, the separate diffusibilities of the former substances being as 1 to 0·7, while that of the latter are as 1 to 0·841. I have not, however, pursued this branch of the subject.

The separation of the same metals from each other may possibly be favoured in another manner. In the preceding experiments (Table VI.) the two metals were in

union with the same acid, or rather both were in the state of chloride. But the metals might be used in combination with different acids, and these acids themselves might be of equal or of unequal diffusibility. If of equal diffusibility, such as nitric and hydrochloric acids, no reason appears why the acids should affect the amount of separation. But if the acids are unlike in diffusibility, the case is not so clear. If, for instance, the potassium were in the form of chloride and the sodium of that of sulphate, might not the diffusion of the potassium be promoted by the highly diffusive chlorine with which it is associated, and the diffusion of the soda, on the other hand, be retarded by its association with the slowly diffusive sulphuric acid? Will, in fine, the separation of the metals be greater from a mixture of chloride of potassium and sulphate of soda, or even from sulphate of potash and chloride of sodium, than from the two chlorides, or from the two sulphates? The inquiry, it will be remarked, raises the whole question of the distribution of acid and base in solutions of mixed salts. It will be illustrated by a comparison of the diffusion of chloride of potassium mixed with sulphate of soda, with the diffusion of sulphate of potash mixed with the chloride of sodium, the salts being taken in equivalent proportions.

TABLE IX.—Diffusion of a mixture of 5.12 per cent. of Chloride of Potassium and 4.88 per cent. of Sulphate of Soda (equivalent proportions), for seven days, at 14°.

| Number of stratum. | Potassium, in grammes. | Sulphuric acid, in grammes. | Total diffusate, in grammes. |
|--------------------|------------------------|-----------------------------|------------------------------|
| 1 | •023 | •002 | •024 |
| 2 | •035 | •002 | •030 |
| 3 | •048 | •004 | •045 |
| 4 | •064 | •009 | •066 |
| 5 | •092 | •016 | •097 |
| 6 | •128 | •032 | •149 |
| 7 | •174 | •058 | •215 |
| 8 | •242 | •105 | •316 |
| 9 | | | •441 |
| 10 | | | •615 |
| 11 | | | •815 |
| 12 | | | 1.042 |
| 13 | | | 1.290 |
| 14 | | | 1.517 |
| 15 and 16 | | | 3.346 |
| | | | 10.008 |

TABLE X.—Diffusion of a mixture of 4·01 per cent. of Chloride of Sodium and 5·99 per cent. of Sulphate of Potash (equivalent proportions), for seven days, at 14°.

| Number of stratum. | Potassium, in grammes. | Sulphuric acid, in grammes. | Total diffusate, in grammes. |
|--------------------|------------------------|-----------------------------|------------------------------|
| 1 | ·028 | ·002 | ·023 |
| 2 | ·034 | ·002 | ·030 |
| 3 | ·049 | ·004 | ·044 |
| 4 | ·064 | ·009 | ·065 |
| 5 | ·092 | ·015 | ·096 |
| 6 | ·128 | ·031 | ·149 |
| 7 | ·172 | ·059 | ·219 |
| 8 | ·242 | ·104 | ·315 |
| 9 | | | ·435 |
| 10 | | | ·600 |
| 11 | | | ·797 |
| 12 | | | 1·025 |
| 13 | | | 1·261 |
| 14 | | | 1·480 |
| 15 and 16 | | | 3·467 |
| | | | 10·016 |

The weight of the mixed salt was always 10 grammes. The diffusions exhibited in the two Tables are strikingly similar, and indeed may be considered as identical. It thus appears that the diffusion of the metals is not affected by the acid with which they are in combination. The result is quite in harmony with BERTHOLLET'S view, that the acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of soda is the same thing as a mixture of sulphate of potash and chloride of sodium, when the mixtures are in a state of solution. With two acids very unequal in their affinity for bases, the result possibly might be very different.

2. *Effect of Temperature on Diffusion.*

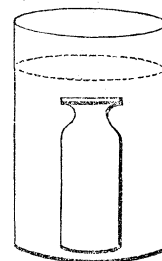
Diffusion is promoted by heat, and separations may accordingly be effected in a shorter time at high than at low temperatures. In a series of observations made upon hydrochloric acid, the diffusion of that substance was carefully determined at 15°·5 (60° F.), and at three higher points, advancing by 11°·11 (20° F.). The ratios of the diffusions observed were as follows:—

| | |
|---|---------|
| Diffusion of hydrochloric acid at 15°·55 (60° F.), | 1 |
| „ „ at 26°·66 (80° F.), | 1·3545 |
| „ „ at 37°·77 (100° F.), | 1·7732 |
| „ „ at 48°·88 (120° F.), | 2·1812. |

The increments of diffusibility, 0·3545, 0·4187, and 0·408 for equal increments of temperature, are probably affected by small errors of observation, but they appear to indicate that the diffusion increases at a higher, although not greatly higher, rate than the temperature. The average increase of diffusibility for the whole range of temperature observed is 0·03543, or $\frac{1}{28}$ for each degree (0·01969, or $\frac{1}{50}$ nearly for 1° F.).

The preceding experiments were made by diffusing a 2 per cent. solution of hydrochloric acid from wide-mouth phials immersed in a jar of water, as in my former experiments*. The times were observed in which an equal amount of the acid (0.777 gramme from three phials) was diffused out. These times of equal diffusion were 72 hours at $15^{\circ}55$ (60° F.); 53.15 hours at $26^{\circ}66$ (80° F.); 40.6 hours at $37^{\circ}77$ (100° F.); and 33 hours at $48^{\circ}88$ (120° F.).

Fig. 2.



The diffusate from a 2 per cent. solution of chloride of potassium in similar circumstances was 0.6577 gramme,

In 101.75 hours, at $15^{\circ}55$ (60° F.); and

In 41.93 hours, at $48^{\circ}88$ (120° F.).

The diffusate from a 2 per cent. solution of chloride of sodium was 0.6533 gramme,

In 124.75 hours, at $15^{\circ}55$ (60° F.);

In 49.60 hours, at $48^{\circ}88$ (120° F.).

In equal times the diffusate would be

For chloride of potassium at $15^{\circ}55$ (60° F.), 1

„ „ at $48^{\circ}88$ (120° F.), 2.426

For chloride of sodium at $15^{\circ}55$ (60° F.), 1

„ „ at $48^{\circ}88$ (120° F.), 2.5151.

As the ratio between the diffusates of hydrochloric acid, at the same two temperatures, was 1 to 2.1812, it appears that the acid is less increased in diffusibility than the salts at the higher temperature; chloride of sodium also is slightly more increased than chloride of potassium. The more highly diffusive the substance the less does it appear to gain by heat. Chloride of sodium appears to be sensibly $2\frac{1}{2}$ times more diffusible at $48^{\circ}88$ (120° F.) than at $15^{\circ}55$ (60° F.): this gives an average increase of 0.014, or $\frac{1}{71}$ for 1 degree (0.025 for 1° F., or $\frac{1}{40}$). The inequality of diffusion which the three substances referred to exhibit at a low temperature, becomes therefore less at high temperatures; and it would appear to be the effect of a high temperature to assimilate diffusibilities. Heat, then, although it quickens the operation of diffusion, does not appear otherwise to promote the separation of unequally diffusive substances.

The results in such experiments are less disturbed by changes of temperature, if at all gradual, than might be supposed. A sensible separation was obtained of hydrochloric acid and chloride of sodium from each other, in a solution containing 2 per cent. of each substance, when the water-jar was heated up from $15^{\circ}55$ to 95° C. in two hours, and maintained at the latter temperature during four hours more. Diffusion appeared to be accelerated about six times at the higher temperature.

At low temperatures, again, diffusion is proportionally slow. The ratio of diffusibility

* Philosophical Transactions, 1850, p. 25.

of the following salts at two different temperatures appeared to be,—

| | |
|---------------------------|---|
| For chloride of potassium | at 5°·3 (41°·5 F.), 1; at 16°·6 (62° F.), 1·4413 |
| For chloride of sodium | at 5°·3 (41°·5 F.), 1; at 17°·4 (63°·4 F.), 1·4232 |
| For nitrate of soda | at 5°·3 (41°·5 F.), 1; at 17°·4 (63°·4 F.), 1·4475 |
| For nitrate of silver | at 5°·3 (41°·5 F.), 1; at 17°·4 (63°·4 F.), 1·3914. |

The salts are unequally affected to a sensible extent; and it will be observed that the superiority of chloride of potassium over chloride of sodium, in diffusibility, is increased at the low temperature.

Within the range of temperature of the preceding experiments, the diffusibility of chloride of sodium being taken as 1 at 17°·4 (63°·4 F.), it becomes 0·7026 at 5°·3 (41°·5 F.); or it diminishes 0·0246, or $\frac{1}{40\cdot7}$, for a depression of 1° (0·0136, or $\frac{1}{73\cdot5}$, for a depression of 1° F.).

3. *Dialysis.*

Passing from liquid diffusion in the water-jar, I may advert first to the diffusion of crystalloids through a gelatinous or colloid mass, the circumstance of the experiment being varied as little as possible from those of jar-diffusion.

Ten grammes of chloride of sodium and 2 grammes of the Japanese gelatine, or gelose of PAYEN, were dissolved together in so much hot water as to form 100 cub. cents. of fluid. Introduced into the empty diffusion-jar and allowed to cool, this fluid set into a firm jelly, occupying the lower part of the jar, and containing of course 10 per cent. of chloride of sodium. Instead of placing pure water over this jelly, it was covered by 700 cub. cents. of a solution containing 2 per cent. of the same gelose, cooled so far as to be on the point of gelatinizing; the jar at the same time being placed in a cooling mixture, in order to expedite that change. The jar with its contents was now left undisturbed for eight days at the temperature 10°. After the lapse of this time the jelly was removed from the jar in successive portions of 50 cub. cents. each from the top, and the proportion of chloride of sodium in the various strata ascertained. The results were very similar to those obtained in diffusing the same salt in a jar of pure water. The diffusion in the gelose appeared more advanced in eight days than diffusion in water for seven days, as will be seen by comparing the gelose experiment below with a water experiment on chloride of sodium which had been conducted at nearly the same temperature (Table III.).

TABLE XI.—Diffusion of a 10 per cent. solution of Chloride of Sodium in the jelly of gelose, for eight days, at 10°.

| Number of stratum. | Diffusate, in grammes. |
|--------------------|------------------------|
| 1 | •015 |
| 2 | •015 |
| 3 | •026 |
| 4 | •035 |
| 5 | •082 |
| 6 | •130 |
| 7 | •212 |
| 8 | •350 |
| 9 | •486 |
| 10 | •630 |
| 11 | •996 |
| 12 | 1•172 |
| 13 | 1•190 |
| 14 | 1•203 |
| 15 and 16 | 3•450 |
| | 9•992 |

Diffusion of a crystalloid thus appears to proceed through a firm jelly with little or no abatement of velocity. With a coloured crystalloid, such as bichromate of potash, the gradual elevation of the salt to the top of the jar is beautifully illustrated. On the other hand, the diffusion of a coloured colloid such as caramel through the jelly, appears scarcely to have begun after eight days had elapsed. The diffusion of a salt into the solid jelly may be considered as cementation in its most active form.

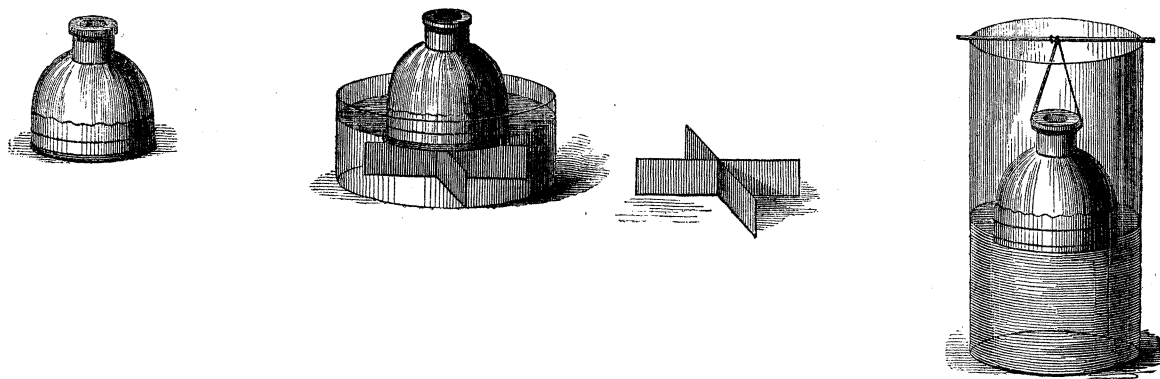
Numerous experiments were made on the diffusion of crystalloids through various dialytic septa, such as gelatinous starch, coagulated albumen, gum-tragacanth, besides animal mucus and parchment-paper, which all tended to prove how little the diffusive process was interfered with by the intervention of colloid matter. Salts appeared to preserve their usual relative diffusibility unchanged. The same partial separation of mixed salts was observed as in the water-jar. With a mixture, for instance, of equal parts of chlorides of potassium and sodium in the dialyser, the first tenth part of the mixture which passed through was found to consist of 59•17 per cent. of chloride of potassium and 40•83 per cent. of chloride of sodium. Double salts also, such as alum, and the sulphate of copper and potash, which admit of being resolved into pairs of unequally diffusive salts, were largely decomposed upon the dialyser, as they are in the water-jar. The effect of heat in promoting diffusion appeared, however, to be diminished in dialysis, at least with a parchment-paper septum. Thus the diffusion from a 2 per cent. solution of chloride of sodium in a constant period of three hours was,—

| | | Ratio. |
|--------------|------------|--------|
| At 10° . . . | 0•738 grm. | 1 |
| At 20 . . . | 0•794 grm. | 1•07 |
| At 30 . . . | 0•892 grm. | 1•20 |
| At 40 . . . | 1•017 grm. | 1•37. |

The rate of diffusion in water alone, without the septum, would have been doubled by an equal rise of temperature instead of being increased one-third only as above.

The small glass bell-jar (fig. 3) formerly used as an osmometer, was conveniently

Fig. 3.—Bulb Dialyser.



applied to dialytic experiments. Two sizes of the bulb were employed, 3.14 and 4.44 inches in diameter respectively, and of which the dialytic septa possessed an area very nearly of $\frac{1}{100}$ dth and $\frac{1}{200}$ dth of a square metre (15.6 and 7.8 square inches). With 100 cub. cents. of fluid in the osmometer (the volume usually employed), the septum of the smaller instrument was covered to a depth of about 20 millimetres (0.8 inch), and the septum of the larger to a depth of 10 millimetres (0.4 inch). The thinner the stratum, the more exhaustive the diffusion in a given time. It is generally unadvisable to cover the septum deeper than 10 or 12 millimetres (half an inch), where a considerable diffusion is desired within twenty-four hours. The following practical observations may be found useful in applying the dialyser to actual cases of analysis. They refer to the parchment-paper septum, which is much the most convenient for use.

With a 2 per cent. solution of chloride of sodium, containing 2 grammes of the salt, and covering a septum of nearly 0.01 square metre (15.6 square inches) in area, to a depth of 10 millimetres, the salt which diffused in five hours amounted to 0.75 gramme, and in twenty-four hours to 1.657 gramme, leaving behind 0.343 gramme, or 17.1 per cent. of the original salt. The following experiments, made with the same osmometer and solution, show the effect of reducing the volume of liquid placed in the dialyser. The proportion of salt which diffused out in twenty-four hours was—

From 100 cub. cents. of solution 86 per cent.

From 50 cub. cents. of solution 92 per cent.

From 25 cub. cents. of solution 96 per cent.

In all cases the volume of water outside into which the salt escaped was ample, being from five to ten times greater than the volume of fluid placed in the dialyser, and it was changed during the continuance of the experiment. A much less volume of external water suffices, provided it is changed at intervals of a few hours. The temperature was

10° to 12°. It will be observed that these volumes correspond to a depth of liquid in the dialyser of 0.4, 0.2, and 0.1 inch respectively.

The time of travelling through the thickness of the parchment-paper itself may be observed, and is worthy of remark.

Of the quality of parchment-paper always used in these experiments, a square metre, when dry, weighed 67 grammes; and when charged with water, 108.6 grammes. Taking the specific gravity of cellulose at 1.46, that of the lighter woods, the parchment-paper described will, in the humid state, have a thickness of 0.0877 millimetre, or $\frac{1}{11.41}$ of a millimetre. Wet parchment-paper so thin is highly translucent. Gelatinous starch, slightly coloured with blue litmus, was applied by a brush to one side of the wet parchment-paper. Immediately afterwards a drop of water, containing $\frac{1}{1000}$ th part of *hydrochloric acid*, was applied on the point of the finger to the other (the lower) side of the paper. The time required by the acid to affect the litmus, in five successive trials, was 6 seconds, 5.5 seconds, 6 seconds, and 5 seconds. The mean is 5.7 seconds, which is therefore the time required by hydrochloric acid, diluted already 1000 times, to travel a distance of 0.0877 of a millimetre, by the agency of diffusion. The temperature was 15°.

With hydrochloric acid diluted twice as much as before (water containing 0.0005 dry acid), the average time of passage was 10.4 seconds, or nearly double the preceding time.

Water containing $\frac{1}{1000}$ th of sulphuric acid (an acid less rapidly diffused than hydrochloric acid) reddened the litmus in 9.1 seconds, and when doubly diluted in 16.5 seconds.

These results are not affected, it is believed, by any sensible diffusive movement on the part of the litmus. The diffusion of that colouring matter, in a colloid medium, is so slow that it may be entirely disregarded. The acid, therefore, is not met in its way by the litmus, but really travels the entire distance expressed by the thickness of the parchment-paper. The first experiments related give a diffusive velocity, in water, to hydrochloric acid, already diluted one thousand times, of 0.0154 millimetre per second, and 0.924 millimetre in one minute.

The few following dialytic experiments may be recorded for the sake of the practical points which they bring out. They were made in the smaller osmometer, with 100 cub. cents. of a solution containing 10 grammes of each of the various substances. The area of the parchment-paper septum was 0.005 square metre, and the depth of the stratum of fluid placed upon it 20 millimetres. The substances diffused were all crystalloids, with the exception of gum-arabic.

TABLE XII.—Dialysis through Parchment-paper during twenty-four hours, at 10° to 15°.

| Ten per cent. solutions. | Diffusate, in grammes. | Relative diffusate. | Osmose, in grammes of water. | Relative osmose. |
|--|---------------------------|------------------------|------------------------------------|---------------------|
| Gum-arabic | 0·029 | ·004 | 5·0 | ·263 |
| Starch-sugar | 2·000 | ·266 | 17·0 | ·894 |
| Cane-sugar..... | 1·607 | ·214 | 15·3 | ·805 |
| Milk-sugar..... | 1·387 | ·185 | 15·0 | ·789 |
| Mannite | 2·621 | ·349 | 17·6 | ·926 |
| Glycerine | 3·300 | ·440 | 17·6 | ·926 |
| Alcohol | 3·570 | ·476 | 7·6 | ·400 |
| Starch-sugar (second experiment) | 2·130 | ·284 | 16·8 | ·884 |
| Chloride of sodium | 7·500 | 1 | 19·0 | 1 |

The experiments were all made through the same portion of parchment-paper, and in the order of the Table; gum-arabic first, and chloride of sodium last. After every experiment the bulb was immersed in water for twenty-four hours, to purify the septum, before it was again used. The diffusion of starch-sugar was repeated early and late in the series of experiments, with little change in the result, showing considerable uniformity in the action of the parchment-paper; the first diffusate of starch-sugar being 2 grammes, and the second 2·13 grammes. Yet the parchment-paper had been in contact with water or some solution for a whole fortnight between the two observations referred to.

A layer of animal mucus, taken from the stomach of the pig, 12 millimetres in thickness (10 grammes of humid mucus being spread over 0·005 square metre of surface), was applied, between two discs of calico, to the diffusion-bulb used above, the parchment-paper being first removed.

TABLE XIII.—Dialysis through Animal Mucus during twenty-five hours, at 10° to 15°.

| Ten per cent. solutions. | Diffusate, in grammes. | Proportional diffusate. | Osmose, in grammes of water. |
|--------------------------|---------------------------|----------------------------|------------------------------------|
| Gum-arabic | ·023 | ·004 | + 29 |
| Starch-sugar | 1·821 | ·360 | + 7·6 |
| Cane-sugar..... | 1·753 | ·347 | + 4·6 |
| Milk-sugar..... | 1·328 | ·262 | + 7·1 |
| Mannite | 1·895 | ·375 | + 5·0 |
| Alcohol | 2·900 | ·573 | + 7·2 |
| Starch-sugar | 1·765 | ·349 | + 7·0 |
| Glycerine | 2·554 | ·505 | + 7·5 |
| Chloride of sodium | 5·054 | 1 | — 0·2 |

The relative diffusibilities of the different substances present a considerable degree of similarity in the two Tables, and are equally analogous to the diffusibilities of the same substances observed in pure water. The intervention of a colloid septum cannot be said to have impeded much the diffusion of any of these substances except the colloid gum.

The dialysis through parchment-paper of several other organic substances, both crystalloids and colloids, may be brought together, in comparison with the chloride of sodium as a standard. The larger osmometer bulb was used, and the parchment-paper

was now changed in each experiment. The substance in solution amounted to 2 grammes, the depth of fluid in the dialyser to 10 millimetres (0·4 of an inch), and the surface of the septum to 0·01 square metre (15·6 square inches).

TABLE XIV.—Dialysis through Parchment-paper during twenty-four hours, at 12°.

| Two per cent. solutions. | Diffusate, in grammes. | Proportional diffusate. |
|-----------------------------|---------------------------|----------------------------|
| Chloride of sodium | 1·657 | 1 |
| Picric acid | 1·690 | 1·020 |
| Ammonia | 1·404 | ·847 |
| Thein | 1·166 | ·703 |
| Salicin | ·835 | ·503 |
| Cane-sugar..... | ·783 | ·472 |
| Amygdalin..... | ·517 | ·311 |
| Extract of quercitron | ·305 | ·184 |
| Extract of logwood | ·280 | ·168 |
| Catechu | ·265 | ·159 |
| Extract of cochineal | ·086 | ·051 |
| Gallo-tannic acid | ·050 | ·030 |
| Extract of litmus | ·033 | ·019 |
| Purified caramel | ·009 | ·005 |

Picric acid and thein were actually diffused from 1 per cent. solutions, and the numbers observed are multiplied by 2. The crystallizable principles, thein, salicin, and amygdalin, appear greatly more diffusible than gallo-tannic acid, or than gum, as has been already seen. Such inequality of rate is likely to facilitate the separation of vegetable principles by the agency of dialysis.

4. *Preparation of Colloid Substances by Dialysis.*

The purification of many colloid substances may be effected with great advantage by placing them on the dialyser. Accompanying crystalloids are eliminated, and the colloid is left behind in a state of purity. The purification of soluble colloids can rarely be effected by any other known means, and dialysis is evidently the appropriate mode of preparing such substances free from crystalloids.

Soluble Silicic Acid.—A solution of silica is obtained by pouring silicate of soda into diluted hydrochloric acid, the acid being maintained in large excess. But in addition to hydrochloric acid, such a solution contains chloride of sodium, a salt which causes the silica to gelatinize when the solution is heated, and otherwise modifies its properties. Now such soluble silica, placed for twenty-four hours in a dialyser of parchment-paper, to the usual depth of 10 millimetres, was found to lose in that time 5 per cent. of its silicic acid, and 86 per cent. of its hydrochloric acid. After four days on the dialyser, the liquid ceased to be disturbed by nitrate of silver. All the chlorides were gone, with no further loss of silica. In another experiment 112 grammes of silicate of soda, 67·2 grammes of dry hydrochloric acid, and 1000 cub. cents. of water were brought together, and the solution placed upon a hoop dialyser, 10 inches in diameter. After four days the solution had increased to 1235 cub. cents., by the action of osmose; colloid

bodies being generally highly osmotic. The solution now gave no precipitate with nitrate of silver, and contained 60·5 grammes of silica, 6·7 grammes of that substance having been lost. The solution contained 4·9 per cent. of silicic acid.

The pure solution of silicic acid so obtained may be boiled in a flask, and considerably concentrated, without change; but when heated in an open vessel, a ring of insoluble silica is apt to form round the margin of the liquid, and soon causes the whole to gelatinize. The pure solution of hydrated silicic acid is limpid and colourless, and not in the least degree viscous, even with 14 per cent. of silicic acid. The solution is the more durable the longer it has been dialysed and the purer it is. But this solution is not easily preserved beyond a few days, unless considerably diluted. It soon appears slightly opalescent, and after a time the whole becomes pectous somewhat rapidly, forming a solid jelly transparent and colourless, or slightly opalescent, and no longer soluble in water. This jelly undergoes a contraction after a few days, even in a close vessel, and pure water separates from it. The coagulation of the silicic acid is effected in a few minutes by a solution containing $\frac{1}{10,000}$ th part of any alkaline or earthy carbonate, but not by caustic ammonia, nor by neutral or acid salts. Sulphuric, nitric, and acetic acids do not coagulate silicic acid, but a few bubbles of carbonic acid passed through the solution produce that effect after the lapse of a certain time. Alcohol and sugar, in large quantity even, do not act as precipitants; but neither do they protect silicic acid from the action of alkaline carbonates, nor from the effect of time in pectizing the fluid colloid. Hydrochloric acid gives stability to the solution: so does a small addition of caustic potash or soda.

This pure water-glass is precipitated on the surface of a calcareous stone without penetrating, apparently from the coagulating action of soluble lime-salts. The hydrated silicic acid then forms a varnish, which is apt to scale off on drying. The solution of hydrated silicic acid has an acid reaction, somewhat greater than that of carbonic acid. It appears to be really tasteless (like most colloids), although it occasions a disagreeable persistent sensation in the mouth, after a time, probably from precipitation.

Soluble hydrated silicic acid, when dried in the air-pump receiver, at 15°, formed a transparent glassy mass of great lustre, which was no longer soluble in water. It retained 21·99 per cent. of water after being kept two days over sulphuric acid.

The colloidal solution of silicic acid is precipitated by certain other soluble colloids, such as gelatine, alumina, and peroxide of iron, but not by gum nor caramel. As hydrated silicic acid, after once gelatinizing, cannot be made soluble again by either water or acids, it appears necessary to admit the existence of two allotropic modifications of that substance, namely, soluble hydrated silicic acid, and insoluble hydrated silicic acid, the fluid and pectous forms of this colloid.

The ordinary soluble silicate of soda is not at all colloidal, but diffuses as readily through a septum as the sulphate of soda does. Several crystalline hydrated silicates of soda are known (FRITZSCHE).

The amorphous silicic acid obtained by drying and calcining the jelly, and the vitreous

acid obtained by igneous fusion, have both a specific gravity of about 2.2, according to H. ROSE*, and appear to be the same colloidal substance; while the specific gravity of crystalloidal silicic acid (rock-crystal and quartz) is about 2.6.

Soluble silicic acid forms a peculiar class of compounds, which like itself are colloidal, and differ entirely from the ordinary silicates. The new compounds are interesting from their analogy to organic substances, and from appearing to contain an acid of greatly higher atomic weight than ordinary silicic acid. Like gallo-tannic acid, gummic acid, and the other organic colloidal acids, silicic acid combines with gelatine; the last substance appearing to possess basic properties. *Silicate of gelatine* falls as a flaky, white and opaque precipitate, when the solution of silicic acid is gradually added to a solution of gelatine in excess. The precipitate is insoluble in water, and is not decomposed by washing. Silicate of gelatine prepared in the manner described, contains 100 silicic acid to about 92 gelatine. This is a greater proportion of gelatine than in the gallo-tannate of gelatine, and requires for soluble silicic acid a higher equivalent than that of gallo-tannic acid. In the humid state the gelatine of this compound does not putrefy.

The acid reaction of 100 parts of soluble silicic acid is neutralized by 1.85 part of oxide of potassium, and by corresponding proportions of soda and ammonia. The *collo-silicates* or *co-silicates* thus formed are soluble and more durable than fluid silicic acid, but they are pectized by carbonic acid or by an alkaline carbonate, after standing for a few minutes. The co-silicate of potash forms a transparent hydrated film on drying *in vacuo*, which is not decomposed by water, and appears to require about ten thousand parts of water to dissolve it. The silicate of soda which FORCHHAMMER obtained by boiling freshly precipitated silicic acid with carbonate of soda, and collecting the precipitate which falls on cooling, contains 2.74 per cent. of soda, and is represented by $\text{NaO} + 36\text{SiO}_2$ (GMELIN). This silicate is probably a co-silicate of soda in the pectous condition. Soluble silicic acid produces a gelatinous precipitate in lime-water, containing 6 per cent. and upwards of the basic earth. This and the other insoluble earthy co-silicates appear not to be easily obtained in a definite state. They gave out a more basic silicate to water on washing. The composition of these salts, and that also of the co-silicate of gelatine, were found to vary according as the mode of preparation was modified. When a solution of gelatine was poured into silicic acid in excess, the co-silicate of gelatine formed gave, upon analysis, 100 silicic acid with 56 gelatine, or little more than half the gelatine stated above as found in that compound prepared with the mode of mixing the solutions reversed. The gallo-tannate of gelatine is known to offer the same variability in composition.

The gelatine used in the preceding experiments was isinglass (*colle de poisson*), purified by solution in hydrochloric acid and subsequent dialysis. As the acid escapes by diffusion, a jelly is formed in the dialyser. This jelly is free from the earthy matter, amounting to about 0.4 per cent. in isinglass, and is not liable to putrefaction.

Cosilicic acid also precipitates both *albuminic acid* and pure *casein*.

* Annales de Chimie, 3 sér. t. lvii. p. 163.

Soluble Alumina.—We are indebted to Mr. WALTER CRUM for the interesting discovery that alumina may be held in solution by water alone in the absence of any acid. But two soluble modifications of alumina appear to exist, alumina and metalumina. The latter is Mr. CRUM's substance.

A solution of the neutral chloride of aluminium (Al_2Cl_3), placed on the dialyser, appears to diffuse away without decomposition. But when an excess of hydrated alumina is previously dissolved in the chloride, the latter salt is found to escape by diffusion in a gradual manner, and the hydrated alumina, retaining little or no acid, to remain behind in a soluble state. A solution of alumina in chloride of aluminium, consisting at first of 52 parts of alumina to 48 of hydrochloric acid, after a dialysis of six days, contained 66·5 per cent. of alumina; after eleven days 76·5 per cent.; after seventeen days 92·4 per cent., and after twenty-five days the alumina appeared to be as nearly as possible free from acid, as traces only of hydrochloric acid were indicated by an acid solution of nitrate of silver. But in such experiments the alumina often pectizes in the dialyser before the hydrochloric acid has entirely escaped.

Acetate of alumina with an excess of alumina gave similar results. The alumina remained fluid in the dialyser for twenty-one days, and when it pectized was found to retain 3·4 per cent. of acetic acid, which is in the proportion of 1 equivalent of acid to 28·2 equivalents of alumina.

Soluble alumina is one of the most unstable of substances, a circumstance which fully accounts for the difficulty of preparing it in a state of purity. It is coagulated or pectized by portions, so minute as to be scarcely appreciable, of sulphate of potash and, I believe, by all other salts; and also by ammonia. A solution containing 2 or 3 per cent. of alumina was coagulated by a few drops of well-water, and could not be transferred from one glass to another, unless the glass was repeatedly washed out by distilled water, without gelatinizing. Acids in small quantity also cause coagulation; but the precipitated alumina readily dissolves in an excess of the acid. The colloids gum and caramel also act as precipitants.

This alumina is a mordant, and possesses indeed all the properties of the base of alum and the ordinary aluminous salts. A solution containing 0·5 per cent. of alumina may be boiled without gelatinizing, but when concentrated to half its bulk it suddenly coagulated. Soluble alumina gelatinizes when placed upon red litmus paper, and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol nor by sugar. No pure solution of alumina, although dilute, remained fluid for more than a few days.

Like hydrated silicic acid, then, the colloid alumina may exist either fluid or pectous, or it has a soluble and insoluble form, the latter being the gelatinous alumina as precipitated by bases. It is evident that the extraordinary coagulating action of salts upon hydrated alumina must prevent the latter substance from ever appearing in a soluble state when liberated from combination by means of a base.

Colloidal alumina possesses also, I believe, a high atomic weight, like cosilicic acid.

The chloride of alumina with excess of alumina referred to above appears to be, either in whole or in part, a colloidal hydrochlorate of alumina, containing the latter substance with its large colloidal equivalent, and may be really neutral in composition. The soluble basic persalts of iron, tin, &c. are likewise all colloidal, and have no doubt a similar constitution. Such colloidal salts are themselves slowly decomposed on the dialyser, being resolved into the crystalloidal acid which escapes and the colloidal oxide which remains behind.

Soluble Metalumina.—Mr. CRUM first pointed out a singular relation of acetic acid to alumina, which has never been explained. Sulphate of alumina, when precipitated by acetate of lead or baryta, gives a binacetate of alumina, with one equivalent of free acetic acid; the neutral teracetate of alumina not appearing to exist. It was further observed that, by keeping a solution of this binacetate in a close vessel at the boiling-point of water for several days, nearly the whole acetic acid came to be liberated, without any precipitation of alumina occurring at the same time. Mr. CRUM boiled off the free acetic acid, or the greater part of it, and thus obtained his soluble alumina. The same result may be arrived at by dialysing a solution of acetate of alumina that has been altered by heat. In three days the acetic acid was reduced on the dialyser to 11 per cent., giving 1 equiv. acetic acid to 8 equivs. alumina; in six days to 7.17 per cent. acid; in thirteen days to 2.8 per cent. acid, or 1 equiv. acid to 33 equivs. alumina. The alumina exists in an allotropic condition, being no longer a mordant; and forming, when precipitated, a jelly that is not dissolved by an excess of acid. Metalumina resembles alumina in being coagulated by minute proportions of acids, bases, and of most salts. Mr. CRUM found the solution of metalumina to require larger quantities of acetates, nitrates, and chlorides to produce coagulation than of the former substances. The solution of metalumina is tasteless, and entirely neutral to test-paper, according to my own observation.

Like alumina, the present colloid has therefore a fluid and a pectous form, the liquid soluble metalumina, and the gelatinous insoluble metalumina.

Soluble Peroxide of Iron.—A solution of hydrated peroxide of iron may be obtained by a process exactly analogous to that for soluble alumina. Perchloride of iron in solution is first saturated with hydrated peroxide of iron, added by small quantities at a time; or carbonate of ammonia may be added in a gradual manner to perchloride of iron, so long as the precipitated oxide continues to be redissolved on stirring. These red solutions of iron have lately been carefully investigated by Mr. ORDWAY (*SILLIMAN'S Journal*, 3 ser. xxxix. 197), by M. BECHAMP (*Annales de Chimie*, 3 sér. lvii. 293), and by M. SCHEURER-KESTNER (*Ib.* lv. 330). It is observed that the act of solution of the hydrated peroxide by the chloride of iron is a gradual process, demanding time. The quantity of oxide taken up will go on increasing for a long time, if digestion in the cold is continued. Mr. ORDWAY found chloride of iron to take up so much as 18 equivalents of peroxide of iron in the course of five months. This slowness of action is highly characteristic of colloids. Only monobasic acids, such as hydrochloric and nitric, serve for

preparing such solutions; sulphuric and other polybasic acids giving insoluble subsalts with excess of ferric oxide, or of any other aluminous oxide. The red liquid so obtained is already a colloidal hydrochlorate of peroxide of iron, but requires to be dialysed for a sufficient time. Such a compound possesses an element of instability in the extremely unequal diffusibility of its constituents. Beginning with perchloride of iron, containing five or six equivalents of peroxide in solution, the whole solid matter also amounting to 4 or 5 per cent. of the liquid, and the latter forming a stratum of the usual depth of about half an inch in the dialyser, it was found that hydrochloric acid diffused out accompanied only by a small proportion of the iron. After eight days, the deep red solution in the dialyser contained peroxide of iron and hydrochloric acid, in the proportion of 97·6 per cent. of the former to 2·4 per cent. of the latter. In nineteen days the hydrochloric acid was reduced to 1·5 per cent., which gives 1 equiv. of acid to 30·3 equivs. peroxide of iron. The last solution was transferred to a phial, in which it remained fluid for twenty days, and then spontaneously pectized.

The peracetate of iron, prepared by double decomposition, is incapable of dissolving hydrated peroxide of iron, as is well known, but still may be made a source of soluble peroxide; as the salt referred to is itself decomposed to a great extent by diffusion on the dialyser. About one-half of the iron was lost by a diffusion of eighteen days, in a particular experiment, leaving on the dialyser a red liquid, in which ninety-four parts of peroxide of iron were still associated with six parts of acetic acid.

Water containing about 1 per cent. of hydrated peroxide of iron in solution has the dark red colour of venous blood. The solution may be concentrated by boiling to a certain point, and then pectizes. The red solution is coagulated in the cold by traces of sulphuric acid, alkalies, alkaline carbonates, sulphates and neutral salts in general, but not by hydrochloric, nitric, and acetic acids, nor by alcohol or sugar. The coagulum is a deep red-coloured jelly, resembling the clot of blood, but more transparent. Indeed the coagulation of this colloid is highly suggestive of that blood, from the feeble agencies which suffice to effect the change in question, as well as from the appearance of the product. The coagulum formed by a precipitant, or in the course of time, without any addition having been made to the solution of peroxide of iron, is no longer soluble in water, hot or cold; but it yields readily to dilute acids. It is, in short, the ordinary hydrated peroxide of iron. Here then, again, we have a soluble and insoluble form of the same colloidal substance. Native hematite, which presents itself in mammillary concretions, is no doubt colloidal.

Soluble Metaperoxide of Iron.—The soluble peroxide of iron of M. PÉAN DE SAINT-GILLES* appears to be the analogue of metalumina. It was also prepared by the prolonged action of heat upon a pure solution of the acetate. The characteristic properties of this substance, which indicate its allotropic nature, are the orange-red colour and the opalescent appearance of its solution. The metaperoxide of iron is entirely precipitated of a brown ochreous appearance by a trace of sulphuric acid, or of an alkaline salt, and

* Comptes Rendus, 1855, p. 568.

is insoluble in all cold acids, even when the latter are concentrated. The solubility of metaperoxide of iron in water appears to be more precarious, if possible, than that of the colloid alumina. It would no doubt be more safely prepared by diffusing away the acetic acid of the altered acetate of iron, than it is by boiling off that acid; as the solution is said to become precipitable by heat before the whole acetic acid is expelled.

Ferrocyanide of Copper.—Many of the insoluble ferrocyanides are crystalline precipitates, but the compound above named, and the different varieties of prussian blue, appear to be strictly colloidal.

Certain anomalous properties long observed in these compounds come thus to be explained. The ferrocyanide of copper precipitated from ferrocyanide of potassium and sulphate of copper, is a reddish-brown gelatinous precipitate, and carries down a portion of the potash salt. It is obtained of greater purity, like the other insoluble ferrocyanides, by the use of ferrocyanic acid as the precipitant. Ferrocyanide of copper is then darker in colour, and still more highly gelatinous. It is well known that this substance appears as a transparent almost colourless jelly, when precipitated from strong solutions. This colloidal matter assumes colour on the addition of water, in consequence of further hydration, following in this respect the analogy of the crystalloid salts of copper. The ferrocyanide of copper, when once precipitated, may be washed without loss, and exhibits no symptoms of solubility. But it has been remarked that the same salt, when produced by mixing the precipitating salts dissolved in not less than two or three thousand times their weight of water, gives a wine-red solution with no precipitate. This is the soluble condition of the colloid. When the red solution is placed in the dialyser the salt of potash diffuses out, and the whole ferrocyanide of copper is retained behind in solution.

Precipitated ferrocyanide of copper is not dissolved by oxalic acid, nor by oxalate of potash, but dissolves freely in about one-fourth of its weight of neutral oxalate of ammonia. The ferrocyanide of copper must be washed beforehand, to ensure solubility. A solution holding 3 or 4 per cent. of ferrocyanide of copper is of a dark reddish-brown colour, intermediate in tint between the acetate and meconate of iron. The solution is transparent, but assumes a peculiar appearance of opacity when seen by light reflected from its surface. The same appearance was observed by PÉAN DE SAINT-GILLES in his metaperoxide of iron.

When a red solution, such as that described, was dialysed, the oxalate of ammonia came away in a gradual manner; 30.6 per cent. of the oxalate of ammonia were found in the colourless diffusate of the first twenty-four hours; 31 per cent. of the same salt in the diffusate of the next three days, and 18.2 per cent. in the diffusates of the following seven days, making altogether 79.8 per cent., or four-fifths of the whole oxalate of ammonia originally introduced. A small portion of the ammoniacal salt is retained with force, as might be expected from a ferrocyanide. Although the diffusate appeared colourless, it was found to contain a little oxide of copper, namely, 0.041 gramme (of which 0.022 gramme diffused out in the first twenty-four hours), from 2 grammes of ferrocyanide of copper placed in the dialyser.

The liquid ferrocyanide of copper, both before and after being dialysed, may be heated without change, but it is pectized by foreign substances with extreme facility. This effect is produced by a minute addition of nitric, hydrochloric, and sulphuric acids in the cold, and of oxalic and tartaric acids with the aid of a slight heat. It is remarkable that acetic acid does not pectize the ferrocyanide of copper and many other colloids. Sulphate of potash, sulphate of copper, and metallic salts generally appear to pectize the red liquid. The oxalate of ammonia, if any is present, remains in solution.

Neutral Prussian Blue.—The blue precipitate from perchloride of iron and ferrocyanide of potassium, or ferrocyanic acid, is a bulky hydrate, which dries up into gummy masses, so far resembling a colloid. The precipitate dissolves readily with the aid of a gentle heat, in one-sixth of its weight of oxalic acid, giving the well-known solution of prussian blue, used as an ink. Prussian blue is equally soluble in the oxalate and binoxalate of potash. When the solution of prussian blue in oxalic acid was placed on the dialyser, no colouring matter came through, but 28 per cent. of the oxalic acid diffused away in the first twenty-four hours, accompanied by traces of peroxide of iron. The oxalic acid appears to leave the colloidal solution very slowly and incompletely, 8 per cent. diffusing away in the second twenty-four hours, 11 per cent. in the next four days, and 2 per cent. in the following six days. The colloidal solution of prussian blue was pectized by small additions of sulphate of zinc and several other metallic salts, but required larger quantities of the alkaline salts for precipitation.

Ferridcyanide of Iron.—The blue precipitate from the ferridcyanide of potassium and a protosalt of iron is soluble in oxalic acid and the binoxalate of potash, but not in the neutral oxalates. This blue liquid is quite incapable of passing through the dialyser, and is equally colloidal with ordinary prussian blue. So also is *basic prussian blue* prepared by the spontaneous oxidation of precipitated ferrocyanide of protoxide of iron. This last colloid might probably be purified with advantage upon the dialyser.

The ammonio-tartrate of iron, ammonio-citrate of iron, and similar pharmaceutical preparations are chiefly colloidal matters.

Sucrate of Copper.—The deep blue liquid obtained by adding potash to a mixed solution of chloride of copper and sugar appears to contain a colloidal substance. Placed on a dialyser for four days, the blue liquid became green, and no longer contained either potassium or chlorine; it in fact consisted of oxide of copper united with twice its weight of sugar. The external liquid remained colourless, and gave no indication of copper when tested with sulphuretted hydrogen. The colloidal solution of sucrate of copper was sensitive in the extreme to pectizing agents. Salts and acids generally gave a bluish-green precipitate; even acetic acid had that effect. The precipitate, or pectous sucrate, after being well-washed, consisted of oxide of copper with about half its weight of sugar, and is therefore a subsucrate. When the green liquid is heated strongly, it gives a bluish-green precipitate, and does not allow the copper to be readily reduced to the state of suboxide. The subsucrate of copper possesses considerable vivacity of colour, and might be used as a pigment. A solution of sucrate of copper absorbs carbonic acid from the air with great avidity.

The sucrate of copper dries up into transparent films of an emerald green colour. These films are not altered in appearance or dissolved in cold or boiling alcohol. In water they are resolved into sugar and the pectous subsucrate of copper.

Sucrate of Peroxide of Iron.—The perchloride of iron with an addition of sugar is not precipitated by potash, provided the temperature is not allowed to rise. The peroxide of iron combined with the sugar is colloidal, and remains on the dialyser without loss. At a certain stage, however, the sugar appears to leave the peroxide of iron, and a gelatinous subsucrate of iron pectizes. The subsucrate of iron thrown down from the soluble sucrate, by the addition of sulphate of potash, consisted of about 22 parts of sugar to 78 parts of peroxide of iron.

Sucrate of Peroxide of Uranium.—A similar solution may be obtained by adding potash to a mixture of the nitrate or chloride of uranium with sugar, avoiding heat. The solution is of a deep orange-yellow colour, and on the dialyser soon loses the whole of its acid and alkali. This fluid sucrate has considerable stability, but is readily pectized by salts, like the sucrate of copper. The subsucrate pectized has considerable solubility in pure water.

Sucrate of Lime.—The well-known solution of lime in sugar forms a solid coagulum when heated. It is probably, at a high temperature, entirely colloidal. The solution obtained on cooling passes through the septum, but requires a much longer time than a true crystalloid like the chloride of calcium.

The blue solution of tartrate of copper in caustic potash contains a colloidal compound, which has not been fully examined.

Soluble Chromic Oxide.—The definite terchloride of chromium, being a crystalloid, diffuses away entirely when placed in solution upon the dialyser. This salt dissolves, with time, a certain portion of freshly-precipitated hydrated chromic oxide, and becomes of a deeper green colour. Such a solution, after dialysis for twenty-two days, contained 8 hydrochloric acid to 92 chromic oxide; and after thirty days, 4.3 acid to 95.7 oxide, or 1 equiv. acid to 10.6 equivs. oxide. After thirty-eight days, the solution gelatinized in part upon the dialyser, and then contained 1.5 acid to 98.5 oxide, or 1 equiv. acid to 31.2 equivs. chromic oxide. This last solution, which may be taken to represent soluble chromic oxide, is of a dark green colour, and admits of being heated, and also of being diluted with pure water without change. It was gelatinized with the usual facility by traces of salts and other reagents which affect colloid solutions, and was then no longer soluble in water, even with the assistance of heat. It appeared to be the green hydrated oxide of chromium, as that substance is usually known. A metachromic oxide may possibly be obtained by heating and dialysing the acetate, but I have not attempted to form it.

Mr. ORDWAY succeeded in dissolving an excess of the hydrated *uranic oxide* and of *glucina* in the chloride of uranium and of glucinum respectively. The dialysis of such solutions may be reasonably expected to yield soluble uranic oxide and soluble glucina.

It appears, then, that the hydrated peroxides of the aluminous type, when free, are

colloid bodies; that two species of each of these hydrated oxides exist, of which alumina and metalumina are the types; one derived from an unchanged salt, and the other from the heated acetate of the base; further, that each of these species has two forms, one soluble and the other insoluble, or coagulated. This last species of duality should be well distinguished from the preceding allotropic variability of the same peroxide. The possession of a soluble and an insoluble (fluid and pectous) modification is not confined to hydrated silicic acid and the aluminous oxides, but appears to be very general, if not universal, among colloid substances. The double form is typified in the fibrin of blood.

The precipitated and gelatinous *peroxide of tin* is largely soluble in the bichloride of the same metal. Such a solution, when placed in the dialyser, allows the whole chlorine of the salt and a portion of the tin to diffuse away. Peroxide of tin, or stannic acid, remains behind, but not in a soluble state. It forms in the dialyser a semitransparent gelatinous cake, which after a few days is entirely free from chlorine. The original solution, containing excess of stannic acid, was diluted to various degrees, but was dialysed always with the same result. The coagulum was insoluble in hot or cold water, but dissolved readily in dilute acids. It was evidently the peroxide of tin unaltered.

The *metastannic acid*, or nitric acid peroxide of tin of BERZELIUS, forms a solid compound with a small quantity of hydrochloric acid. This compound is not dissolved by an excess of acid, but is soluble in pure water. The solution placed in the dialyser is readily decomposed, and leaves behind a semitransparent gelatinous mass of pure hydrated metastannic acid, insoluble both in water and acids. There appears, then, to be no soluble form of either hydrated stannic or metastannic acid, although both are colloidal substances.

Precipitated *titanic acid* was dissolved in hydrochloric acid and submitted to dialysis. The hydrochloric acid readily diffused away, leaving hydrated titanic acid, gelatinous and insoluble, upon the dialyser. The proportion of titanic acid, which escaped from the dialyser and was lost, amounted to 0.050 gramme out of 2.5 grammes. Titanic acid thus resembles stannic acid in not presenting itself in the form of a fluid colloid.

Metallic protoxides are not soluble in their neutral salts, and cannot therefore be submitted to dialysis in the same conditions as the preceding peroxides. It was observed, however, that oxide of copper and oxide of zinc, when dissolved in ammonia, are capable of diffusing through a colloidal septum, and are therefore not colloids themselves. The water outside the dialyser should be charged with ammonia in such an experiment.

5. *Dialysis of Organic Colloid Substances.*

Tannin.—The tannin employed was that extracted from gall-nuts by the ether process of PELOUZE. A two per cent. solution of this substance, covering a surface of paper-parchment of the area of about $\frac{1}{100}$ th of a square metre, or 15.6 square inches, to a

depth of 10 millimetres, was diffused at 10° to 13° of temperature. The diffused matter amounted, in successive periods of twenty-four hours, to .073, .040, .021, .021, .024 and .024 gramme, derived from the two grammes in solution. Probably the earlier diffusates were increased by the presence of a little gallic acid, which, being a crystalloid, would no doubt be rapidly eliminated by diffusion. The latter observations indicate that tannin passes through a paper-parchment septum about 200 times less rapidly than chloride of sodium does, in similar circumstances as to temperature and strength of solution. The diffusates from the tannin solution gave a precipitate with gelatin, and therefore contained tannin unaltered. But the diffusates probably contained also throughout some products of decomposition of a crystalloid character.

To the low diffusibility of tannin may be ascribed the remarkably slow penetration of skins by that substance in the ordinary operation of tanning leather. Tannin appears to form compounds of much stability with certain other colloids, as tanno-gelatine, and the compound with albumen which appears to be the primary basis of the vegetable cell (FRÉMY).

Gum.—The diffusate obtained from a solution containing 2 grammes of gum-arabic, in experiments corresponding in their conditions with the experiments upon tannin just related, was .013 gramme per day. The power of gum to penetrate the colloid septum appears, therefore, to be one-half less than that of tannin, and 400 times less than the diffusibility of chloride of sodium. Gum gave the same amount of diffusate with a mucus septum as with parchment-paper. When substances of the crystalloid class are mixed with the gum, the diffusion of the latter appears to be still further reduced, and may even be entirely extinguished. The separation of colloids from crystalloids by dialysis is, in consequence, generally more complete than might be expected from the relative diffusibility of the two classes of substances.

Vegetable gum, which FRÉMY has shown to be a gummate of lime, can be purified by a dialytic method, which may be found applicable with advantage in other cases. Oxalic acid, it is known, precipitates lime from the gum very imperfectly. Hydrochloric acid may be used to separate that base from a solution of gum placed upon the dialyser, with more effect. It is only necessary to add to a strong solution of gum 4 or 5 per cent. of hydrochloric acid, and to dialyse till the gum solution gives no precipitate with nitrate of silver. In an experiment made upon a 20 per cent. solution of gum, the ash was reduced to 0.1 per cent. of the gum in five days. The gummic acid possesses a sensible acid reaction, about equal to that of carbonic acid. This acid reaction was neutralized in 100 parts of gummic acid by 2.85 parts of potash. This amount of potash is very nearly equivalent to the lime originally present in the gum (1.72 lime, or 3.07 carbonate of lime, being equivalent to 2.89 potash). When the gummate of potash itself was dialysed without addition, the potash gradually diffused away, possibly in the state of carbonate, and left the gum again possessed of an acid reaction. Gummic acid, well-dried at 100° , becomes insoluble in water, but swells up in that liquid, like gum-tragacanth. We appear to have here the pectous form of gummic acid.

It is worthy of inquiry whether such native gums as are insoluble in water are not the pectous form of soluble gum, rather than allotropic varieties of that substance. So also of the metagummic acid of FRÉMY, formed by the action of strong sulphuric acid on mucilage. This last substance is insoluble in water, but was found by FRÉMY to afford, when neutralized by lime and alkalies, a soluble gum undistinguishable from gum-arabic.

Gummic acid produces a remarkable compound with gelatine. When solutions of these two colloids are mixed, oily drops fall and form a nearly colourless jelly on standing. This jelly is very fusible, melting at 25° , or by the heat of the hand. The *gum-mate of gelatine* may be washed without decomposition, but is soluble to a certain extent in pure water, and still more so in a solution of gelatine. Prepared with gummic acid in excess, the compound, when dried at 100° , consisted of 100 gummic acid with 59 gelatine. The drops and the jelly contained 83.5 per cent. of water. Solution of gelatine is not precipitated by unpurified gum, nor by the gummate of potash.

Dextrin.—A two per cent. solution of dextrin, prepared from starch, was diffused in the same conditions as the preceding substances, but through a mucus septum. It gave in twenty-four hours .034 gramme of diffusate from 2 grammes, or about three times more diffusate than was given by gum-arabic.

Caramel.—The dialytic examination of this substance adds to the accurate information on the subject lately supplied by M. A. GÉLIS*, and places caramel indisputably in the colloid class. The crude caramel obtained by heating cane-sugar at 210° — 220° , when placed on the dialyser, allows certain intermediate coloured substances (Caramelane and Caramelene of GÉLIS) to diffuse out with considerable facility, while the compound containing the largest proportion of carbon remains behind. The latter substance, as obtained by me, possessed five times the colouring power of the original crude caramel, weight for weight. This highest soluble member of the caramel series may also be obtained, more quickly, by precipitation from its aqueous solution by means of alcohol. But I found it necessary to repeat the precipitation four times, or till the mass thrown down, from being plastic at first became pulverulent. A solution containing 10 per cent. of the caramel so purified is gummy; and on standing, it formed a tremulous jelly entirely soluble in hot or cold water. Evaporated *in vacuo*, the solution dries up into a black shining mass, which is tough and elastic, while it still possesses a certain proportion of water, like gum containing some water. Once thoroughly dried at a low temperature, this soluble caramel may be heated, afterwards, to 120° and retain complete solubility. But if a solution of the same caramel be directly evaporated to dryness by the heat of a water-bath, the whole matter is rendered insoluble in hot or cold water. The soluble and insoluble caramel have the same composition, and appear to illustrate the usual double form of colloids. The proportion of carbon in the fluid caramel was found as high as 54.59 per cent., which comes nearer to $C_{24}H_{15}O_{15}$ (requiring C 55.17) than any other formula in which the oxygen and hydrogen are assumed to be present in the pro-

* Annales de Chimie, &c., sér. 3. t. lii. p. 352.

portion of water. In the analysis by GÉLIS of his carameline, the proportion of carbon did not exceed 51·33 per cent., which does not apply to the present substance.

Fluid caramel is wholly tasteless, and appears to be neutral. It exhibits the same excessive sensibility to crystalloidal reagents which is witnessed in fluid silicic acid and alumina. The solution is precipitated or pectized by mere traces of any mineral acid, by alkaline sulphates, chloride of sodium, by most other salts, and by alcohol. The caramel then forms a brownish black pulverulent substance, insoluble in hot or cold water. The presence of sugar and of the intermediate brown substances protects fluid caramel in a remarkable way from the action of crystalloids, and accounts for the preceding properties not being observed in crude caramel. This colloid appears also to be precipitated by certain substances of its own class, such as peroxide of iron.

Pectous caramel may readily have its solubility restored. Placed in dilute potash, the caramel swells and appears gelatinous, and is dissolved on the application of heat. When this solution is dialysed, the potash is quickly reduced to the proportion of about 9 per cent., which forms a neutral compound. If an excess of acetic acid now be added, the whole potash is soon diffused away, and pure soluble caramel remains on the dialyser. Even carbonic acid will carry away the potash.

The extremely low diffusibility which has been assigned to caramel in former Tables, belongs to that substance as last described; the brown intermediate substances which accompany it in crude caramel being considerably more diffusive, although they again are much less diffusive than any variety of crystallizable or uncrystallizable sugar. When the molasses of the cane-sugar are diffused, much the greater portion of the colouring matters remains in the dialyser.

With the parchment-paper septum the fluid caramel appeared even less dialysable than gum, the diffusate in twenty-four hours from a 2 per cent. solution of the former being ·009 gramme only, while that of the latter was ·013. Caramel may be stated, approximately, to be 600 times less dialysable than chloride of sodium, and 200 times less so than sugar. Hence liquids coloured with caramel, such as porter and coffee, may be dialysed for a day with the passage of very little colouring matter.

Before leaving caramel, the analogy may be referred to which the insoluble form of that substance presents to *coal*. Caramelization appears the first step in that direction,—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages.

Albumen.—The purification of albumen is effected with much advantage upon the dialyser. The solution of egg-albumen is mixed freely with acetic acid and then dialysed. The earthy and alkaline salts are speedily got rid of, and in three or four days the albumen burns without leaving a trace of ash. Although the acetic acid used in the process appears to diffuse off entirely, albumen prepared in the manner described has a faint acid reaction. It also coagulates milk when mixed with the latter and heated. Albumen so prepared retains its constituent sulphur.

The passage through parchment-paper of pure albumen prepared by the unobjection-

able process of M. WURTZ is so slow, that several days are required to produce a sensible result. Thus the diffusate from a solution of 2 grammes of albumen in 50 grammes of water was 0.052 gramme in eleven days, which gives 0.005 gramme in a single day. Albumen, then, appears to be about $2\frac{1}{2}$ times less dialysable than gum, and 1000 times less so than chloride of sodium.

Even combination with an alkali does not appear to enable albumen to pass through the colloid septum. To half a gramme of pure albuminic acid dissolved in 50 grammes of water, .05 gramme of hydrate of soda was added (one-tenth of the weight of the albumen), and the liquid was placed upon parchment-paper. No albumen could be discovered in the diffusate of several days, but it gave .069 gramme of carbonate of soda, equivalent to .053 gramme of hydrate of soda; that is the whole soda originally added to the albumen. The separation of the soda from the albumen may possibly have been aided by the presence of carbonic acid in the water, but certainly the entire separation of the alkali from albumen by diffusion through a colloidal film is a remarkable fact. Hydrate of potash was found to diffuse away from albumen in the same manner.

A solution of *Emulsin* is precipitated by albuminic and gummic acids, but not by unpurified albumen or gum-arabic. The precipitates are white and opaque, pulverulent, and not gelatinous. They are soluble in acetic acid.

A thin stratum of pure albumen coagulated by heat appears to intercept completely the passage of liquid albumen of the egg. Forty grammes of undiluted egg-albumen, representing 5.6 grammes of dry albumen, were placed on a dialyser of the small size, composed of two sheets of calico well-impregnated with albumen and coagulated by heat of steam, as in the albumenized osmometer*. After twelve days the volume of liquid within the instrument had increased to 117 grammes by osmose, while a diffusate had passed through the dialyser of 0.243 gramme, or 4.34 per cent. of the original dry albumen. This diffusate consisted of salts chiefly, with some organic matter, but no portion of the latter was coagulable by heat.

Neither gelatinous starch, animal gelatine dissolved in water, nor extract of flesh appears to be capable of diffusing through a colloid septum in a sensible degree, although salts and other crystallizable substances, which are mixed with the former, diffuse through the septum readily, and may thus be separated from the former substances.

6. *Separation of Arsenious Acid from Colloidal Liquids.*

Dialysis may be advantageously applied to the separation of arsenious acid and metallic salts from organic solutions in medico-legal inquiries. The process has the advantage of introducing no metallic substance or chemical reagent of any kind into the organic fluid. The arrangement for operating is also of the simplest nature.

The organic fluid is placed, to the depth of half an inch, on a dialyser formed of a hoop of gutta percha 10 or 12 inches in diameter, covered with parchment-paper (fig. 1, page 186). The dialyser is then floated in a basin containing a volume of water about

* Philosophical Transactions, 1854, p. 189.

four times greater than the volume of organic fluid in the dialyser. The water of the basin is generally found to remain colourless after the lapse of twenty-four hours, and after being concentrated by evaporation, it admits of the application of the proper reagents to precipitate and remove a metal from solution. One-half to three-fourths of the crystalloidal and diffusible constituents of the organic fluid will generally be found in the water of the basin.

In the few illustrative experiments which follow, the 4-inch bulb dialyser, having an area of 16 square inches, or about $\frac{1}{100}$ th part of a square metre, was generally made use of (fig. 3, p. 201). The volume of liquid placed in the bulb was 50 cubic centimetres, and accordingly covered the dialyser to a depth of 5 millimetres, or about 0.2 inch. The outer volume of water (in the jar) was not less than 1 litre, or twenty times the volume of the solution on the dialyser.

1. A solution of arsenious acid, in pure water, was first placed on the dialyser, the water containing 0.5 per cent. of arsenious acid, or 0.25 gramme of that substance, for twenty-four hours. The dialyser being then removed, the outer fluid was concentrated by heat, and then precipitated by sulphuretted hydrogen. It gave 0.300 gramme of tersulphide of arsenic, equivalent to 0.241 gramme of arsenious acid. It appears, then, that about 95 per cent. of the arsenious acid had diffused from the dialyser into the water-jar in twenty-four hours.

2. Water, with one-fourth of its volume of fluid egg albumen and 0.25 gramme, or 0.5 per cent. of arsenious acid, was now placed on the dialyser as before. The diffusate gave, with sulphuretted hydrogen, after being acidulated with hydrochloric acid, 0.267 gramme of tersulphide of arsenic, equivalent to 0.214 gramme of arsenious acid.

3. The water contained 10 per cent. of gum-arabic and 1 per cent. arsenious acid, the latter amounting to 0.5 gramme. From the diffusate was derived 0.505 gramme of tersulphide of arsenic, equivalent to 0.406 gramme of arsenious acid. The dialyser still gave out arsenious acid when immersed for a second day in water. The outer fluid contained no gum.

It may be added that a similar 1 per cent. solution of arsenious acid, without the gum, gave a diffusate of 0.45 gramme arsenious acid in the same time, that is, nine-tenths of the whole acid.

4. A solution in hot water of 1 per cent. isinglass and 0.5 per cent. of arsenious acid (0.25 gramme), formed a jelly upon the dialyser on cooling. The diffusate from this jelly gave 0.260 tersulphide of arsenic, equivalent to 0.209 arsenious acid, with no gelatine. The escape of the arsenious acid appears then to have been slightly retarded by the fixing of the gelatinous solution. This is probably due to the arrest of mechanical movement within the gelatinous stratum, and not to any sensible impediment offered by the jelly to diffusion.

In another experiment, similar to the last, but continued for four days instead of twenty-four hours, the tersulphide of arsenic weighed 0.320 gramme, equivalent to 0.257 arsenious acid.

5. A quantity of white of egg, amounting to 50 grammes, to which 0.01 gramme of arsenious acid in solution had been added, was coagulated by heat. The solid mass was then cut up into small pieces and placed on the dialyser, mixed with 50 grammes of water; after the usual period of twenty-four hours, the diffusate gave 0.01 gramme of tersulphide of arsenic, equivalent to 0.008 gramme arsenious acid. Here, of the mass upon the dialyser, the arsenious acid formed only $\frac{1}{10,000}$ th part, yet four-fifths of it are recovered.

6. One hundred grammes of milk, charged with $\frac{1}{10,000}$ th part of arsenious acid (0.01 gramme), and forming a stratum on the dialyser of 10 millimetres, gave a diffusate which yielded 0.010 tersulphide of arsenic, equivalent to 0.008 gramme of arsenious acid. The outer liquid was colourless, and gave no indication of casein, but it contained of course the salts and the sugar of the milk.

7. The same experiment was repeated with sized writing-paper, as the septum, applied to the same bulb. The result was a slight increase in the quantity of arsenious acid recovered.

It appears, then, that arsenious acid separates on the dialyser from gum, from gelatine, albumen, fluid or coagulated, and from casein, and is obtained in a solution fit for the application of reagents.

8. Half a litre of dark-coloured porter, with 0.05 gramme of arsenious acid added ($\frac{1}{10,000}$ th part of arsenious acid) was placed on a hoop dialyser, 8 inches in diameter, and the whole floated in an earthenware basin containing 2 or 3 litres of water. After twenty-four hours the latter fluid had acquired a slight tinge of yellow. It yielded, when concentrated and precipitated by sulphuretted hydrogen, upwards of one-half of the original arsenious acid in a fit state for examination.

9. In a similar experiment on 200 grammes of defibrinated blood charged with $\frac{1}{4000}$ th part of arsenious acid (0.05 gramme), and placed in a similar dialyser to the last for twenty-four hours, the diffusate of arsenious acid was recovered with the same facility, and appeared to be equally considerable.

10. Animal intestines, charged with the usual minute proportion of arsenious acid, were cut into small pieces and digested in water, about 32° C., for twenty-four hours. The whole was then thrown upon a dialyser for an equal time. Arsenious acid diffused out so free from colloidal matter that the action of reagents was not interfered with. A high temperature in digesting the intestines is quite unnecessary, and appeared indeed to increase the difficulty of diffusing out the arsenious acid afterwards.

The *tartrate of potash and antimony*, mixed in the small proportion of $\frac{1}{10,000}$ th, with defibrinated blood and with milk, was separated by dialysis quite as effectually as arsenious acid above.

Strychnine also was separated from organic fluids in the same manner, a small addition of hydrochloric acid being first made to the fluid on the dialyser.

Dialysis then appears of general application in the preparation of a liquid for examination by chemical tests, whether the poison looked for be mineral or organic. All

soluble poisonous substances, whatever their origin, appear to be crystalloids, and accordingly pass through colloidal septa.

7. *Colloidal Condition of Matter.*

I may be allowed to advert again to the radical distinction assumed in this paper to exist between colloids and crystalloids in their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass.

The colloidal character is not obliterated by liquefaction, and is therefore more than a modification of the physical condition of solid. Some colloids are soluble in water, as gelatine and gum-arabic; and some are insoluble, like gum-tragacanth. Some colloids, again, form solid compounds with water, as gelatine and gum-tragacanth, while others, like tannin, do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes, notwithstanding their differences.

The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature, usually occurring in the act of solution, becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced and precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents, as has already been explained.

While soluble crystalloids are always highly sapid, soluble colloids are singularly insipid. It may be questioned whether a colloid, when tasted, ever reaches the sentient extremities of the nerves of the palate, as the latter are probably protected by a colloidal membrane, impermeable to soluble substances of the same physical constitution.

It has been observed that vegetable gum is not digested in the stomach. The coats of that organ dialyse the soluble food, absorbing crystalloids and rejecting all colloids. This action appears to be aided by the thick coating of mucus which usually lines the stomach.

The secretion of free hydrochloric acid during digestion—at times most abundant—appears to depend upon processes of which no distinct conception has been formed. But certain colloidal decompositions are equally inexplicable upon ordinary chemical views. To facilitate the separation of hydrochloric acid from the perchloride of iron,

for instance, that salt is first rendered basic by the addition of peroxide of iron. The comparatively stable perchloride of iron is transformed, by such treatment, into a feebly-constituted colloidal hydrochlorate. The latter compound breaks up under the purely physical agency of diffusion, and divides on the dialyser into colloidal peroxide of iron and free hydrochloric acid. The super-induction of the colloidal condition may possibly form a stage in many analogous organic decompositions.

A tendency to spontaneous change, which is observed occasionally in crystalloids, appears to be general in the other class. The fluid colloid becomes pectous and insoluble by contact with certain other substances, without combining with these substances, and often under the influence of time alone. The pectizing substance appears to hasten merely an impending change. Even while fluid a colloid may alter sensibly, from colourless becoming opalescent; and while pectous the degree of hydration may become reduced from internal change. The gradual progress of alteration in the colloid effected by the agency of time, is an investigation yet to be entered upon.

The equivalent of a colloid appears to be always high, although the ratio between the elements of the substance may be simple. Gummic acid, for instance, may be represented by $C_{12}H_{11}O_{11}$, but judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule.

With silicic acid, which can exist in combination both as a crystalloid and colloid, we have two series of compounds, silicates and cosilicates, the acid of the latter appearing to have an equivalent much greater (thirty-six times greater in one salt) than the acid of the former. The apparently small proportion of acid in a variety of metallic salts, such as certain red salts of iron, is accounted for by the high colloidal equivalent of their bases. The effect of such an insoluble colloid as prussian blue in carrying down small proportions of the precipitating salts, may admit of a similar explanation.

Gelatine appears to hold an important place as a colloidal base. This base unites with colloidal acids, giving a class of stable compounds, of which tanno-gelatine only appears to be hitherto known. Gelatine is precipitated entirely by a solution of metaphosphoric acid added drop by drop, 100 parts of gelatine uniting with 3.6 parts of the acid. The compound formed is a semitransparent, soft, elastic, and stringy solid mass, presenting a startling resemblance to animal fibrin. It will be an interesting inquiry whether metaphosphoric acid is a colloid, and enters into the compound described in that character, or is a crystalloid, as the small proportion and low equivalent of the acid would suggest. Gelatine is also precipitated by carbolic acid.

The hardness of the crystalloid, with its crystalline planes and angles, is replaced in

the colloid by a degree of softness, with a more or less rounded outline. The water of crystallization is represented by the water of gelatination. The water in gelatinous hydrates is aptly described by M. CHEVREUL as retained by "capillary affinity," that is, by an attraction partaking both of the physical and chemical character. While it is here admitted that chemical affinity of the lowest degree may shade into capillary attraction, it is believed that the character of gelatinous hydration is as truly chemical as that of crystalline hydration. Combination of a colloid with water is feeble, it is true, but so is combination in general with the colloid. Notwithstanding this, anhydrous colloids can decompose certain crystalloid hydrates. The water in alcohol of greater strength than corresponds with the density 0.926, which represents the definite hydrate $C_4H_6O_2 + 6HO$, is certainly in a state of chemical union. But alcohol so high as 0.906, contained in a close vessel, is concentrated in a notable degree by contact with dry mucus, gelatine, and gum, and sensibly even by dry parchment-paper. Dilute alcohol divided from the air of the atmosphere by a dry septum of mucus, gelatine, or gum, is also concentrated by evaporation, as in the well-known bladder experiment of SÖMMERING. The selective power is here apparent of the colloid for water, that fluid being separated from alcohol, and travelling through the colloidal septum by combination with successive molecules of the latter, till the outer surface is reached and evaporation takes place. The penetration in this manner of a colloid by a foreign substance may be taken as an illustration of the phenomena of cementation. Iron and other substances which soften under heat, may be supposed to assume at the same time a colloidal constitution. So it may be supposed does silica when fused into a glass by heat, and every other vitreous substance.

Gelatinous hydrates always exhibit a certain tendency to aggregation, as is seen in the jelly of hydrated silicic acid and of alumina. With some the jelly is also adhesive, as in glue and mucus. But unless they be soluble in water, gelatinous hydrates, when once formed, are not in general adhesive. Separated masses do not reunite when brought into contact. This want of adhesiveness is very remarkable in the gelose of PAYEN, which resembles gelatine so closely in other respects. Layers of a gelose solution, allowed to cool and gelatinize in succession in a diffusion-jar (p. 199), do not adhere together.

Ice itself presents colloidal characters at or near its melting-point, paradoxical although the statement may appear. When ice is formed at temperatures a few degrees under $0^{\circ} C.$, it has a well-marked crystalline structure, as is seen in water frozen from a state of vapour, in the form of flakes of snow and hoar-frost, or in water frozen from dilute sulphuric acid, as observed by Mr. FARADAY. But ice formed in contact with water at 0° , is a plain homogeneous mass with a vitreous fracture, exhibiting no facets or angles. This must appear singular when it is considered how favourable to crystallization are the circumstances in which a sheet of ice is slowly produced in the freezing of a lake or river. The continued extrication of latent heat by ice as it is cooled a few degrees below $0^{\circ} C.$, observed by M. PERSON, appears also to indicate a molecular change subsequent to the first freezing. Further, ice, although exhibiting none of the viscous

softness of pitch, has the elasticity and tendency to rend seen in colloids. In the properties last mentioned, ice presents a distant analogy to gum incompletely dried, to glue, or any other firm jelly. Ice further appears to be of the class of adhesive colloids. The redintegration (regelation of FARADAY) of masses of melting ice, when placed in contact, has much of a colloid character. A colloidal view of the plasticity of ice demonstrated in the glacier movement will readily develop itself.

A similar extreme departure from its normal condition appears to be presented by a colloid holding so high a place in its class as albumen. In the so-called blood-crystals of FUNKE, a soft and gelatinous albuminoid body is seen to assume a crystalline contour. Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute?

8. *Osmose.*

Little has been said in the present paper respecting osmose, a subject closely connected with colloidal septa. It now appears to me that the water movement in osmose is an affair of hydration and of dehydration in the substance of the membrane or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic result, otherwise than as it affects the state of hydration of the septum.

Osmose is generally considerable, through membranous and other highly hydrated septa, with the solution of any colloid (gum, for instance) contained in the osmometer. Yet the diffusion outwards of the colloid is always minute, and may sometimes amount to nothing. Indeed, an insoluble colloid, such as gum-tragacanth, placed in powder within the osmometer, was found to indicate the rapid entrance of water to convert the gum into a bulky gelatinous hydrate. Here no outward or double movement is possible.

The degree of hydration of any gelatinous body is much affected by the liquid medium in which it is placed. This is very obvious in fibrin and animal membrane. Placed in pure water, such colloids are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose. The contact of the saline fluid is thus attended by a continuous catalysis of the gelatinous hydrate, by which it is resolved into a lower gelatinous hydrate and free water. The inner surface of the membrane of the osmometer contracts by contact with the saline solution, while the outer surface dilates by contact with pure water. Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose, by equalizing the condition as to

saline matter of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmose, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum.

The substances fibrin, albumen, and animal membrane swell greatly when immersed in water containing minute proportions of acid or of alkali, as is well known. On the other hand, when the proportion of acid or alkali is carried beyond a point peculiar to each substance, contraction of the colloid takes place. Such colloids as have been named acquire the power of combining with an increased proportion of water, and of forming superior gelatinous hydrates, in consequence of contact with dilute acid and alkaline reagents. Even parchment-paper is more elongated in an alkaline solution than in pure water. When so hydrated and dilated, the colloids present an extreme osmotic sensibility. Used as septa, they appear to assume or resign their water of gelatination under influences apparently the most feeble. It is not attempted to explain this varying hydration of colloids with the osmotic effects thence arising. Such phenomena belong to colloidal chemistry, where the prevailing changes in composition appear to be of the kind vaguely described as catalytic. To the future investigation of catalytic affinity, therefore, must we look for the further elucidation of osmose.