



## LXI. On velocity of molecular and chemical reactions in heterogeneous systems

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LXI. *On Velocity of Molecular and Chemical Reactions in Heterogeneous Systems.* By Dr. MEYER WILDERMAN, Ph.D., B.Sc. (Oxon.)\*.

PART I.

[Plates XVII. & XVIII.]

I. *On Velocity of Molecular Reactions in Heterogeneous Systems and the so-called Diffusion Theory.*

§1. IN the report of the British Association, 1896, *Zeitschrift für physikalische Chemie*, 1899, xxx. pp. 348-368, and *Phil. Mag.* July 1901, p. 50, and some other publications, I showed that the velocity of all molecular reactions between two parts of the heterogeneous system, such as transformation of water into ice, ice into water, separation of salt from an oversaturated solution, solution of salt, evaporation of liquids, condensation of vapour, solidification of solutions to solids or to solid solutions, &c., all follow the same law :

$$\frac{dt}{d\tau} = C(t_o - t)(t - t_{ov}) = c\Sigma_{\tau}(t_o - t),$$

i. e. the velocity of reaction is at the time  $\tau$  directly proportional to the remoteness of the system at the time  $\tau$  from the point of equilibrium,  $t_o - t$ , and to the surface of contact of the reacting parts of the heterogeneous system,  $t - t_o^*$ , which is proportional to  $\Sigma_{\tau}$ . Further improvements in the methods employed and the photographing of the reactions showed, however, the necessity of introduction of the constant  $K$ , which I called the "instability constant," i. e.

$$\frac{dt}{d\tau} = C(t_o - t)(t - t_{ov} + K)$$

(see the above papers in the *Zeitsch. für physikalische Chemie* and *Phil. Mag.*)

$$= K(t_o - t) \text{ for constant surface.}$$

The above equation was therefore given by me in a most general way, including the solution and separation of salts, as a particular case only, in a series of publications before Noyes and Whitney (*Zeitsch. phys. Chem.* 1897, xxiii. p. 689), before L. Bruner and Tolloczko (*Zeitsch. phys. Chem.* 1900, xxxv. p. 283), and long before Nernst and E. Brunner (*Zeitsch. phys. Chem.* 1904, xlvii. p. 52), who all use it for the particular case of solutions of salts only. The equation

\* Communicated by the Author.

used by Noyes and Whitney is  $\frac{dt}{d\tau} = C(t_0 - t)$  (they take the surface to remain constant); Bruner and Tolloczko use my equation  $C\Sigma_{\tau}(t_0 - t)$ ; the equation used by Nernst and Brunner is  $\frac{dt}{d\tau} = \frac{D}{\delta}\Sigma(t_0 - t)$ , where  $\frac{D}{\delta}$  are also constants, i. e. the equation of the above authors is identical with the first (less accurate one) of mine. As my papers were published also in the very same *Zeitsch. für phys. Chem.* in which these and other authors \* later published their papers, I must clearly uphold here my priority rights, since all these authors do is to give their own interpretation to my constant. All the more so, since Nernst and E. Brunner, L. Bruner and Tolloczko, give us in an arbitrary manner (with their methods, see §2) for a part of the curve what was established by me before, on careful experiments, for the whole curve; my reactions were photographed and carried out by methods of infinitely greater accuracy and reliability than theirs.

In my general equation the assumption was made that the volume remains the same during the whole time of the reaction. Mr. Drucker also investigated the effect of the volume upon the speed of solution of solids, and found that the speed is indirectly proportional to the volume of the liquid. I wish to add that, from the standpoint of my general equation, this is, at a constant surface of the solid, a self-understood, unavoidable necessity. Because, as the reaction goes on *at the surface of the solid in contact with the liquid*, the amount of substance going into solution is, at a constant surface, at the time  $\tau$  only dependent upon the concentration of the solution, and this amount is according to our conception subsequently distributed by the stirrer, through the *whole volume* of the liquid. If the volume is, for example, twice as large, the increase in its concentration must be twice as slow, i. e. the speed of solution, *as measured from the concentrations of the solution*, will be twice as small. This naturally applies to *all molecular reactions*, of which solution of solids forms only one particular case. But I wish clearly to point out, that *this dependence upon the volume is only an apparent one*, for the reason that we are able only to measure the concentrations of the solution. The *true reaction* takes place only *at the surface of the solid*, and here the phenomenon of solution is independent of the volume of the rest of the solution. Only the surface of contact and the concentration of the solution in contact with the solid are the working factors and come into consideration here.

\* See Karl Drucker (*Zeitsch. für phys. Chem.* 1901, p. 173, and p. 693), who wrongly attributes my equation to Noyes & Whitney.

§2. *On the Method of Investigation.*

- (a) *On the artificial production of solid blocks suitable for investigation in this region. Also on the solids used by Nernst and E. Brunner and others to prove the Diffusion Theory.*

The speed of reaction is directly proportional to the surface of the solid, and it is quite evident that no reliable research at a constant surface is possible, and still less are comparative quantitative experiments possible, so long as we cannot procure a solid, with a sufficiently large surface, which is quite uniform throughout its whole thickness, which can be reproduced every time we want it, which is chemically pure, which is suitable for quick and reliable measurements of concentration, and which represents a reaction free from subsidiary reactions and from other complications. To get all these requirements realized at once is by no means easy. Metals seem to answer the requirements of surface, but, except Pt, Ag, and the liquid mercury, they all cannot be got chemically pure, and insurmountable difficulties are created for correct measurements of the speed of reaction by the interference of local action due to small variations in the impurities. Again, some of the minerals, such as marbles, gypsums, and some other few substances, present the best material for getting suitable blocks for an investigation, but these minerals are seldom chemically pure, few of them are uniformly the same everywhere, and still fewer of them are substances which are suitable for a rapid and reliable titration. The solid substances, which are most suitable and desirable for research, are for this reason those which are artificially prepared in the laboratory, but the difficulty is that these substances are almost without exception obtainable either in small crystals or powders, &c., while we require for the investigation blocks with large surfaces. How Nernst and Brunner try to overcome the difficulties here is best to be seen from the *two principal substances of their investigation*, upon which they tried to build up experimentally their diffusion theory, namely, benzoic acid and "magnesium hydroxide."

About the first we read that, to create a block, they "melted the benzoic acid in a test-tube, poured it into a porcelain cover of a crucible, 5 cm. diameter. On cooling the same separated from the cover, and they fixed it in again with shellac; the surface was then rubbed down with a knife and sandpaper. The surface still clearly retained its crystalline structure. This cake still contained scratches at the rim, and they filled these now up with paraffin." With

this method we always get air-tubes and spaces enclosed in the acid, and this cannot be avoided even by removing the air from the liquid acid in vacuum or by very slow cooling of the acid in a double-walled air-bath. The substance does not crystallise as one uniform mass. Photo (1) (Pl. XVII.) gives the surface of the block of benzoic acid as soon as the top thin film is removed during the reaction. There is no need for me to add that such a block cannot possibly be suitable for any comparative quantitative measurements. This process of melting can naturally find only a limited application, cannot e. g. be applied to inorganic substances requisite for the research. From among the last Nernst and Brunner chose for their research "magnesium hydroxide." We are told that they "took advantage of the property of calcined  $\text{MgO}$  mixed with water, to dry to a thick mass and to become hard." As a matter of fact, ordinary analysis shows that the  $\text{Mg}(\text{OH})_2$  always contains, under their conditions of work, very much carbonate, and we find that  $\text{Mg}(\text{OH})_2$  cannot stick together without it. I find that if we mix  $\text{MgO}$  with water and let it dry in an ebonite lid with vertical rims over  $\text{CaCl}_2$  in vacuum, so as to prevent absorption of  $\text{CO}_2$  by the  $\text{MgO}$  or  $\text{Mg}(\text{OH})_2$ , we get the block as in photo (2); if we dry pure  $\text{Mg}(\text{OH})_2$  mixed with  $\text{H}_2\text{O}$  over  $\text{CaCl}_2$  in vacuum, we get a block as in photo (3) (in which one part of the surface has been polished). Both of them show a great contraction on drying, contain numerous air-holes, before and after their surfaces are cut away with a razor, contain big cracks across, and *fall to pieces as soon as they come into contact with water*, as is to be seen from photo (4), in which the breaking up of  $\text{Mg}(\text{OH})_2$  under water is shown. If we mix  $\text{MgO}$  with 10 per cent. gum-arabicum, fill with it the ebonite lid and dry over  $\text{CaCl}_2$ , we get a disk, which sticks together as in photo (5), which at the same time shows the enormous contraction of the mixture; but as soon as we bring this disk in contact with water it breaks up to pieces as is seen from photo (6). *There is no possible way of getting a block of pure  $\text{Mg}(\text{OH})_2$  which could be brought into contact with water without falling at once to pieces!* I lost quite a considerable time in my attempts to produce such a block, but entirely failed, though I was with my method quite successful in a great number of other cases, namely: I compressed the mixture of  $\text{MgO}$  and  $\text{H}_2\text{O}$  directly after they were mixed, and the mixture  $\text{MgO}$  and  $\text{H}_2\text{O}$  after standing in a closed up vessel for about two weeks; then I compressed dry  $\text{Mg}(\text{OH})_2$ , as well as  $\text{Mg}(\text{OH})_2$  mixed with water in moulds, under a pressure of several thousand atmospheres; and though I succeeded with a conical piston in

this way in getting beautiful uniform blocks free from air-holes and cracks and the blocks seemed quite excellent, yet when the same were brought into contact with  $H_2O$  they immediately fell to pieces. The solids on coming into contact with  $H_2O$  expand again to such a degree that they fall in no time to pieces. On the contrary,  $MgCO_3$  shows no such property, but gives excellent blocks which stand water very well. Photo 7 gives a block of  $MgCO_3$  compressed under 2500 atmospheres, in which the impression of the piston in the centre is still to be seen, and then allowed to remain under water. Photo 8 shows a block of  $MgCO_3$ , which was compressed in an ebonite lid in a special arrangement by means of a screw, after it was first mixed with water to a paste, and then allowed to remain under water. Photo 9 shows  $MgCO_3$  as got in an ebonite lid after the same was mixed with water to a paste and dried, and then the lid and the dry disk were allowed to remain for a long time under a dilute  $HCl$  solution; for they show at the same time that water does not break up the same. Nernst and Brunner give us, on p. 79 of their paper, a series of apparent reasons why their theory does not require to hold good in case of Oxides, Carbonates, &c. which do not agree with their theory, and why this one substance,  $Mg(OH)_2$ , is to be of all substances the substance to be taken for the test of their theory, and we are invited to accept their theory on the basis of " $Mg(OH)_2$ ," alone. Now we find that Nernst and Brunner's so-called  $Mg(OH)_2$  is nothing but a mixture of oxide, hydroxide, and carbonate of magnesia. Not contented with this, since their "magnesium hydroxide" blocks do not hold sufficiently well, they mix it with gum arabicum, which, as known, is the potassium and calcium salt of "Arabinsäure" or "Gumisäure," and so their mixture contains besides also the Magnesium salt of "Arabinsäure." As the conditions of preparation of their blocks were never identical in respect of time, quantity of gum arabicum used, &c., the composition of their mixture was never the same. And with such mixtures Nernst and Brunner give us their quantitative experiments upon speed of reaction, their comparative experiments, their principal experimental proofs of the diffusion theory!

The method I use for getting from a substance chemically pure and suitable for the research, blocks of any desired thickness, of the same uniformity through the whole of its mass, free from air and cracks, and enabling us to use the same blocks for a series of experiments for comparative experiments and to reproduce the same, consists in their *artificial preparation under the very high pressure of several*

thousand atmospheres. The substance is brought into a steel ring of an internal diameter=51 mm., external diameter=127 mm., placed in the steel base (Pl. XVIII.), and is compressed here under several thousand atmospheres with the piston, which is 51 mm. diameter and 12 cm. long. The diameter of the piston is 51 mm., or very nearly 2 inches. The diameter of the ram of the hydraulic press is 10 inches, the ram is compressed to 75 or 100 atmospheres on the gauge, thus producing a pressure on the piston and the substance of  $75 \times 25 = 1875$ , or  $100 \times 25 = 2500$  atmospheres per square inch. The maximum compression of the solid usually takes place much below these pressures, already at about 1000 to 1400 atmospheres, and often below this. The substances are left under the above pressure usually for 16 to 24 hours, when the pressure is generally released; the base is then removed from the ring containing the compressed block of the substance, and the latter is pushed out from the ring (the pressure usually required is 70 to 350 atmospheres per square inch), with the piston, into a steel ring of a larger diameter placed below the ring, it being arranged that the disk should fall on a piece of soft felt below. The ring, base, and piston must be perfectly polished so as to get a perfect uninjured block. The ring itself was a little modified, made internally a little conical (a fraction of a mm. suffices) from top to bottom, in order that the block of substance shall leave the ring at once, as soon as it is moved by the piston, instead of its requiring to be pressed through the ring through its whole thickness. In such a way we get beautiful disks, with perfect surfaces, free from any air-holes, cracks, &c., requiring no admixtures in order to make the substance stick well together, with perfect uniformity through their whole thickness; whether the substance is crystalline or amorphous, an organic or inorganic solid, a compound or an element (S, C, metal powders, &c.), it is crushed to a uniform body; one disk 1.5 to 2 cm. thick is quite enough for carrying out a long series of comparative experiments, and we are able to *polish* and to rectify over and over again the surface of the same block for the same experiment, because it must be a strict rule to allow the solid to corrode during solution only as little as possible and to repolish the same as often as is practicable. We can keep the dissolving surface of the solid always at nearly the same height in the liquid, by fixing the blocks to ebonite disks of different thicknesses. Photo 10 (Pl. XVII.) shows a disk of benzoic acid before treatment; photo 10 A shows the block of benzoic acid after solution in water

during two hours. The surface is still excellent. I find, however, that while some of them (such as benzoic acid, most organic substances,  $\text{MgCO}_3$ , &c.) remain on placing the disk into water (under stirring) in perfect condition; others, such as  $\text{Mg}(\text{OH})_2$ ,  $\text{Fe}_2(\text{OH})_6$ , &c., break up mechanically at once, since when the disks are brought into contact with water they suffer too great an expansion. All the same, the above method now opens the way for a true and reliable investigation in this region, putting at our disposal an exceedingly great number of chemically pure substances, suitable and desirable for this research, while before we practically had none, and we were dependent upon minerals, which are seldom perfectly pure. Care was taken to use only the purest chemicals for this research, and the firm of Merck prepared the same for me with special care and under special instructions; and where minerals had for special reasons to be used, only the best and purest specimens procurable were employed.

(b) *On the Arrangement of Constant Speeds of Stirrer.*

If we have a super-cooled or a super-saturated solution, so that very fine particles of ice or salt separate from the whole of the liquid, and through the whole of the liquid, then, by the use of an effective stirrer creating currents in all directions, a uniform state of the whole system during the reaction can be obtained, as can be seen from the photographic curves in my paper (*Zeitschr. für phys. Chemie*, 1899) giving the speed of these reactions. When, however, we have a solid piece, salt or ice in a liquid mass, so that the contact between the solid and the liquid is only local, and reduced to a comparatively very small surface of contact, it is extremely difficult to get the liquid uniform through the whole mass, as already mentioned in the above paper. Nernst and Brunner use an air-motor, which is known to be inconstant, and the variations of its speed were, according to Nernst and Brunner, as much as 10, 15, sometimes even 30 per cent. The direct experiments with pieces of rubber, of the same specific gravity as water, showed me, that if we keep the solid fixed at the bottom and move the liquid by the stirrer, the number of revolutions which the liquid makes past the solid is not directly proportional to the number of revolutions of the stirrer, but is considerably smaller. The liquid is also never equally moved in all its layers, as is to be seen from the fact, that a cone is formed in it with the apex (smallest speed) on the stem of the stirrer, and the base (biggest speed) above it, which is the higher the quicker the



stirring. For this reason I preferred to fix the solid disk, as Drucker did, to the stirrer itself, so as to make the number of revolutions of the same equal to the number of revolutions of the stirrer, and I placed the investigated disk, always of nearly the same thickness, between the two stirring plates of the double stirrer (see Pl. XVIII. fig. 1), so that, besides moving the block, the liquid was stirred above and below it. The double stirrer is made of ebonite, which is affected neither by acids nor by alkalis. The two stirrers are connected with ebonite rods forming a cage for the block of substance to be investigated. The last is covered with paraffin of a high melting-point at all surfaces except the top, a rubber ring is put on it and prevents it from being damaged after it is fixed between the rods. Though apparently little work had to be done, I found that to get constant speeds I had to use a powerful electromotor ( $\frac{1}{8}$  H.P.) to prevent its heating up, and that constant voltage as well as a regulation of the speed had to be provided for. Both the field and armature were supplied with a series of resistances and with continuous spiral resistance when required. In all experiments I usually employed 200 volts thrown upon the common terminals connecting the field and armature. For the variation of speed within very great limits, I used in the first instance different sets of wheels of different diameter, which could be changed as desired, and the wheels were driven by a flexible steel spiral which could be applied to all of them by means of the arrangements seen in fig. 2 (Pl. XVIII.). To get the variations of speed in still greater limits the volts thrown upon the field and armature were different, use being made of accumulators. I was thus able to change *the speed of the stirrer* from about 1 revolution per minute to about 500 and to keep the speed practically constant. The best results were obtained for speeds of about 100 to 150 revolutions per minute, when the variation after hours did not amount to 1 revolution per minute, and which I adopted for my investigations. As the effective stirring depends more upon the construction of the part of the stirrer in the liquid than upon the number of revolutions, I reduced the last by improvements in the first, and this enabled me to get with an ordinary one-fifth second stop-watch, easy, reliable counting of the number of revolutions of the stirrer, which usually were kept at about 130 per minute. The speed-indicator was used only for speeds above 250 revolutions per minute. I found that no permanent speed could be got for longer periods when ordinary cords are used, because as these stretch under work the speed changes also. A thin steel wire was for this reason

wound to a spiral on a lathe supplied with small hooks and used instead of cords. This has a wonderful flexibility, gives an excellent grip, and allows good adjustment, if required, by cutting off a few rings or by forcible stretching of a few of them, and gives always the same constant speed. By an arrangement, as seen at C of the photograph (fig. 2), the same spiral can be used for the different pulleys.

(c) *Further details of the Method* (see fig. 1, Pl. XVIII.).

The beaker with 1500 c.c. of the liquid was kept in a bath of a constant temperature, a 1/10 degree thermometer having been immersed in the liquid, with its bulb close to the solid block; the effect of stirring upon the temperature of the liquid seemed to be but small, but had to be adjusted sometimes by the temperature of the outer bath, which was continuously stirred by the second stirrer driven by a pulley from the first. In case of substances of very small solubility, such as the gypsums, which do not admit sensitive titration, especially since very dilute solutions had to be investigated here, the method of electric conductivity after Kohlrausch had to be used. Two platinum electrodes (see fig. 1) were fixed in the ebonite lid of the beaker, for making these measurements, the electrodes coming into the middle between the two stirrers. A series of known concentrations of the same  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ , which later on had to be investigated as a solid disk, was prepared, and small intervals of concentrations were investigated with a series of resistances, and so a scale was got for them on the bridge, for the same temperature and speed of stirrer, which subsequently was used when the solution of the disk was investigated. The water used in these experiments was the same. The volume of the solution remained for the whole series the same, namely 1500 c.c.

In case of other substances, such as benzoic acid, or of mixtures, the speed of reaction was measured by taking out samples and titrating the same. The samples were drawn off with a 10 c.c. pipette through the glass tube fixed in the ebonite lid of the beaker, always from the same place between the two stirrers; after the pipette was first twice filled with the solution, and the solution let back into the beaker, the final filling of the pipette for titration was carried through within the last 5 to 10 seconds of the minute.

Very great and quite exceptional precautions had to be taken with the titrations of this acid. I titrated the benzoic acid with a .088 normal baryta, back titrating the same with a .022 normal benzoic acid. The baryta was added from a

thin well-running tube, 1 mm. of which indicated .01 c.c., and I read the tube with a lens to about .2 mm. or to .002 c.c., and the excess of baryta had to be titrated with the more dilute .022 normal benzoic acid so that the last drop should not affect the result much, and this operation had to be repeated twice to further reduce the reading-error. As 50 c.c. of ordinary distilled water contain already an amount of  $\text{CO}_2$  corresponding to 0.3–0.4 c.c. of a .022 normal solution, and at least 50 c.c. of water are required for washing out the sample bottles and for titration, the  $\text{CO}_2$  of the water alone is enough to cause an error of 10, 20, or 30 per cent. in the total difference measured. Therefore the water in the wash-bottle had to be freed from  $\text{CO}_2$  by boiling and then protected by a tube of soda-lime to prevent its contamination with  $\text{CO}_2$  from the air or through our blowing, the total amount of wash-water used for each titration had to be kept the same in each experiment, and the water itself had to be titrated and the samples freed from  $\text{CO}_2$  before titration by boiling. As rapid stirring mixes energetically the solution with the air containing  $\text{CO}_2$ , and the experiment lasts for several hours, the water in the beaker had to be protected against contamination with  $\text{CO}_2$ , as shown in fig. 1 (Pl. XVIII.). The glass cylinder was closed up with a thick ebonite piece and sealed up with Crooks' cement between glass and ebonite. In the ebonite piece a circle was eccentrically cut out to allow the blades of the stirrer mixing the solution to pass through it into the beaker. A deep circular groove 17 mm. wide was cut out in the remaining ring, concentric with the cut-out circle; to the stem of the stirrer a circular lid with a deep projecting circular rib 7 mm. thick, cut out of one piece of ebonite, was fixed, and the stirrer was fixed so that the circular rib entered deep into the groove, leaving 5 mm. free space all round without touching the circular ring at the bottom; this groove was filled with distilled water sufficient to form a secure seal with the rotating circular rib of the lid of the stirrer, and the stirrer was thus always kept in the same position in the beaker. None of these very necessary precautions in the titration were taken by Nernst and Brunner, Bruner and Tolloczko, and others.

All the above precautions in the preparation of the blocks, in the arrangement of constant speeds, in the titration &c., I had to take before I was able to get the constants, as I give them in this paper, which are considerably worse than those supplied by Nernst and Brunner and others. It is true, Nernst and Brunner tell us, that "the greater variations of A were omitted if they differed much from the rest," but

this is a very strange thing to do, when we are asked to take their results as quantitative measurements and to give them all the credence we have to give the quantitative results, instead of leaving it to the reader to see for himself what value those A's really possess. Especially is this regrettable when we are invited to accept a theory on the basis of conclusions which are mostly based upon differences in the values of A, which, it is quite evident, are often smaller than the experimental error of the method itself.

§ 3. *The Theory of Molecular Reaction, including the Solution of Solids in a Solvent. Also on the Diffusion Theory.*

In the first place let me state again, in somewhat greater detail, the content of my equation as far as it concerns the solution of salts, before I pass to the consideration of its content according to the diffusion theory. I assume that every substance has a solution pressure, which causes the solid to pass into the solvent, whenever brought into contact with the same; that this goes on until the solution becomes saturated, so that the solution pressure of the solid is kept in equilibrium by the counter osmotic pressure of the saturated solution, which (leaving out of consideration galvanic cells where we have to deal with electrostatic forces) at equilibrium are equal; that in case of an unsaturated solution, before equilibrium is reached, the solution pressure of the solid is greater than the counter osmotic pressure of the solution, and the substance of the solid is still driven into the solution by a force, which is directly proportional to the difference of the existing solution pressure and the counter osmotic pressure, or to the difference of the osmotic pressure of the solution at equilibrium (which is equal to the solution pressure of the solid) and the osmotic pressure of the solution at the time  $\tau$ , or also directly proportional to the difference of the concentration of the solution at equilibrium and its concentration at the time  $\tau$ , since the osmotic pressure is directly proportional to the concentration. Similarly, in case of an over-saturated solution, the solution pressure of the solid is smaller than the counter osmotic pressure of the solution, and the substance in solution is driven into the solid by a force, which is directly proportional to the difference of the existing osmotic pressure of the solution and the solution pressure of the solid (or osmotic pressure of the solution at equilibrium). The speed with which the solid passes into the solution or from the solution into the solid, I therefore take to be directly proportional to the driving force, and the number of molecules passing from the solid

into the solution, and *vice versa*, is evidently the greater, the larger the surface from which they pass into the solution, or the larger the surface of contact of the solid and liquid, because the reaction goes on all along at every point of the solid in contact with the solution. Hence my equation

$$\frac{dt}{d\tau} = C\Sigma\tau(t_0 - t).$$

These extremely simple and clear conceptions about the cause of the shape of my *general* equation, Noyes and Whitney, Bruner and Tolloczko, Nernst and Brunner tried to replace, singling out a special case of solution of solids from all the rest of the reactions, by other conceptions. Let us now see what these conceptions are, how they simplify matters purely theoretically, and how far they are confirmed by true experiments. Noyes and Whitney, dealing with solubility of salts, write :—" We can imagine that the solid substance is always surrounded with an infinitely thin layer of a saturated solution, and that the process consists in a diffusion from this layer to the rest of the solution, which is kept by stirring homogeneous. Then according to the known laws of diffusion the speed of reaction will be directly proportional to the differences of concentration of the saturated solution

and that of the solution, i. e.,  $\frac{dx}{d\tau} = A'(C' - C).$ " This view

was adopted first by L. Bruner and Tolloczko, who went a step further, and assumed that the velocity constant is nothing else but the *diffusion constant*, and later on they introduce also the idea of a finite layer  $\delta$  &c. The views of these investigators were later on fully adopted and followed by Nernst and Brunner, who instead of  $D$  use Bruner and

Tolloczko's  $\frac{D}{\delta}$ , and make a step further still, by trying to

explain the equations of Boguski, Spring, Haber, and Lorenz, giving speed of chemical reactions in heterogeneous systems, as diffusion equations also. With the last we shall deal in detail later on. In this first publication I shall restrict myself principally to molecular reactions only.

Returning to the work of Bruner and Tolloczko, as  $\frac{D}{\delta}$

had to be made equal to the velocity constant, they soon got the result that if the diffusion constants were not to upset the theory,  $\delta$  or the layer of Noyes and Whitney cannot be taken to be "infinitely thin," but must have a measurable thickness. In this, as well as in my identical equation,

every letter denotes the same thing, but  $C'$  is in my conception the concentration of saturation which the system is striving to reach, owing to *the solution in contact with the solid being unsaturated*,  $C' - C$  being directly proportional to the force driving it to the state of equilibrium, while Noyes and Whitney assume that the concentration of saturation is *always* present near the solid salt, while the concentration of the rest of the solution is entirely another one. To make, however, this assumption of constant saturation at a surface possible, Bruner and Tolloczko had further to introduce the conception of infinite speed of reaction at the surface of the solid, while following them Nernst *further introduced also the idea of "infinitely great forces acting at the surface,"* since without such assumptions the above explanation cannot, evidently, be upheld; and then to suit the idea of the  $\delta$  a second hypothesis had to be made, by Tolloczko and Bruner, also adopted by Nernst and Brunner, *that the solution cannot be mixed up to the solid itself, but the mixing stops at a distance from the solid.* Since without this mysterious property we get from  $\frac{D}{\delta} = K$ , that if  $\delta$  were according to

Noyes and Whitney infinitely small,  $D$ , or the diffusion constants as calculated from this equation, would only prove the *falsity* of the theory. This is how the original hypothesis of Noyes and Whitney, which seemed to be very simple, grew up into a conglomerate of assumptions. I shall now test, step by step, what this theory and all its assumptions are really worth.

(a) Let us now first see, how Noyes and Brunner support their hypothesis, following in all essential features the ideas given by Bruner and Tolloczko. About the first Noyes writes: "At the surface of contact of two phases (or parts) of the heterogeneous system equilibrium is extremely quickly established." "This," in Nernst's opinion, "follows already *a priori* theoretically as a necessity, because otherwise noticeable difference of the chemical potential would exist at the separating surface, *i. e.*, at infinitely near points, which evidently would lead to infinitely great forces and velocities of reaction. This, however, means nothing else than that in the immediate vicinity of the two surfaces the equilibrium is established with infinite speed. If we assume what is more nearly true, that the surface of separation is not a mathematically sharp plane, we have still to deal with dimensions of the order of the spheres of action of molecular forces, and if we can no longer speak of infinitely great velocities of reaction, still they must be of a very great order, which practically

amounts to the same." This says in so many words what Bruner and Tolloczko told us before (*Zeitsch. für anorg. Chemie*, 1901, p. 328) that "the saturated solution at the surface of the solid is formed instantaneously." Now, this fundamental assumption of Nernst is quite wrong, as can be seen from the following: when we mix two liquids, say in equal parts, and a reaction goes on between them, we have, in the first instance, a certain difference of chemical potentials acting between the molecules in the system, since otherwise no reaction would go on; secondly, the acting molecules can only be removed from one another by double the distance of the spheres of the molecules themselves. According to Nernst all such reactions, such as solution of anilin in acetic acid, &c. ought to go on with an infinitely great speed in the homogeneous system.

Now, a very great number of reactions in *organic* chemistry are carried out by mixing two liquids together in the above manner, and all organic reactions, with few exceptions, belong to the *slow, often to the extremely slow*, not to the instantaneous, reactions. On the other hand, many reactions, *even in very dilute solutions*, go on almost instantaneously, though the reacting molecules in the solution are very considerably removed from one another. This is so well known to every chemist, that I need not dwell upon it any longer to show the utter futility of the above assumption. Nernst's assumption that "infinitely great forces" are acting between different parts of the heterogeneous system, when it is not in equilibrium, is therefore absolutely unsupported by daily experience. Here we have to deal with ordinary solution of solid salts, where no electrostatic forces come into play, and consequently where the osmotic pressure of the solution at equilibrium equals the total solution pressure of the solid. We shall see later on that the forces coming into consideration here for the different kinds of reaction are not "infinitely great," but of measurable, and often of very small values indeed. So far I much prefer the less detailed views of Bruner and Tolloczko, who speak of "instantaneous reactions," without binding themselves to "infinitely great forces."

(b) I now turn my attention to Nernst and Brunner's support of the hypothesis that at the surface of the solid a saturated solution is formed, which is only capable of passing into the region of the action of the stirrer by diffusion. My question is, where is the proof for the same? What is there to prevent the liquids from passing to the very solid? In my opinion neither their deduction of the equation on p. 63, nor

their own experiments on p. 62, giving the variation of the constant  $A$  with temperature—the only experiments which ought to have brought some support to their assumptions—tend to support their views, but on the contrary disprove the same. The equations (3) and (4) of Nernst and Brunner are not deduced according to proved conceptions, but are nothing else than a graphical adaptation to the above mentioned conceptions, which became unavoidable, to make them artificially fit into a known equation. But as Nernst and Brunner admit, that it is impossible to assume that there should be on the one hand a layer of complete rest, where the equalization takes place only by diffusion, and on the other hand a layer outside the same, where equalization takes place only by convection caused by the stirring,—it follows from this that even if Bruner and Tolloczko's, Nernst and Brunner's assumption of two layers be made, a gradual transformation of the second layer into the first under a gradual diminution of convection must take place; the straight line  $AB$  is therefore arbitrary, and must be replaced by a curve, of an unknown equation, in all probability by a logarithmic curve, and the value  $D$  is not  $CB$ , but a value which may be considerably greater; and the whole deduction of equation 4, that is of my equation, from the diffusion conceptions is arbitrary: the strict existence of my equation is, in my opinion, for this reason, if anything, a proof that their conceptions are wrong, not that they are right. Moreover, for all we know, there is no reason whatever to assume, that even if a saturated solution be formed at the surface of the solid, this should not form only an infinitely thin film, as originally assumed by Noyes and Whitney, that this film should not be of the size of the sphere of a molecule, that is of the dimensions  $10^{-15}$  mm. instead of Nernst's 0.02 mm., and that the liquid from outside this film should not enter it, *i. e.* should not reach the very surface of the solid itself diluting the same. Indeed, in case of solidification of water in a U-tube, *i. e. even without stirring*, the water reaches the ice or the ice the water to a proximity of about  $10^{-15}$  mm.—why should this not be the case with the liquid in contact with the solid especially when it is stirred? The very value calculated by Nernst and Brunner, by the use of diffusion constants, for " $\delta$ " as being equal to 0.02 mm., which seems to them "as very probable," seems to me on the contrary *very improbable*, in view of the results obtained for solidification of water. With these much more natural assumptions for  $\delta$ , &c., their deduction of equation (4) would again cease to hold good, and *the actual values of the diffusion*



constants would present, in my opinion, a striking proof that the application of the above diffusion conceptions here is entirely out of place.

(c) Not only is there no proof for their values of  $\delta$ , but the assumption of the existence of the layer at all is extremely unnatural, and is evidently wrong. My equation holds good also for evaporation of solids and liquids, where the diffusion of the gas into the whole gaseous space is instantaneous, and where there is nothing to keep the gas saturated at the surface of the solid, and in the rest of the space unsaturated, where there is nothing to prevent the moving molecules from reaching the very solid on its way. If this is so for the gaseous space, where is the need and the force of these most unnatural assumptions as regards the solution?

Note also, that the laws of Boyle and Gay Lussac and the whole kinetic theory were deduced without the assumption of the existence of such a layer and presuppose that the gas can reach the very solid. Note, that van't Hoff's laws of Boyle and Gay Lussac in solutions presuppose that the substance in solution behaves in a similar manner to the substance in the gaseous space. All this is, in my opinion, a solid proof against the above fundamental assumptions of the diffusion theory.

(d) I now pass to an important experimental test of the diffusion theory, and this is the influence of temperature upon the speed of reaction. If the velocity of reaction is, as we are told, regulated by diffusion, then  $A$  must vary with temperature as the diffusion constant  $F$  does. This, in my opinion, would be a serious proof for the diffusion theory if it proved to hold good, since it would have represented a quantitative test of the theory instead of remaining a mere assertion with no proof whatever. Now Nernst and Brunner investigated the speed of solution of benzoic acid at different temperatures. They find  $A$  at  $20^\circ = 2.30$ , at  $30^\circ = 1.5 \times 2.30$ , i. e. an increase of 5 per cent. per degree, while it ought to have been only 2.5 per cent. according to the variation of the diffusion constant. One would say, this is a most decisive proof against their theory; but there is always, according to Nernst and Brunner, a way out of the difficulty. It is enough for this to assume that the adhesion and with it the thickness of the layer  $\delta$ , become smaller with temperature. The sole effect of the introduction of this layer  $\delta$  is to prove something without proof. To this  $\delta$  all sorts of properties are now attributed, without, however, the least evidence being produced. The diffusion-constant  $F$  is a clear, known physical

constant and can be tested in an independent manner, while  $\delta$  presents no such embarrassing feature, as it *cannot be tested in any independent way*. It will be shown later on that the apparent proof of " $\delta$ " consisting in *the would-be fact, according to Nernst and Brunner, that the speed of solution of magnesium hydroxide, magnesium metal in benzoic acid, is the same as the speed of solution of benzoic acid itself, does not exist and is based only upon quite arbitrary experiments*. About this  $\delta$  we read:—"This  $\delta$  should depend only upon speed of stirring and temperature and not upon the nature of the substance in solution;" but a little further again "this, however, is not the case, because this layer has a resting surface on one side and moving on the other, and the effect of the last becomes the greater the more we are removed in this layer from the resting surface," "nor is it independent of the value F itself" (*i. e.* it depends upon the nature of the substance), "nor is it the same at all places of the surface of the solid," and lastly, "whether  $\delta$  depends only upon temperature and speed of stirring it is difficult to say in advance." In short we know absolutely *nothing about this very  $\delta$ , about which we ought to know everything and upon the value and existence of which the whole theory depends*.

It is quite evident that until some independent way be used to determine the value  $\delta$  in each case, so as to show that my velocity-constant A is, in each case, really composed of the two known values F and  $\delta$ , *not an atom of evidence* can be brought for the existence of such a relationship. All Nernst and Brunner do is to divide F by my constant A, so as to get the value which  $\delta$  *ought* to have, in order that  $\frac{F}{\delta}$  *should* be equal to A which is found in the experiment, as required by their theory, while what *we* wish to know, *require* to know, is, *does  $\delta$  really possess such a value, and does it exist at all?*

I now give here a very careful investigation of the *influence of temperature upon the velocity-constant*, carried through with the same benzoic acid which Nernst and Brunner investigated, and for a series of temperatures between 1° C. and 60° C.

In the following table—

$b'$  gives the number of cc. Baryta requisite for neutralization of 10 cc. of the benzoic acid in solution.

$C_1$  gives the concentration of benzoic acid in solution at the time  $\tau$ , if the concentration of the benzoic acid solution saturated at 17°·5 C. is taken as unit and 10 cc. are put equal to 10.

$v$  is the volume of the solution at the time  $\tau$ .

$C$  is the concentration of the benzoic acid at the given temperature, expressed in unit concentrations of the benzoic acid saturated at 17°·5 C., which we denote with letter ( $a$ ).

$A$  is  $\frac{v}{d\tau} \ln \frac{C-C_1}{C-C_2}$  or the *velocity constant* of the reaction of solution of benzoic acid.

TABLE I.

*Influence of Temperature upon the Velocity Constant of Molecular Reactions at different Temperatures.* (Speed of solution of benzoic acid in water at 60° C., 40° C., 31° C., 17°·5 C., 1°·5 C.)

No.	$b'$ .	$C_1$ .	$v$ .	$C - C_1$ .	$d\tau$ .	$A$ .	
<i>Speed of solution of benzoic acid in water at 60° C.</i>							
1 ...	0·843	3·338	1490	41·862	10	8·797	14th May, 1907.
2 ...	1·449	5·738	1480	39·462	10	9·327	$T=333^\circ$ .
3 ...	2·058	8·150	1470	37·050	10	10·610	$C$ at equilibrium at 60° C.
4 ...	2·711	10·73	1460	34·47	10	9·487	=1·2132 gr. in 100 cc. of
5 ...	3·259	12·90	1450	32·30	10	9·947	water; <i>i. e.</i> 10 cc. of the
6 ...	3·798	15·04	1440	30·16	10	10·340	saturated solution = 45·2 cc.
7 ...	4·325	17·13		28·07			of ( $a$ ).
Average ...							$n=130$ rev. per minute.
							Corr. for water = 0·05 cc.
							Pipette = 10 cc.
<i>Speed of solution of benzoic acid in water at 40° C.</i>							
1 ...	0·428	1·695	1470	18·985	42	5·089	21st May, 1907.
2 ...	1·077	4·265	1450	16·415	22	5·775	$T=313^\circ$ .
3 ..	1·425	5·642	1440	15·038	30	5·543	$C$ at equilibrium at 40° C.
4 ...	1·839	7·282	1430	13·398	31	5·883	=0·5551 gr. in 100 cc. of
5 ...	2·244	8·886	1420	11·794	30	5·819	water; <i>i. e.</i> 10 cc. of the
6 ...	2·588	10·250		10·430			sat. sol. = 20·68 cc. of ( $a$ ).
Average ...							$n=130$ rev. per minute.
							Corr. for water = 0·03 cc.
							Pipette = 10 cc.

TABLE I. (continued).

No.	$b'$ .	$C_1$ .	$v$ .	$C-C_1$ .	$d\tau$ .	A.	
<i>Speed of solution of benzoic acid in water at 31° C.</i>							
1 ...	0.656	2.598	1500	13.222	19	4.826	10th May, 1907. $T=30.4^\circ$ . C at equilibrium at 31° C. $=0.4247$ gr. in 100 cc. of water; <i>i. e.</i> 10 cc. of the sat. sol. = 15.82 cc. of (a). $n=130$ rev. per minute. Correction for water = 0.045 cc. Pipette = 10 cc.
2 ...	0.854	3.382	1490	12.438	20	4.748	
3 ...	1.048	4.150	1480	11.670	30	4.453	
4 ...	1.302	5.157	1470	10.663	25	4.819	
5 ...	1.514	5.996	1460	9.824	33	4.806	
6 ...	1.744	6.907	1450	8.913	39	4.787	
7 ...	2.016	7.984	1440	7.836	60	4.037	
8 ...	2.322	9.197	1430	6.623	69	4.214	
9 ...	2.630	10.415		5.403			
Average ...						<u>4.524</u>	
<i>Speed of solution of benzoic acid in water at 17.5° C.</i>							
1 ...	.05	.2154	1480	9.7846	6	3.168	7th May, 1907. $T=29.5^\circ$ . C at equilibrium at 17.5° C. $=0.2684$ gr. in 100 cc. of water; <i>i. e.</i> 10 cc. of the sat. sol. = 10 cc. of (a). $n=120$ rev. per minute. Volume of pipette = 9.19 cc.
2 ...	.079	.3404	1465	9.6596	25.5	2.782	
3 ...	.185	.7971	1445	9.2029	46.5	2.31	
4 ...	.3425	1.475	1430	8.525	39.75	2.568	
5 ...	.4785	2.062	1420	7.938	31.5	2.254	
6 ...	.5685	2.449	1410	7.551	23.5	3.325	
7 ...	.663	2.856		7.144			
8 ...	.593	2.555	1490	7.445	18.5	2.482	
9 ...	.643	2.770	1475	7.230	66.5	2.503	
10 ...	.824	3.55	1460	6.45	30.5	3.088	
11 ...	.9175	3.953	1445	6.047	59.0	2.395	
12 ...	1.048	4.516	1430	5.484	24.5	2.191	
13 ...	1.095	4.718		5.282			
14 ...	1.078	4.645	1490	5.355	36.5	2.793	
15 ...	1.16	4.999	1480	5.001	38.0	2.351	
16 ...	1.228	5.292		4.708			
17 ...	1.550	6.679	1485	3.321	162.0	3.387	
18 ...	1.788	7.705	1465	2.295	157.5	2.533	
19 ...	1.915	8.252		1.748			
Average ...						<u>2.676</u>	

No.	$b'$	$C_1$	$v$	$C-C_1$	$dr$	$A$	
<i>Speed of solution of benzoic acid in water at 1°·5 C.</i>							
1 ...	·011	·0436	1400	6·2494	23·75	1·326	9th May, 1907. $T=274^{\circ}\cdot 5$ . $C$ at equilibrium at $1^{\circ}\cdot 5$ C. $=0\cdot 1689$ gr. in 100 cc. of water; i. e. 10 cc. of the sat. sol. = $6\cdot 293$ cc. of (a). $n=129$ rev. per minute. Correction for water = $0\cdot 045$ cc. Volume of pipette = 10 cc.
2 ...	·044	·1742	1480	6·1188	19·25	1·558	
3 ...	·075	·2970	1470	5·996	30·0	1·881	
4 ...	·132	·5228	1460	5·7702	50·0	1·627	
5 ...	·211	·8356	1450	5·4574	58·0	1·377	
6 ...	·285	1·128	1440	5·1650	60·0	2·218	
7 ...	·398	1·584	1430	4·709	45·0	1·225	
8 ...	·445	1·762	1430	4·531	40·0	1·487	
9 ...	·492	1·948	1430	4·345			
Average ...						<u>1·587</u>	

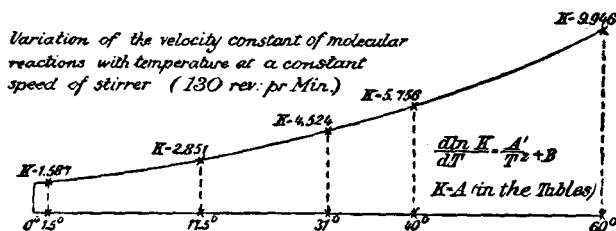


Diagram 1

*Influence of Temperature upon the Velocity Constant A of Molecular Reactions.*

We find

$$\frac{d \ln K}{dt} = \frac{A'}{T^2} + B; \text{ if } B=0, \frac{d \ln K}{dT} = \frac{A'}{T^2}$$

and

$$\ln K = -\frac{A'}{T} + \text{const.} \quad \ln K_{T_0} - \ln K_{T_1} = A' \left( \frac{T_0 - T_1}{T_0 T_1} \right)$$

$t =$	$1^{\circ}\cdot 5$	$17^{\circ}\cdot 5$	$31^{\circ}$	$40^{\circ}$	$60^{\circ}$
$T =$	$274\cdot 5$	$290\cdot 5$	$304$	$313$	$333$
$A =$	$1\cdot 587$	$2\cdot 851$	$4\cdot 524$	$5\cdot 756$	$9\cdot 946$

It follows from this :

$$\ln \frac{2\cdot 851}{1\cdot 587} = \frac{A' \times 16}{274\cdot 5 \times 290\cdot 5} \quad \text{and } A' = 2920;$$

$$\ln \frac{4\cdot 524}{2\cdot 851} = \frac{A' \times 13\cdot 5}{290\cdot 5 \times 304} \quad \text{and } A' = 3020;$$

$$\ln \frac{5\cdot 756}{4\cdot 524} = \frac{A' \times 9}{304 \times 313} \quad \text{and } A' = 2550;$$

$$\ln \frac{9\cdot 946}{5\cdot 756} = \frac{A' \times 20}{333 \times 313} \quad \text{and } A' = 2850.$$

*Thus I find that the law regulating the variation of the velocity-constant with temperature is for molecular reactions similar to the law of van't Hoff for homogeneous reactions; it has the same thermodynamic explanation, i. e. is in connexion with the maximum work performed during the reaction in a reversible cycle. I will show in my publication on chemical reaction in heterogeneous systems that the same equation holds good in case of reaction of acids &c. upon little soluble solids and confirm it also upon data taken from the investigations of other reliable scientists.*

The above is a very strong and reliable proof against the diffusion conceptions of Noyes and Whitney, Bruner and Tolloczko, Nernst and Brunner. As to the percentage increase of  $A$ , this gradually drops from 5.1 per cent. per degree between  $1^{\circ}5$  C. and  $17^{\circ}5$  C. to 3.64 per cent. between  $40^{\circ}$  C. and  $60^{\circ}$  C., instead of being 2.5 per cent., as required by the diffusion theory; and this increase of  $A$  drops with rise of temperature instead of rising.

(e) My further question is, what do we gain by the Bruner-Tolloczko's, Nernst and Brunner's hypothesis? Nothing either in clearness or in generality of conception. In the first instance, what has become of the speed with which the solid passes into the thin film of the solution, the heterogeneous reaction proper? and which law regulates this reaction? What do we know of the "infinite forces at play," mentioned by Nernst? Are we to be satisfied by mere assertions without proof, or are we going to know anything about this speed and about the forces at play and the mode of their action? In the theory of galvanic cells we are, at any rate, consistent, we calculate and measure the solution-pressures, whether they be only an integration-constant or not. We get solution-pressures of  $10^{15}$  or  $10^{-15}$  atmospheres, to which many a serious scientist objected, but we, from our point of view, adhere to them. These forces are great enough and small enough to show us that if Nernst and Brunner's theory of the process of the ordinary solution of solids at their surface be true, this theory, as given to us at present, still teaches us nothing about the heterogeneous reactions proper even in the sphere of pure abstraction. I, for one, would object to this method of treating the subject of molecular reactions as a clear and lucid conception of a phenomenon which we wish to know, even if pure abstractions were all that interested us. Our conceptions, instead of becoming simpler, became complicated, and we are thrown face to face with new unknown problems which are very difficult and inaccessible to test, while the content and the conceptions contained in the equation,

as given by myself, are very clear and simple, are almost axiomatic in their character.

I return to the argument I have already given in the Rep. Brit. Assoc. Liverpool, 1896, in connexion with Co. My equation is shown to hold for *all* molecular reactions, including such reactions as the transformation of ice into water, water into ice, &c., where concentration does not come into consideration. *It is evident that a law of such a generality cannot find an explanation in diffusion*, which can have only a limited application. This is evident *proof* that there is no necessity whatever in diffusion conceptions to explain the meaning of my equation, and that to give the correct natural interpretation to its meaning, we must take as a basis the *general* features underlying *all* of them, as I did in my papers and here, and not follow the particular line of diffusion.

The *analogy* between the equation for velocity of solution of salt with the equation for diffusion evidently seemed to Noyes and Whitney, Bruner and Tolloczko, Nernst and Brunner peculiar and led them to try to *identify* them and to adapt the conceptions accordingly.

This coincidence may appeal to some as remarkable, but is of no value *so long as the physical constants do not prove this identity*, because buoyancy is also regulated by a law of a similar nature, so is the law of Newton for cooling &c. Why not *identify* velocity of molecular reaction with the law of Newton? With many assumptions, plenty of hypothesis, and no experimental proof, a much more fascinating theory could be developed here. But, as already explained in my paper (Phil. Mag. July 1901) in great detail, there is no more and no less analogy between *all* these phenomena (speed of molecular reaction, diffusion, buoyancy, conduction of heat), they *all* have in common, that, whenever a kind of energy (chemical, thermal, &c.) is removed from the state of equilibrium, the speed with which it strives to attain the same is directly proportional to its remoteness at the time  $\tau$  from its point of equilibrium. This, nevertheless, does *not* make all these phenomena *identical*.

(*f*) Let us now assume for a moment that the speed of solution is regulated by

$$\frac{dt}{dy} = \frac{F}{\delta} \Sigma (C-c) \quad \text{or} \quad \frac{F'}{\delta} (C-c), \quad \text{for } \Sigma=1.$$

Now the velocity of evaporation also follows my equation, and the well established thermodynamic analogy between solution and evaporation makes this also self-evident. In case of gases the diffusion constant D is about 10,000 times greater

than in water ;  $\delta$ , if it existed at all, is evidently much smaller than in solution (we look away from the fact that it is inconceivable that a layer of gas should be formed near the solid the molecules of which cannot move into the rest of the gaseous space, or that the gas from the total volume should not be capable to reach the solid). In view of the above equation for solution, the velocity of evaporation ought to go on with an infinitely greater speed than velocity of solution. We find, however, on the contrary, that the speed of evaporation of liquids and solids belongs in comparison to the slow reactions, as is to be seen already from the fact how difficult it is to reach the maximum of vapour-pressure in all the researches.

This is a further proof against the diffusion conceptions.

(*g*) I shall next deal with the variation of the constant  $A$  with the number of revolutions of the stirrer. There is no reason why the ordinary velocity-constant should not change with the speed of the stirrer, considering that it does so enormously change with the solvent, with the size and dimensions of the apparatus and other mechanical conditions, but whatever its cause, I will show, however, that this variation of the velocity-constant with the number of revolutions proves, if anything, the *improbability* of the diffusion conceptions of Nernst and Brunner. Formerly Tolloczko and Bruner found by the very same method which Nernst and Brunner use, that the speed of solution of the same benzoic acid is directly proportional to the speed of stirring—a rate of variation which does not seem probable for the layer  $\delta$ . Nernst and Brunner seem to have got at first the same results, but they tell us that this was due to some cracks at the rims of the acid, and that as soon as these cracks were filled up with paraffin the value of  $A$  changed as the two-thirds power of the speed of the stirrer. It will, however, be seen from the details of the method used by Nernst and Brunner (dealt with in § 2) and from the photographs of the benzoic acid which I obtained by their method, that their benzoic acid was never free from holes, that the speed of their motor changed too considerably for accurate measurements to be carried out in this region, and that even their titrations were not arranged accurately enough for the very dilute solutions they dealt with. With such a method they nevertheless changed the variations of speed (see pp. 60–61) of their stirrer only from 144 to 202 and from 135 to 180, *i. e.* only by 25 to 30 per cent., which is not enough to distinguish between the results calculated after one equation or the other, even when the



results are obtained with very much better methods. On page 61 they give us

$$n=200 \text{ rev. and } A=2.63; \quad n=177 \text{ rev. and } A=2.76,$$

*i. e.* a diminution of  $A$  with the increase of the speed, showing the lack of sensitiveness of their method. On page 72 they give us the variation of  $A$  for their so-called "Magnesium hydroxide" in benzoic acid:—

$$n=135; \quad A=1.35, 1.88, 1.76=\text{aver. } 1.66.$$

$$n_1=182; \quad A_1=2.14, 1.71, 1.90, 1.87, 1.89=\text{aver. } 1.92.$$

$$n_2=178; \quad A_2=2.14, 2.08=\text{aver. } 2.11.$$

If we take the velocity constant to be directly proportional to the speed of the stirrer, we get—

$$\frac{n_1}{n} = \frac{182}{135} = 1.348 \quad \text{and} \quad \frac{A_1}{A} = \frac{192}{166} = 1.157,$$

*i. e.*, a difference of 14.2 per cent.

$$\frac{n_2}{n} = \frac{178}{135} = 1.318 \quad \text{and} \quad \frac{A_2}{A} = \frac{211}{166} = 1.272,$$

*i. e.*, a difference of 3.5 per cent.

If we take, with Nernst and Brunner, the velocity constant to be directly proportional to the two-third power of the speed of the stirrer we get:

$$\frac{\lg 192 - \lg 166}{\lg 112 - \lg 135} = .487 \text{ instead of } .667,$$

*i. e.*, a difference of -26.98 per cent.; and

$$\frac{\lg 211 - \lg 166}{\lg 178 - \lg 135} = .8676 \text{ instead of } .667,$$

*i. e.*, a difference of +30.08 per cent.

Thus Nernst and Brunner's data, if anything, prove more direct proportionality and not the two-third power of  $n$ , and in reality they can neither be used for the proof of one nor for the proof of the other, especially considering the fact that besides general great experimental errors of their method their "Magnesium hydroxide" proves also to have been a mixture of  $\text{MgO}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{MgCO}_3$ , &c., &c.

I now give here a careful investigation of this point carried out with speeds from about 2 to 400 revolutions per minute and more. (See Table II. and diagram 2.)

TABLE II.—*Variation of the Velocity Constant with the number of revolutions of the stirrer per minute.*

$$\frac{v}{d\tau} \log \frac{C-C_1}{C-C_2} = K_1; \quad K_1 \times 2.3026 = A_1.$$

No.	Benzoic acid. Molecule normal <i>a.</i>	C <sub>1</sub> . Benzoic acid in c. c. of the saturated solution of benzoic acid Elect. conduct.	C'. by Titration	C - C <sub>1</sub> Electric conduct.	C - C'. By titration.	<i>v.</i>	<i>dτ</i> in minutes.	Electric conductivity. $K_1 \times 2.3026 = A_1.$	Titration. $R' \times 2.3026 = A'.$	
<i>Diffusion of benzoic acid in water, when not stirred.</i>										
1'...	·000896	·4072	·4376	9·5928	9·5624	1470	1060	·09554	·10130	2nd May, 1907.
2'...	·002302	1·046	1·1110	8·954	8·8890					
1''.	·003560	1·618	1·653	8·382	8·347	1430	2500	·07182	·07392	Temp. 16°·0-16°·5 C.
2''.	·005737	2·607	2·665	7·393	7·335					
1'''.	·006533	2·968	3·015	7·032	6·985	1410	1008	·05584	·06316	
2'''.	·007137	3·243	3·322	6·757	6·678					
<i>i. e., the velocity constant of diffusion seems to become smaller, the greater the concentration of the solution.</i>										
<i>Speed of solution of benzoic acid in water at 2·42 rev. per minute.</i>										
1 ...	·005737	2·607	2·665	7·393	7·335	1420	367	·1937	·1892	30th April, 1907.
2 ...	·003533	2·968	3·015	7·032	6·985					
<i>Speed of solution of benzoic acid in water at 2·86 rev. per minute.</i>										
1 ...	·000108	0·0491	0·0198	9·9509	9·9802	1490	115	·2276	·1969	Temp. 17°·6 C.
2 ...	·000489	0·2222	0·1703	9·7778	9·8297					
3 ...	·000896	0·4072	0·4376	9·5928	9·5624	1480	152	·1861	·2685	
Average...								·2068	·2326	
<i>Speed of solution of benzoic acid in water at 3·00 rev. per minute.</i>										
1 ...	·002451	1·114	1·111	8·886	8·8890	1460	113·5	·2811	·3267 ?	
2 ...	·002873	1·306	1·336	8·694	8·664					
3 ...	·003345	1·520	...	8·480	...	1450	152	·2376	·2271	
4 ...	·003560	1·618	1·653	8·382	8·347	1440	76	·2203	...	
Average...								·2464	·2588	

TABLE II. (continued).

No.	Benzoic acid. Mol. norm. a.	C <sub>1</sub> . Elect. cond.	C'. Titra- tion.	C—C <sub>1</sub> . Elect. cond.	C—C'. Titra- tion.	v.	dτ.	K <sub>1</sub> × 2.3026 = A <sub>1</sub> .	K' × 2.3026 = A'.	
<i>Speed of solution of benzoic acid in water at 53 rev. per minute.</i>										
1...	·000740	·3364	·4222	9·6636	9·5778					21-22 May, 1907.  Temp. 17°·75 C.
2...	·001085	·4931	·6075	9·5069	9·3925	1470	19·8	<b>1·383</b>	<b>1·443</b>	
3...	·001582	·7190	·8530	9·2810	9·1460	1460	26·5	<b>1·326</b>	<b>1·465</b>	
4...	·002089	·9496	1·120	9·0504	8·880	1450	28·5	<b>1·279</b>	<b>1·502</b>	
5...	·002573	1·1170	1·309	8·8820	8·691	1440	29·75	<b>·909 ??</b>	<b>1·041</b>	
6...	·003068	1·3950	1·572	8·6050	8·428	1430	31·75	<b>1·187</b>	<b>1·385</b>	
7...	·003983	1·8100	1·895	8·1900	8·105	1420	53·0	<b>1·464</b>	<b>1·047</b>	
8...	·005015	2·2790	2·343	7·7210	7·657	1410	64·25	<b>1·294</b>	<b>1·248</b>	
9...	·005780	2·6270	2·778	7·3730	7·222	1400	53·25	<b>1·212</b>	<b>1·538</b>	
10...	·006538	2·9720	3·102	7·0280	6·893	1390	50·0	<b>1·332</b>	<b>1·277</b>	
Average...								<b>1·266</b>	<b>1·327</b>	
<i>Speed of solution of benzoic acid in water at 122 rev. per minute (17°·5 C.).</i>										
1...	·000484	·220	·2154	9·7800	9·7846					15-20 March 1907.  Temp. 17°·8 C.
2...	·000692	·3145	·3404	9·6855	9·6596	1480	6·0	<b>2·397</b>	<b>3·168</b>	
3...	·001665	·7568	·7971	9·2432	9·2029	1465	25·5	<b>2·675</b>	<b>2·781</b>	
4...	·003204	1·456	1·475	8·544	8·525	1445	46·5	<b>2·452</b>	<b>2·309</b>	
5...	·004407	2·003	2·062	7·997	7·938	1430	39·75	<b>2·381</b>	<b>2·567</b>	
6...	·005282	2·401	2·449	7·599	7·551	1420	31·5	<b>2·303</b>	<b>2·254</b>	
7...	·005887	2·676	2·856	7·324	7·144	1410	23·5	<b>2·212</b>	<b>3·324</b>	

TABLE II. (continued).

No.	Benzoic acid. Mol. norm. <i>a</i> .	C <sub>1</sub> . Elect. cond.	C'. Titra- tion.	O—C <sub>1</sub> . Elect. cond.	C—C'. Titra- tion.	<i>v</i> .	<i>dr</i> .	$K_1 \times 2.3026$ $= A_1$ .	$K' \times 2.3026$ $= A'$ .	
8...	·005556	2·525	2·555	7·475	7·445	1490	18·5	<b>2·895</b>	<b>2·482</b>	Temp. 17°·4 C.
9...	·006137	2·789	2·770	7·211	7·230	1475	66·5	<b>2·224</b>	<b>2·503</b>	
10...	·007655	3·479	3·55	6·521	6·450	1460	30·5	<b>2·703</b>	<b>3·088</b>	
11...	·008440	3·837	3·953	6·163	6·047	1445	59·0	<b>2·443</b>	<b>2·395</b>	
12...	·009729	4·422	4·516	5·578	5·484	1430	24·5	<b>2·099</b>	<b>2·191</b>	
13...	·010163	4·619	4·718	5·381	5·282					
14...	...	...	4·645	...	5·355	1490	36·5	...	<b>2·793</b>	Temp. 17°·7 C.
15...	...	...	4·999	...	5·001	1480	38·0	...	<b>2·351</b>	
16...	...	...	5·292	...	4·708					
17...	...	...	6·679	...	3·321	1485	162	...	<b>3·387</b>	Temp. 17°·4 C.
18...	...	...	7·705	...	2·295	1465	157	...	<b>2·533</b>	
19...	...	..	8·252	...	1·748					
Average...								<b>2·413</b>	<b>2·676</b>	
<i>Speed of solution of benzoic acid in water at 204 rev. per minute.</i>										
1...	·001022	·4645	...	9·5355	...	1480	10·0	4·188	...	19-22 April 1907.
2...	·001607	·7304	...	9·2696	...	1470	15·0	4·598	...	
3...	·002532	1·151	1·045	8·8490	8·955	1460	15·4	4·914	4·911	Temp. 18° C.
4...	·003515	1·598	1·497	8·4020	8·503	1450	14·8	4·46	3·495	
5...	·004338	1·972	1·795	8·0280	8·205	1440	22·5	4·246	4·918	
6...	·005471	2·487	2·402	7·5130	7·598	1430	20·7	5·163	3·949	
7...	·006664	3·028	2·824	6·9720	7·176	1420	21·8	4·02	4·393	
8...	·007581	3·445	3·292	6·5550	6·708	1410	22·0	3·857	4·175	
9...	·008425	3·828	3·715	6·1720	6·285					
Average...								<b>4·426</b>	<b>4·306</b>	

No.	Benzoic acid. Mol. n. a.	C <sub>1</sub> . Elect. cond.	O'. Titra- tion.	C-C <sub>1</sub> . Elect. cond.	C-O'. Titra- tion.	v.	dτ.	K <sub>1</sub> × 2·3026 = A <sub>1</sub> .	K' × 2·3026 = A'.	
Speed of solution of benzoic acid in water at 365 rev. per minute.										
1...	·000605	0·2749	...	9·7251	...	1490	4	6·132	...	3 May 1907.
2...	·000953	0·4332	...	9·5668	...		"	4	5·235	
3...	·001251	0·5686	...	9·4314	...	"	10	5·702	...	Temp. 17°·5 C.
4...	·002030	0·9227	...	9·0773	...		"	2	4·992	
5...	·002163	0·9832	0·9465	9·0168	9·0535	1480	3	4·987	4·656	
6...	·002362	1·074	...	8·926	...		"	4		
7...	·002675	1·216	...	8·784	...	"	5	5·174		
8...	·003032	1·378	...	8·622	...	"	2·5	5·112	5·757	
9...	·003194	1·452	1·323	8·548	8·677	1470	10·5	5·188		
10...	·003879	1·763	...	8·237	...	"	4·5	5·317	5·135	
11...	·004172	1·896	1·818	8·104	8·182	1460	15·5	4·743		
12...	·005048	2·294	...	7·706	...	"	9	4·721	5·345	
13...	·005534	2·515	...	7·485	...	1450	24	5·216		
14...	·006896	3·134	3·105	6·866	6·895	1440	32	4·969	5·345	
15...	·008476	3·852	3·877	6·148	6·123					
Average...								5·268	5·222	
Speed of solution of benzoic acid in water at 470 rev. per minute.										
1...	·000597	·2713	...	9·7287	...	1500	2	4·559	...	7 May 1908.
2...	·000727	·3304	...	9·6696	...		"	3	4·835	
3...	·000932	·4235	...	9·5765	...	"	2	4·26	...	Temp. 18° C.
4...	·001051	·4776	...	9·5224	...		"	4	5·043	
5...	·001330	·6045	...	9·3955	...	"	3	4·444	...	
6...	·001513	·6875	...	9·3125	...		"	7	5·158	
7...	·001999	·9085	...	9·0915	...	"	12	4·951	...	
8...	·002777	1·262	...	8·738	...	"	1·5	5·389	...	
9...	·002879	1·309	...	8·691	...	"	8·5	4·974	...	
10...	·003413	1·551	...	8·449	...	"	4	5·504	...	
11...	·003683	1·674	...	8·326	...	"	15	4·145	...	
12...	·004428	2·013	...	7·987	...					
Average...								4·835	...	

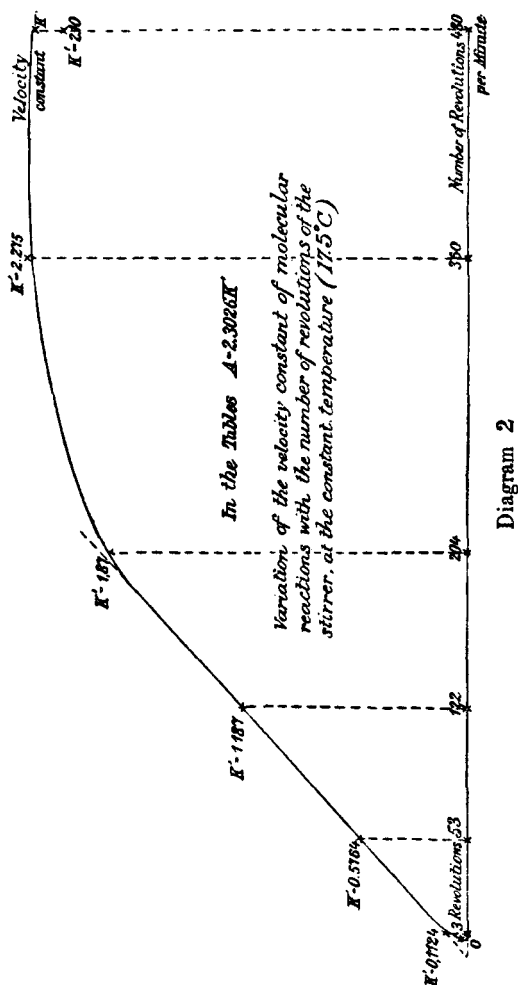


Diagram 2

The results found here are therefore the following:—

1. When the liquid is not stirred at all, the only way for the substance, passing into the solution from the surface of the solid, to pass into the rest of the solution is naturally, as known long ago, by diffusion. The amount passing in this manner is, however, in comparison with what passes at the maximum revolutions or even at any ordinary speeds, only

a small fraction of a per cent. As the assumption that the stirring should produce such a variation in the diffusion-layer is not at all probable, this certainly is, in my opinion, a proof against the diffusion theory.

2. Up to about 3 revolutions of the stirrer, the increase of  $A$  is greater than in direct proportion to the number of revolutions, as the same follows from the curve between 3 and 180 revolutions; the preponderating effect of stirring over that of diffusion is seen even at these slow speeds; the speed of solution is here due to stirring and to diffusion, and the last cannot yet be neglected.

3. From about 3 revolutions to about 180 revolutions the value of  $A$  is directly proportional to the number of revolutions of the stirrer (into this region fall the investigations of Bruner and Tolloczko under their experimental conditions, who found the same result). Thus from about 3 revolutions already the value of transportation due to diffusion no longer interferes with the value of speed of solution, as effected by stirring only.

4. From about 180 to about 400 revolutions, the increase in the value of  $A$  first gradually becomes smaller, until it becomes independent of the number of revolutions of the stirrer, *i. e.* the maximum value for  $A$  has been reached. Into this region fall the experiments of Lorenz and Siegrist under their experimental conditions.

It is, however, evident that the more soluble a substance is, the less will be the number of revolutions requisite to reach a constant maximum value of  $A'$ .

Nernst and Brunner's idea that diffusion is the sole factor in transportation of benzoic acid from the surface of the solid to the rest of the solution is, in my opinion, in no way supported by the character of the above results; quite the contrary. One or two revolutions of the stirrer already transports considerably more than the whole process of diffusion can possibly do alone without stirring; and I fail to see any reasonable support, any reliable proof, that diffusion alone should be operative and that as such it should be (owing to variation of  $\delta$ ) *accelerated* by stirring to such an enormous extent *instead of being more or less destroyed* by the same, owing to the *destruction* of the drop in concentration near the surface of the solid, which is naturally formed when the liquid is not stirred at all. Indeed, as already mentioned, there is nothing to prevent the stirrer from mixing the liquid up to the very solid, and if the liquid can reach the solid during

solidification to a proximity of about  $10^{-15}$  mm., when the liquid is not stirred, we have no reason whatever to assume that the liquid does not reach the solid to the same proximity when we stir the same. For the diffusion conceptions to find any application at all it is necessary *to prove*, not that a saturated solution can be formed at the surface of the solid (when not stirred), but that the solution *is incapable of entering* the layer near the solid when it is moved into it by the stirrer, diluting the same. The assumption that a *saturated* solution is formed at the solid which passes into the rest of the solution by diffusion, overlooks also the fact that *the solid in contact with its saturated solution ought to be in equilibrium with it, ought not to be able to dissolve any more*, and that a reaction of solution of the solid cannot possibly go on, unless the layer in the immediate contact with the solid is *unsaturated*. In this notion we are confirmed by the behaviour of a solid in contact with its gas, and this forms at present an axiomatic notion, which existed for ever so long in physics and chemistry, which led to many useful and fruitful results which cannot be given up for the sake of peculiar diffusion conceptions, even if they should seem capable of explaining some particular case.

(h) I will next consider the "important argument" of Nernst and Brunner "for the conception of the diffusion process." They tell us:—"The true size of the surface is of no importance; when the originally smooth surface of the solid becomes corroded, the velocity constant  $A$  does not change, in spite of the great increase of the surface. Only the quadratic dimensions or contour of the surface and not the microscopic properties of the same are of importance; the last should be of importance, if the reaction takes place on the surface itself." Assuming, however, that this is true, which it is not \*, it is not to be seen, how this is to be taken as a proof for the diffusion conceptions of Nernst and Brunner? If the diffusion layer  $\delta$  were, in comparison with the depth of corrosions, very thick, so that the depths of the corrosions could be neglected, such a conclusion would be admissible. But when the diffusion layer  $\delta$  is even according to Nernst and Brunner only 0.02 mm. thick, while the corrosions according to them can be as deep as 1 mm. (without affecting the constant), it is quite evident that the diffusion layer or surface will be as large as the corrosive surface of the

\* In my next publication I shall furnish further experimental proof that reaction *does take place at the surface* of the solid even in case of substances of no small solubility.



solid itself, and the increase of the diffusion surface will be the same as that of the surface of the solid during corrosion, *i. e.*, we gain nothing whatever here by the assumption of a diffusion layer.

The true position of the facts here is, in my opinion, the following:—

Surfaces which appear to the naked eye smooth are in reality, on inspection with a lens, corroded surfaces, and such surfaces are not always essentially smaller than the surface of the same solid when its corruptions are perceivable; influences of an opposite kind may often counteract one another: on the other hand, I must assert that *very often* we find an increase of the velocity constant with the increase of corrosion, when this is still very far below the values mentioned by Nernst and Brunner, and I find that repeated polishing of the surfaces is in this region imperative.

## PART II.

(i.) I now pass to the most important and most direct test of the diffusion theory. This is given to us by the investigation:—(1) of the *speed of solution of different modifications of the same substance in the same solvent*; (2) of the *speed of solution of the same crystal, cut in different directions to its axis, in the same solvent*. Because if the velocity, with which a solid dissolves, depends, as we are told, upon the speed of diffusion of its saturated solution from the solid into the rest of the solution, and if the saturated solution is formed instantaneously at the solid, then all the  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  of the different Gypsums giving the same saturated solution\* must dissolve with the same speed, and the same crystal Selenite must dissolve in different directions of its axis with the same speed. *If this is not the case, this is the most decisive and direct proof one can possibly imagine, that these fundamental assumptions of the diffusion theory do not hold good, and the whole diffusion theory tumbles to the ground.* Bruner and Tolloczko found (*Zeitsch. für anorg. Chemie*, 1901, p. 325) for Alabaster, the velocity constant  $A=0.00230$  ( $V=2000$  cc.,  $f=22.91$  cm.<sup>2</sup>, number of revolutions 400) and for Marienglass or Selenite  $A=0.00079$  ( $V=2400$  cc.,  $f=20.9$  cm.<sup>2</sup>, number of revolutions 400), *i. e.*  $A$  Alabaster :  $A$  Marienglass =  $3.44 : 1$ . In *Zeitsch. für anorg. Chemie*, 1903, pp. 29, 30, they try to get over this difficulty. They

\* See the investigations of Kohlrausch and Rose and others.

give us  $A$  Alabaster :  $A$  Marienglass =  $2.5 : 1$ , but they inform us that the surface of Marienglass is smooth, the surface of Alabaster not, and when we polish Alabaster to a smooth surface the constant  $A$  drops to half its value. The impression is thus created, that the constants of both are really the same. Note in the first instance, that this explanation is now brought forward by Bruner and Tolloczko, who were the first to find : "The important argument for the diffusion theory consisting in the fact that corrosion as deep as 1 mm. has no effect on the velocity constant;" that they no longer accept this statement in case of Alabaster, which very easily gives perfect surfaces, much better than marble, while they do not take into account the corrosion of all other substances used by them, which are not able to give such smooth surfaces as Alabaster, but for which they nevertheless furnish us with perfect and impossible constants, under conditions when the substances must have corroded during the reaction very considerably ! With "Plâtre" Bruner and Tolloczko found  $A$  to be twice as big as that of Alabaster, but according to them this is only due to the fact that some substance is coming off from the solid. As the method of Bruner and Tolloczko seemed to me quite unsuitable for a reliable investigation here, this matter had to be investigated again. The solubility of the Gypsums is only about 2 gr. per litre, and some of the solutions and differences investigated by them contained no more than .003 gr. in the 25 cc. which they investigated. Such amounts of gypsums Bruner and Tolloczko wish to measure quantitatively either by evaporation or by the more complicated and unreliable method of precipitation with oxalic acid (collecting, washing the same), the decomposition with  $\text{SO}_4\text{H}_2$  and titration with permanganate, and yet they supply us by such methods with constants differing in a series only by about 2 per cent. ! To remove, however, all possible doubt here about the reason for the difference found between Marienglass and Alabaster and to investigate the same in very dilute solutions, when the surface had no time yet to corrode except but very little, I employed the method of electric conductivity as described in paragraph 2, which enables us to make very much more accurate and instantaneous measurements than it is possible to expect from the methods of Bruner and Tolloczko, and very great care was taken to polish the surfaces of the gypsums as perfectly as possible.

Table III.  $A$  gives the speed of solution of the following Gypsums  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  :—Selenite or Marienglass from

Italy, Alabaster from Leicester, fibrous Gypsum from Nottingham, all perfect specimens, perfectly polished and washed and dried up well and quickly; their surface is almost the same, about 4 sq. in., all were investigated at the same temperature of very near  $17^{\circ}5$  C., with the same speed of stirrer (130 to 132 revolutions per minute) and the same volume (1500 cc.) which remained constant during the whole time of the reaction. The surface of the selenite exposed to solution was the flat large side of the twin-crystal, the surface of the fibrous gypsum was cut along the fibre, quite parallel to the same, while the surface of alabaster could be taken in any direction. Photos 11, 12, 13 (Pl. XVII.) show Selenite, Alabaster, fibrous Gypsum, their structure and their surfaces *after* solution. It will be seen from the same that their surfaces were not allowed to corrode. The selenite is transparent like glass, and what we see on the photo is the paraffin below the bottom surface. On the contrary, in case of alabaster and fibrous gypsum, the photos show their structure, not corrosions, which are extremely small. The velocity constant of Selenite is from .48 to about .65, of the fibrous Gypsum is about 2.0, of the Alabaster from 3.1 to about 4.0, the average ratio of the constants of Selenite : fibrous Gypsum : Alabaster at the same surface is about 1 : 3.5 : 5.4. Thus Marienglass and Alabaster give, not as Bruner and Tolloczko lead us to think almost equal constants, but very different constants indeed, and all the three above specimens of the same Gypsum give undoubtedly different constants, whether we take extremely dilute solutions given by the first three dilutions in the above tables, where the ratio is 1 : 4 : 6, or the more concentrated ones. Therefore, as the solubility of all modifications is the same, it is sufficient that the same monoclinic crystal should configurate itself once into a twin-crystal, another time into a fibrous structure, another time into a granular crystalline form; and this physical modification in the configuration of the very same components is already alone sufficient to cause the solid to acquire some new physical properties, of which the speed of solution is one. All the above three specimens are as we find them in nature, their velocity constants undoubtedly increase as the reaction goes on, and this may be due either to corrosion or also to some other influences. It is not likely to be due to the presence of some more easily soluble substances as impurities, because the velocity constants ought in such a case to decrease with time, instead of increasing.

TABLE III A.

Molecule normal. $C_1$ .				Molecule normal. $C_1$ .				Molecule normal. $C_1$ .			
$d\tau$ in minutes.				$d\tau$ in minutes.				$d\tau$ in minutes.			
$O - C_1$ .				$O - C_1$ .				$O - C_1$ .			
$v \log \frac{O - C_1}{d\tau} \times 2.3026 = K$ .				$v \log \frac{O - C_1}{d\tau} \times 2.3026 = K$ .				$v \log \frac{O - C_1}{d\tau} \times 2.3026 = K$ .			
A. <i>Selenite or Marienglass</i> (from Italy). $18^\circ \text{C}$ .; 131 rev. per minute; $v = 1500 \text{ cc}$ .; $\Sigma = 26 \text{ cm}^2$ . 14-15th May, 1908.				B. <i>Fibrous Gypsum</i> (from Nottingham). $17^\circ 55 \text{ C}$ .; 131 rev. per minute; $v = 1500 \text{ cc}$ .; $\Sigma = 25.5 \text{ cm}^2$ . 20th May, 1908.				C. <i>Alabaster</i> (from Leicester). $17^\circ 8 \text{ C}$ .; 131 rev. per minute; $v = 1500 \text{ cc}$ .; $\Sigma = 27.56 \text{ cm}^2$ . 16th May, 1908.			
0001600	25	0143000	4864	0001730	5	0142870	2.065	000093	3	0143670	3.143
0002754	20	0141846	5026	0002720	5	0141880	1.925	0001830	3	0142770	3.413
0003701	20	0140899	5571	0003629	6	0140971	1.987	0002802	3	0141798	3.287
0004743	10	0139857	6638	0004743	6	0139857	1.823	0003730	3	0140870	3.333
0005360	10	0139240	5700	0005758	6	0138842	1.883	0004665	3	0139935	3.580
0005890	10	0138710	5764	0006802	6	0137798	1.811	0005662	3	0138938	3.574
0006420	10	0138180	6080	0007797	6	0136805	1.866	0006654	3	0137946	3.450
0006980	10	0137620	6610	0008815	23	0135785	1.840	0007603	3	0136997	3.640
0007585	15	0137015	6683	0012586	19	0132014	1.860	0008597	3	0136003	3.430
0008499	15	0136101	6578	0015750	19	0128850	2.176	0009524	6	0135076	3.547
0009392	15	0135208	6976	0019255	15	0125345	1.848	0011428	3	0133172	3.357
0010328	15	0134272	6398	0021550	15	0123050	1.902	0012320	3	0132280	3.573
0011182	15	0133418	6365	0023860	15	0120730	1.807	0013292	3	0131308	3.763
0012026	15	0132574	6658	0026030	15	0118570	2.017	0014278	6	0130322	3.513
0012910		0131690		0028300	15	0116300	2.037	0016096	8	0128504	3.597
		Average	6137	0030740		0113860		0018540		0126060	
						Average	1.923	0020640	7	0123960	3.602
Polished block again.				Polished block again.				0026380	19	0118220	3.742
001291	15	0131690	6407	0032010	16	0112580	1.960	0029320	10	0115280	3.778
001375	15	0130852	6002	0034340	15	0110250	1.738	0037800	30	0106800	3.820
001453	30	0130070	6050	0036250	16	0108350	1.845			Average	3.534
0016096	15	0128504	7054	0038360	23	0106240	2.285	Polished block again.			
001700		012760		0042020	18	0102580	2.031	0051860	12	0092740	3.180
		Average	6378	0044490	19	0100110	1.937	0054190	15	0090410	3.625
Excellent surface, transparent like glass.				0046920	44	0097680	2.094	0057410	15	0087190	3.750
For $\Sigma = 20.4 \text{ cm}^2$				0052740	15	0091860	2.247	0060620	46	0083980	3.540
$K' = .49$ (average)				0054780	17	0089820	2.328	0069260	30	0075340	3.300
.40 (in the three greatest dilutions).				0057120	13	0087480	2.330	0074070	29	0070530	3.779
				0058870		0085730		0079040	31	0065560	3.457
						Average	2.080	0083560	30	0061040	3.695
				Excellent surface.				0087910	30	0056690	3.594
				For $\Sigma = 20.4 \text{ cm}^2$				0091830	30	0052770	3.992
				$K' = 1.7$ .				0095880	30	0048720	
										Average	3.563
								Excellent surface.			
								For $\Sigma = 20.4 \text{ cm}^2$			
								$K' = 2.6$ (average)			
								$= 2.4$ (in the three greatest dilutions).			

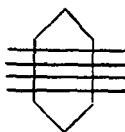
TABLE III B.

Molecule normal. $C_1$ .	$d\tau$ in minutes.	$C - C_1$ .	$\frac{v}{d\tau} \log \frac{C - C_1}{C - C_2} \times 2.3026 = K$ .
A'. Selenite or Marienglass (the large, flat surface of the twin crystal). 18° C.; 131 rev. per min.; $v=1500$ cc.; $\Sigma=26$ cm. <sup>2</sup>			
·0001600	25	·0143000	·4864
·0002754	20	·0141846	·5026
·0003701	20	·0140899	·5571
·0004743	10	·0139857	·6638 ?
·0005360	10	·0139240	·5700
·0005890	10	·0138710	·5767
·0006420	10	0138180	·6080
·0006980	10	·0137620	·6610
·0007585	15	·0137015	·6683
·0008499	15	0136101	·6578
·0009392	15	·0135208	·6976
·00110328	15	·0134272	·6398
·0011182	15	·0133418	·6365
·0012026	15	·0132574	·6658
·0012910		·0131690	
		Average	·6137
Block polished again.			
·001291	15	·0131690	·6407
·001375	15	·0130852	·6002
·001453	30	·0130070	·6050
·0016093	15	·0128504	·7054
·001700		·0127600	
		Average	·6378
Excellent surface.			
For $\Sigma=20.4$ cm. <sup>2</sup> $K'=49$ (average). ·40 (in the three greatest dilutions).			
Molecule normal. $C_1$ .	$d\tau$ in minutes.	$C - C_1$ .	$\frac{v}{d\tau} \log \frac{C - C_1}{C - C_2} \times 2.3026 = K$ .
B'. Selenite or Marienglass (surfaces cut vertically to the surface of A' and cemented with paraffin). 17°·3 C.; 130 rev. per min.; $v=1500$ cc.; $\Sigma=24$ cm. <sup>2</sup> 25th May, 1908.			
·0001392	1	·0143208	3·457
·0001722	1	·0142878	3·018
·0002019	1	·0142581	2·970
·0002308	1	·0142292	3·595
·0002634	1	·0141966	3·035
·0002929	2	·0141671	3·376
·0003555	6	·0141045	3·415
·0005470	3	·0139130	3·620
·0006472	7	·0138762	3·895
·0008964		·0138128	
		Average	3·376
Excellent surface.			
For $\Sigma=20.4$ cm. <sup>2</sup> $K'=2.87$ .			
Molecule normal. $C_1$ .	$d\tau$ in minutes.	$C - C_1$ .	$\frac{v}{d\tau} \log \frac{C - C_1}{C - C_2} \times 2.3026 = K$ .
C'. Selenite or Marienglass (powdered and compressed to a disk under 2500 atm. during 16 hours). 17°·4 C.; 131 rev. per min.; $v=1500$ cc.; $\Sigma=20.4$ cm. <sup>2</sup>			
·0000680	1	·0143920	2·590
·0000930	2	·0143670	2·740
·0001452	2	·0143148	3·240
·0002067	2	·0142533	2·858
·0002611	2	·0141989	2·742
·0003130	2	·0141470	2·902
·0003674	2	·0140926	2·900
·0004220	2	·0140380	3·004
·0004780	4	·0139820	2·920
·0005864	2	·0138736	2·728
·0006367	8	·0138233	2·931
·0008514	10	·0136086	2·955
·0011171	15	·0133429	2·977
·0015082	21	·0129518	3·016
·0020454	12	·0124146	2·950
·0023390	11	·0121250	2·973
·0025910	23	·0118690	2·990
·0031230		·0113370	
		Average	2·907
Very good surface.			
For $\Sigma=20.4$ cm. <sup>2</sup> $K'=2.9$ .			

TABLE III c.

Molecule normal. $O_1$ .	$dt$ in minutes.	$O - O_1$ .	$\frac{C - O_1}{dt} \log \frac{C - O_1}{O - O_1} \times 2.3026 = K$ .	Molecule normal. $O_1$ .	$dt$ in minutes.	$O - O_1$ .	$\frac{C - O_1}{dt} \log \frac{C - O_1}{O - O_1} \times 2.3026 = K$ .	
A". $\text{CaSO}_4 + 2\text{H}_2\text{O}$ precipitated; with excess of water dried in open air; compressed under 2500 atm. for 16 hrs. $18^\circ \text{C}$ .; 131 rev. per min.; $v = 1500 \text{ cc}$ .; $\Sigma = 20.4 \text{ cm}^2$ 29th May, 1908.				B". Anhydride $\text{CaSO}_4$ , Nova Scotia: cut to a disk of 50 mm. diameter; $17.5^\circ \text{C}$ .; 132 rev. per min.; $v = 1500 \text{ cc}$ .; $\Sigma = 19.63$ . 10th June, 1908.				C". $\text{CaSO}_4$ Anhydride, precipitated. Got by heating at $310^\circ \text{C}$ . for 4 to 5 hours, compressed to a disk at 2500 atm.; $\Sigma = 20.4 \text{ cm}^2$
.000067	1	.0143930	2.797	.000050	8	.0144100	.5698	From the top surface powder comes off, <i>i.e.</i> cannot be investigated. It is well known that while $\text{CaSO}_4$ prepared from $\text{CaSO}_4 + 2\text{H}_2\text{O}$ at $80^\circ \text{C}$ . in air current absorbs water rapidly forming $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and dissolving in water, the $\text{CaSO}_4$ prepared from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by heating at about $300^\circ \text{C}$ . (as in our case) absorbs water and dissolves in water very slowly.  Thus, again, the speed of solution of the same $\text{CaSO}_4$ -Anhydride, differently prepared, is <i>different</i> , the speed of combination of the $\text{CaSO}_4$ 's with water, which is also a heterogeneous reaction, is different, and the speed of reaction is <i>dependent</i> upon the physical state of the solid, <i>not</i> independent of the same.
.000094	1	.0143660	3.142	.000094	8	.0143660	.6173	
.000124	1	.0143360	3.039	.000141	4	.0143190	.6302	
.000153	1	.0143070	3.384	.000165	6	.0142950	.6792	
.000185	1	.0142750	2.837	.0002040	7	.0142560	.6140	
.000212	2	.0142480	3.004	.0002444	8	.0142155	.5820	
.000269	3	.0141910	3.056	.0002889	10	.0141711	.5971	
.000355	3	.0141045	3.073	.0003452	15	.0141148	.6536	
.000442	6	.0140178	3.063	.0004372	6	.0140228	.6636	
.000613	6	.0138471	3.029	.0004743	?	.0139857	?	
.000780	11	.0136803	2.986	.0005060	20	.0139540	.6754	
.001076	45	.0133839	3.166	.0006314	15	.0138286	.6557	
.002289	43	.0121710	3.087	.0007217	18	.0137383	.6782	
.003330	27	.0111300	3.213	.0008332	17	.0136268	.6886	
.003965	30	.0104950	2.908	.0009392	20	.0135208	.6976	
.004558	10	.0099020	3.090	.0010642	20	.0133958		
.004760	10	.0097000	3.156	Average			.643	
.004962	10	.0094980	2.852	Excellent surface; polishes better than marble.				
.005141		.0093190						
Average				3.054				
Excellent surface.				For $\Sigma = 20.4 \text{ cm}^2$ $K' = .67$ .				
For $\Sigma = 20.4 \text{ cm}^2$ $K' = 3.054$ .								

In Table III. B the same selenite is investigated in two different directions in the crystal: the first one is the large flat surface of the twin-crystal already mentioned before (A Selenite, photo 11); the second is a surface cut vertically to the surface A, as in the annexed figure.



I cut the selenite crystal, as in the figure, into several strips and connected the vertical surfaces to one surface, the cut-off strips separating into several thin plates, and I made up a block connecting the same by means of paraffin (see photo 14). The surface of the crystal without paraffin was 49 mm. in length and 49 mm. in width; through the paraffin it became 49 mm. in length and 52 mm. in width. As in case of all other gypsums, all sides were covered with paraffin, except one which was exposed to the action of the solution. The surface was perfectly polished, as is to be seen also from photo 14; the velocity constant obtained for this vertical surface is about 3.376, *i.e.* about 6 times as large as the velocity constant of solution of the other surface of the same crystal (which is .6378), a difference which is truly enormous, and cannot possibly be attributed either to the difference in the surface or to the method employed. This experiment proves beyond any possible doubt that the same crystal dissolves at different rates in different directions to the axis of the crystal, and is at the same time an absolute proof that the fundamental assumptions of the diffusion theory mentioned above are thoroughly wrong and belong only to the world of pure imagination. This experiment also explains the reason, why the different modifications of gypsum give us different velocity constants. In the fibrous gypsum all the crystals of which the gypsum is formed configurate in one direction and not in the other; in the selenite the crystals configurate in all directions of the twin-crystal; while in alabaster, precipitated  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ , or in powdered selenite they configurate in no direction. Owing to this in the selenite twin-crystal in the large side of the same, always the same surfaces of all the crystals (which are least easily dissolving) are exposed to solution, in the fibrous gypsum the surfaces of the crystals lying in two directions are exposed to solution, but not the surfaces in the third direction, which combine to form the fibre, while in the alabaster the surfaces of the crystal in all three directions are exposed to solution in equal or nearly equal shares. So we find for  $\Sigma = 20.4 \text{ cm.}^2$  the velocity constant of alabaster is about 2.6; the velocity constant of selenite in powder and compressed to a disk is for the same surface = 2.9, while the velocity constant of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

precipitated and compressed to a block is for the same surface = 3.0, *i. e.* is only a little different (photograph 15 shows block of powdered selenite *after* solution; the corrosion is visible); which seems to prove that when the crystal has no special configuration and all its surfaces are equally exposed to solution, the speed of solution is practically the same.

It should be noted at the same time that the powdered and compressed selenite (see Selenite) and the fine precipitated and compressed  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  seem to give a very good constant from beginning to the end, without any essential increase in the same.

(ii.)  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  and  $\text{CaSO}_4$  Anhydride.—If a substance forms a saturated solution at the surface of the solid with infinitely great speed, and if it passes from the surface of the solid to the rest of the solution only by diffusion, then  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  must dissolve with greater speed than anhydride  $\text{CaSO}_4$ . Because the  $\text{CaSO}_4$  must either first form  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  in the solution at the surface of the solid, before it diffuses into the rest of the solution in which we know it only as  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ , not as  $\text{CaSO}_4$ , or  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  must be formed first on the solid  $\text{CaSO}_4$  itself, as a thin solid layer, under the action of water, and then as such pass into the solution. Whether this reaction of transformation of  $\text{CaSO}_4$  into  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  be quick or slow, whether it takes place at the solid or in solution, the passing of  $\text{CaSO}_4$  into the whole of the solution by diffusion can only be longer, but not shorter than in the case of  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ , if the fundamental assumptions of the diffusion theory be true, and a reverse phenomenon should not be possible. Table III. c gives the speed of solution of anhydride  $\text{CaSO}_4$ , Nova Scotia (photo 16 gives Nova Scotia *after* solution), which was turned to a disk of 50 mm. diameter. The velocity constant of the same is about .64 for its surface; on the other hand, we found the Selenite  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  gave for the same surface  $\Sigma = 20.4 \text{ cm.}^2$ , and under all other identical conditions of temperature, stirring, volume of solution, &c., a constant of about .49; an inspection of the two blocks Selenite and Nova Scotia after they were dissolving in solution, also show a greater corrosion in the last, which is indicative of a greater speed of solution, than in the case of Selenite.

#### *Conclusion.*

I have thus proved, both theoretically and experimentally, that the explanation of my equation for molecular reactions in case of solution of salts, as a diffusion equation, and all



the fundamental assumptions connected with the diffusion conceptions of Nernst, Brunner, and others, have no theoretical and no experimental support whatever. I have traversed in this first publication almost all the experimental material of Bruner and Tolloczko, Nernst and Brunner, so far as it deals with molecular reactions in solution. I have shown step by step, that all their experimental proofs here are nothing but arbitrary experiments, that as soon as they are replaced by accurate reliable results the very same substances furnish us with a solid proof against the diffusion theory. In my next publication I will deal with the speed of *chemical* reaction in heterogeneous systems, and I shall have then a still wider opportunity to show, traversing again the whole of the experimental material of Nernst and Brunner, that from the beginning to the end there is not one experiment which is not arbitrary, and which, when replaced by correct results, does not most decidedly refute the so-called diffusion theory with all its numerous and unnatural assumptions. It is a theory, which is neither theoretically sound, nor is it supported in the least degree by direct experiment.

Davy-Faraday Laboratory  
of the Royal Institution, London,  
January 1909.

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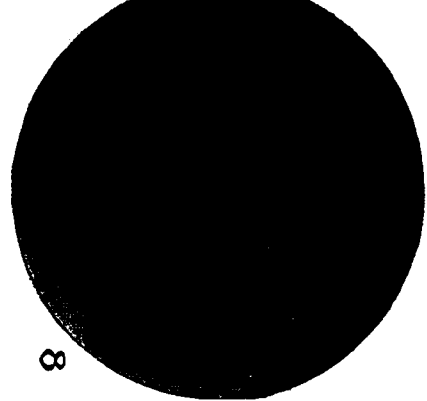
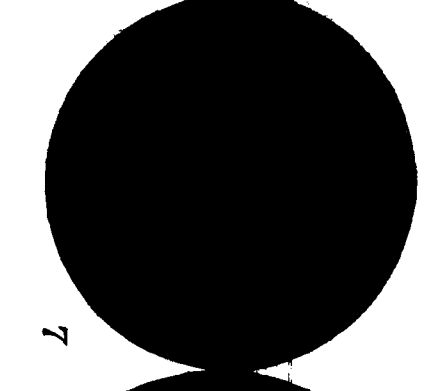
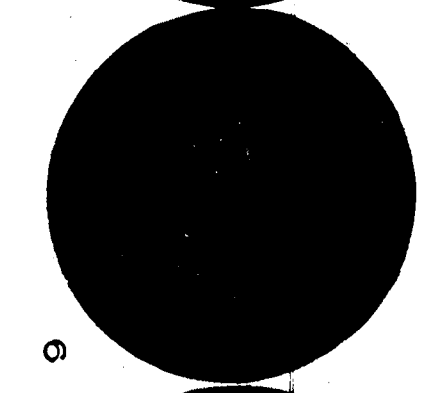
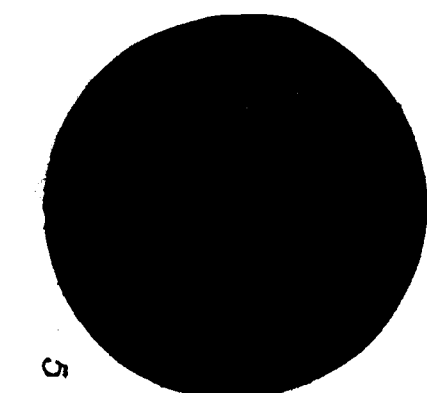
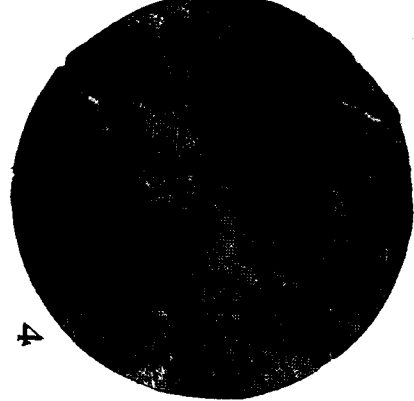
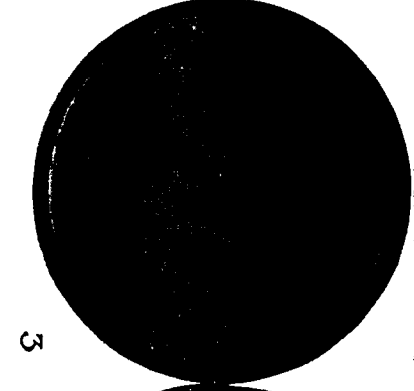
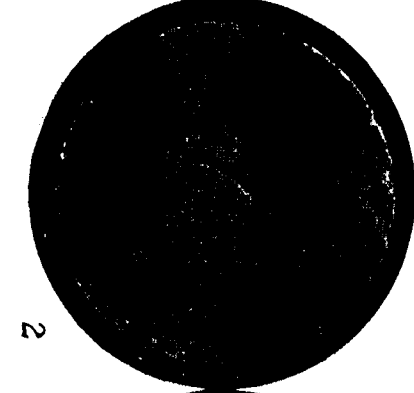
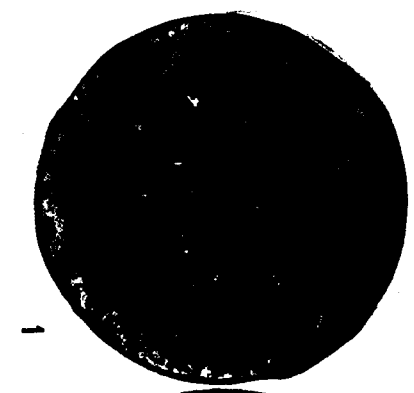
LXII. *On the Radioactivity of certain Lavas.*

*By J. JOLY, F.R.S.\**

SOME months ago, when determining the radium content of lavas from various parts of the world, I noticed with surprise the relatively large amount of radium contained in one from Vesuvius. This lava was from the eruption of 1855. The reading was so high that before accepting it I re-determined it upon a second chip taken from the interior of the same hand specimen. I obtained identically the same value.

Returning to the subject at a more recent date I examined the series of dated Vesuvian lavas in the Museum of Geology in Trinity College, and found quantities of radium in every case supporting my original determination. But the fact seemed brought out that the earlier lavas of the last three hundred years possessed a lower radium content than the more recently ejected rocks. At this stage Prof. Johnston-Lavis was so kind as to send me some samples of the lava-flow of April 1906. Subsequently he also supplied me with one of the oldest lavas: what he has classified as Dyke No. 1 of the ancient volcano of Monte Somma. This last rock is—

\* Communicated by the Author.



WILDERMAN.

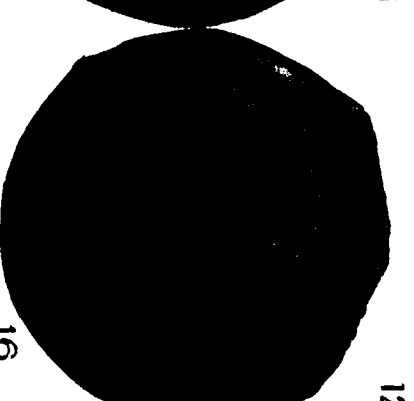
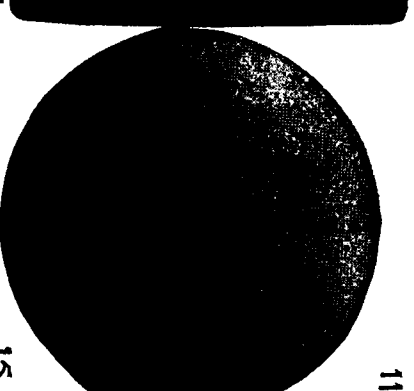
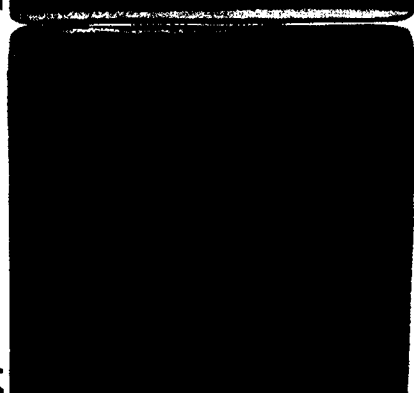
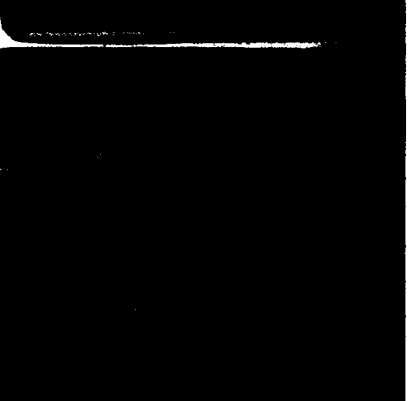
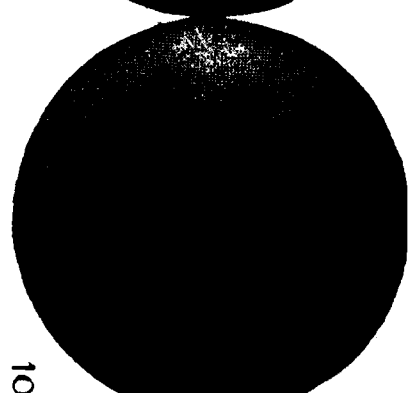
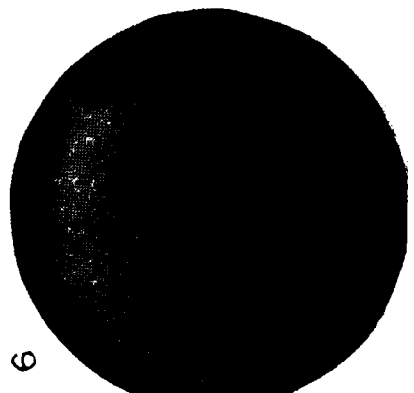
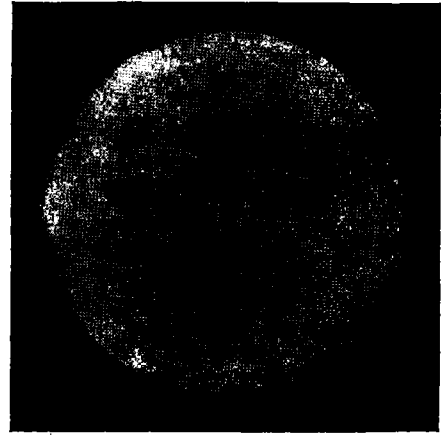


FIG. 1.

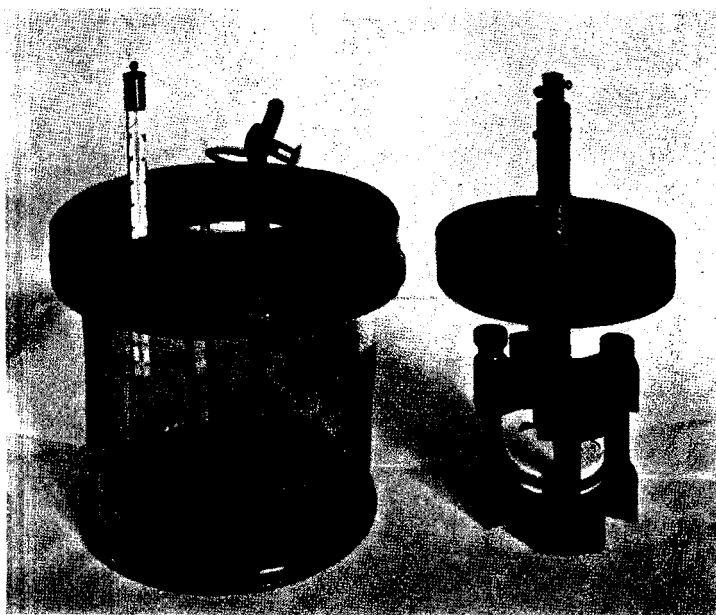


FIG. 2.

