

## On certain Molecular Constants

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XXXIX. *On certain Molecular Constants.*

By FREDERICK GUTHRIE.\*

[Plates XV. &amp; XVI.]

*Liquid Slabs. Metallic Diffusion.*

§ 1. *Liquid Slabs.*—When a little liquid is poured upon a flat horizontal surface which is not attacked by the liquid, a circular disk of liquid is formed, the shape of the edge of which has been very fully examined by Quincke and others. In most such cases, one of the most important factors is the specific relationship in the sense of adhesion between the solid and the liquid. In fact the question, like all questions of capillarity, involves density (and gravitation), cohesion, adhesion, and surface-tension. Such experiments show the relationship between two bodies as well as the physical attributes of one. About twenty years ago I made an attempt to get rid of the factor adhesion, with partial success, by examining the size of a liquid drop. But I soon found that other factors, notably the shape of the solid bodies from which the dropping occurred, and the rate of dropping, introduced arbitrary conditions which removed the measurements from the class of simple physical constants.

§ 2. The plan adopted in the following experiments is the endeavour to support a mass of liquid above a plane surface in such a way that no actual contact ensues, not even such as takes place between clean glass and mercury. If such can be done, it is clear that we shall have a circular flat slab with rounded edges, and into the shape of that slab the influence of adhesion by no means enters. If the thickness of the slab be found to be a constant, we shall have a constant as characteristic as density, and, like density, varying for the same mass only according to volume, such volume-change in our case being brought about by heat alone. Such slab-thickness has for its negative influence the action of gravity (density), for its positive the cohesion and surface-tension.

§ 3. The actual measurements of the slab-thickness I have performed in two ways :—(1) by a spherimeter which, when used as such, gives results trustworthy to the  $\frac{1}{100000}$  of an inch.

\* Communicated to the Physical Society during the Session 188283.



Fig. 1.

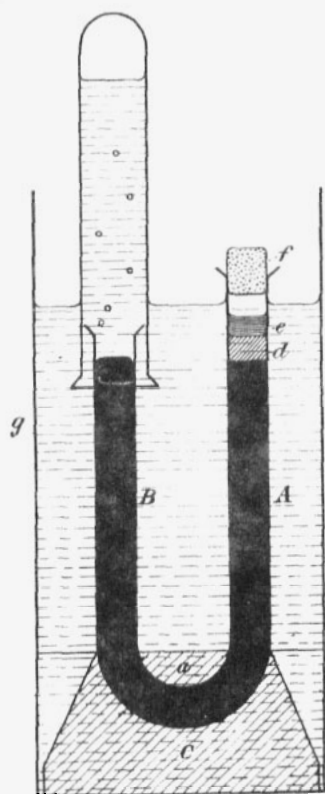


Fig. 2.



Fig. 3.

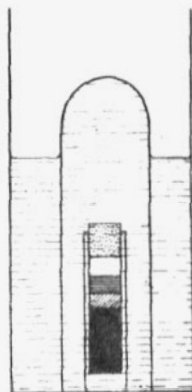


Fig. 4.

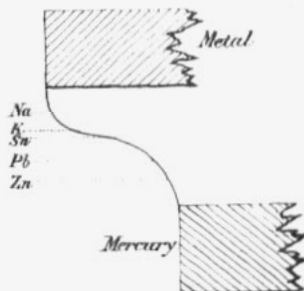
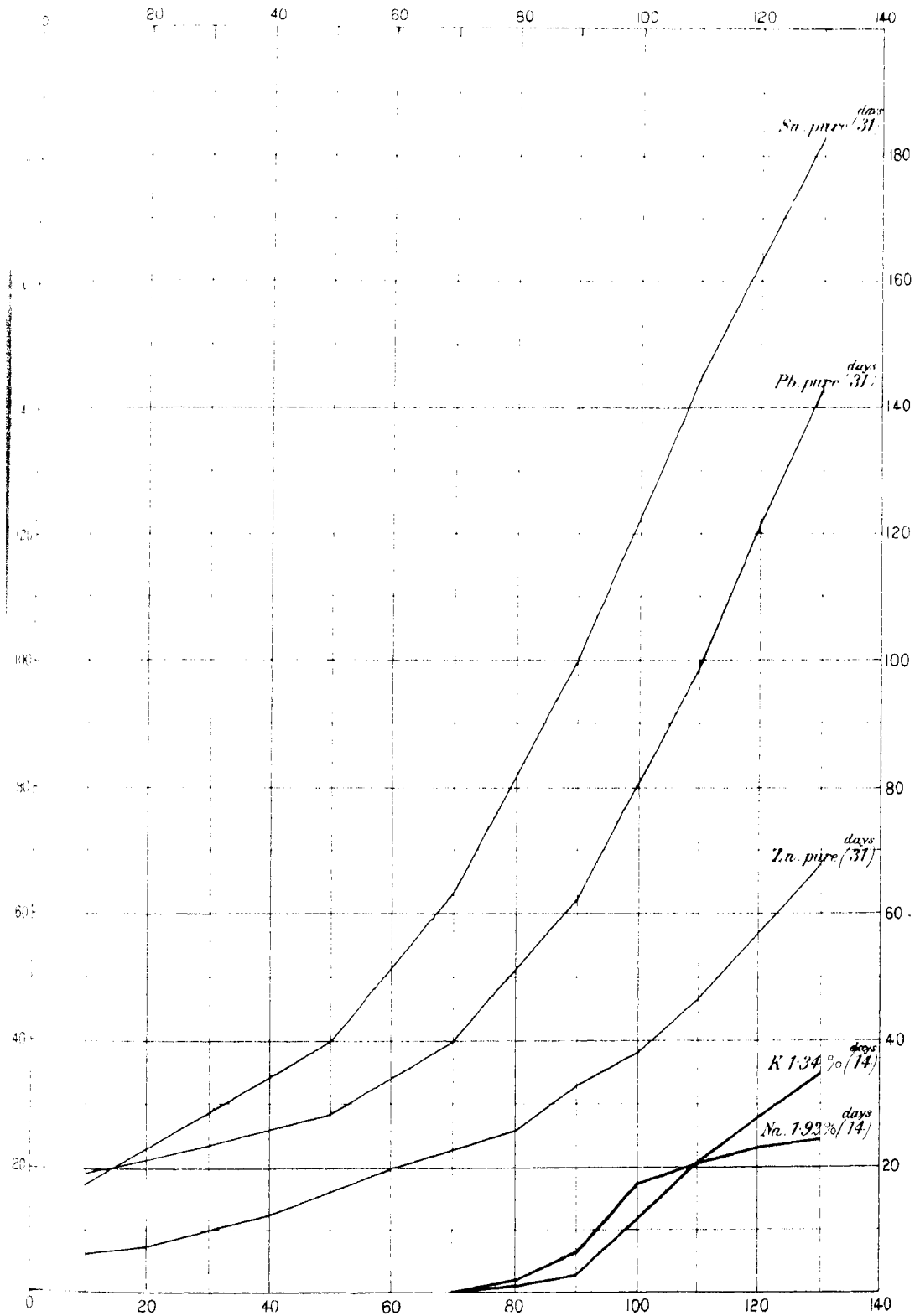


Fig. 5.



But the upper of the two surfaces whose distance has to be measured being liquid, and the lower one not very hard, the spherimeter cannot be used by the method of touch. Accordingly I have measured the slab-thickness indirectly. A known volume of the liquid is poured on the surface, and teased into the circular form if it shows any noticeable departures from it. Four or five diameters are measured by means of a small horizontal cathetometer. The mean being taken, an allowance has to be made for the meniscus. This reduces the shape to the cylindrical, from which the thickness  $h$  is deduced by means of the equation

$$h = \frac{V}{\pi r^2}.$$

§ 4. In regard to the actual apparatus:—Upon a thick round slab of paraffin, a foot in diameter and 4 inches thick, a massive foot of plaster is cast. The whole is placed on a three-screw levelling support. The surface of the paraffin is scraped into a true plane. When water was being examined, the surface of the paraffin was lightly powdered with lycopodium and the water poured on vertically from a fine opening. With some care a perfectly round slab of water 6 inches in diameter can be formed, which is so free to move that the greatest nicety of adjustment in the levelling-screws is necessary. Precisely the same arrangement can be adopted for mercury. But it was found that for the latter liquid a sheet of blotting-paper wetted and allowed to dry on a sheet of plate-glass gave results identical with those of the paraffin surface. The paper surface was used in some of the experiments. As to the allowance for the meniscus, it is clear that this is of less consequence with large slabs than with small ones. Indeed, with slabs a few inches in diameter the meniscus might be neglected. This was imperfectly shown in the case of mercury by adding exactly equal volumes to a small slab. After the slab had passed 2 inches in diameter, each additional volume produced a “parabolic” increase in the diameter. Data derived from this and from the measurement of an enlarged photograph of the edge gave me as a mean 2 millim. to be deducted from the diameter in the case of mercury. Assuming it to be the same for water,

the error incurred, after making this reduction, could not in a 6-inch slab be more than  $\frac{1}{500}$  of the diameter. This would be negligible in the deduced thickness.

§ 5. I give the following datum for mercury on account of the accidental coincidence of the experimental numbers with numbers easy of remembrance, excepting as to the temperature, which is, however, not far from the conventional temperature of 60° F.

100 cub. centim. of mercury at 14° C. has an extreme radius of 100 millim.

$$h = \frac{100,000}{3 \cdot 1416 \times 99^2};$$

thickness of mercury slab = 3.248 millim.

In the case of water it was found so difficult to get a nearly circular slab with 100 cub. centim., that only 50 were employed. The slab may then be teased into a circular form by means of a stick of paraffin covered with lycopodium.

50 cub. centim. of water at 14° C. has an extreme radius of 54.8 millim.

$$h = \frac{50,000}{3 \cdot 1416 \times (53.8)^2};$$

thickness = 5.50 millim.

Glycerine\* is a beautiful liquid in this respect. It is kept off from the paraffin surface by a very faint blush of lycopodium, and it travels very slowly. It can be got into a circular slab more easily than water; but, perhaps on account of its capillary action towards its lycopodium props, it is more persistent in its motion. In fact, unless there be hills of that substance to confront it, it rolls along (for that is the motion of a slab however large) and forms a "level," which requires a very steady support to avoid the notion that its motion is affected by the gravity of the observer.

50 cub. centim. of glycerine at 14° C. has an extreme radius of 59 millim.

$$h = \frac{50,000}{3 \cdot 1416 \times (58)^2};$$

thickness = 4.731 millim.

\* Commercial, "Price's."

§ 6. Accordingly, taking the slab thickness of water as unity, we may begin a table which will at some future time assuredly be extended.

*Specific Slab-thickness (at 14° C.).*

Water .	=1.0000,
Glycerine	=0.8602,
Mercury	=0.5906,

These numbers may be, with instruction, considered in reference to the numbers in table vii., which concern the drop-sizes of the same three liquids, in the 'Proceedings of the Royal Society,' 1864, p. 17 ["Recess"]. It will, I have no doubt, appear that in all cases the greater the drop-size the greater the slab-thickness. Water will, no doubt, again assert its singularity and exhibit the greatest slab-thickness.

§ 7. Restrained as slabs are in their form by skin-tension as well as cohesion, it is found that the addition of a liquid which diminishes the former diminishes also the slab-thickness. Taking 25 cub. centim. of water at 14° C., a slab was formed having 38 millim. corrected radius. This gives a thickness of 5.51 millim. Such a slab is unchanged if touched in the middle by a drop of glycerine. But on touching it with "glacial" acetic acid, it instantly acquires a corrected radius of 44 millim., or thickness of 4.16 millim. This means a diminution in thickness of very nearly 25 per cent., or one quarter. The question therefore presented itself, What is the slab-thickness of "glacial" acetic acid?

I reserve the results of my experiments in the direction of the relationship between the liquids and the alteration of skin-tension.

§ 8. The mercury slab, like the water slab, has what virtually amounts to a skin; and it became interesting to examine the conditions of this skin or region of surface-tension. If lycopodium be strewn upon the surface of a mercury slab, and a little tin, zinc, or lead, or amalgam of these metals be made to touch the slab in the middle, no noticeable disturbance takes place. But if such a slab be touched by an amalgam of K or Na, the slab instantly expands, and the film of lycopodium-powder on its surface cracks radially, exposing the

brilliant metallic surface, which is seen to be agitated over its whole extent. In a few seconds the slab contracts to its original size and the lycopodium cracks heal.

Does this extension of the slab depend upon the diminution of the cohesion of the mass of the mercury, or upon a surface effect?

§ 9. I frequently in my researches have had recourse to the fact, which I first described in the year 1863, that a little sodium added to mercury enables that metal to touch with positive capillarity metals which in its and their ordinary state are not wetted by the liquid metal. I here make use of the same fact. A platinum tube (fig. 1, Pl. XV.), 6 millim. in internal diameter and 2 centim. in height, is rubbed and soaked in some weak sodium amalgam, and then washed in several quantities of pure mercury. Placing such a tube vertically in the middle of a slab of mercury so that its lower edge is clear of the surface upon which the mercury slab rests, we have the condition shown in fig. 1. A little grain of sodium amalgam dropped into the platinum tube causes no immediate change; but in a time measurable by seconds, say 20 to 30 seconds, the slab starts on its expansion and reaches its maximum size, apparently immediately. It seems, then, that since the effect is not instantaneous, it is a surface effect. The effect when produced is due to an alteration of the surface between the tube and the outer portion of the slab. By dipping the platinum tube further down into the slab so as to be within  $\frac{1}{50}$  of an inch of the bottom, I have found the effect to be distinctly delayed.

§ 10. The fact mentioned in § 9, that the release of the mercury skin-tension by sodium is brought about after a time, short indeed, but appreciable when introduced into the central part of a liquid slab inside the platinum tube, points to the existence of a true diffusion between the metals; and this leads to the second part of this communication. For I have examined already a few such cases, which I will now describe, because I believe the subject of elementary diffusion has been neglected excepting in the case of gases, and even here but little is really known.

§ 11. *Metallic Diffusion.*—The metals potassium and sodium suggested themselves of course at once. They offer excep-



tional facilities for the determination of the composition of the mixture, when they have diffused through mercury, because the mere addition of water translates the alkaline metal into hydrogen. The neutralization of the alkalized water, say, by hydrochloric acid, and subsequent evaporation and weighing, give a control upon the hydrogen translation of the alkaline metal. The mercury is thereupon left nearly ready for weighing.

On the other hand, I have not yet been able to establish a column of mercury having an unlimited stock of pure cold alkaline metal above pure mercury at the same temperature below. I do not see the possibility of it. Granted that when such metals as tin, or lead, or gold, or silver dissolve in mercury, heat may move, such movement of heat is, I should think, swamped in its power of causing convection-currents by the conductivity of the mass. But in the case of the alkaline metals the first contact of the two metals is accompanied by so much heat that the conditions obtainable with other metals are here far more difficult. Perhaps mercury and sodium brought into contact at a temperature far below the freezing-point of mercury might give the required starting-point. If their contact were real and the elevation of temperature very gradual and well controlled, we might have a trustworthy condition; but scarcely so at a single temperature.

Such a condition would represent a certain fixed sodium potential (not infinite, because the sodium has to be disintegrated), on the one hand, and a lower, but not zero, on the other; and between the two the integral of the resistances of the various amalgams after the first contact.

§ 12. This being so, I elected to employ sodium amalgam and potassium amalgam rather than the free metals.

On mixing sodium with mercury, the two combine with great energy and liberate so much heat as to point to a loss of volume. Is this loss of volume, if it take place under any circumstance, so great as to give rise to an amalgam having a greater density than mercury itself?

If  $\frac{m_1}{v_1}$  be the density of mercury and  $\frac{m_2}{v_2}$  that of sodium, and if  $v_3$  be the volume of the amalgam, then the density of

the amalgam would be equal to that of the mercury, if

$$\frac{m_1 + m_2}{v_3} = \frac{m_1}{v_1},$$

or

$$v_3 = v_1 \left( 1 + \frac{m_1}{m_2} \right).$$

If  $v_3$  should be less than this for any ratio between the constituents, the convection-currents of sodium would at all events begin to flow down if such an amalgam were at the top of the mercurial column.

On this point, without making a study of the specific gravity of alloys of sodium of different strengths, I have satisfied myself that, as long as the amalgam is liquid, it is lighter than mercury. This is easily shown by introducing mercury into one limb and the various liquid amalgams of sodium into the other limb of a long U-tube : whereupon the pure mercury always prevails in weight. Now when a solid amalgam of sodium is brought into contact with mercury, heat may be either set free or absorbed. Chemists will understand me if I remind them that  $a$  pounds of water mixed with  $b$  pounds of chloride of calcium will give a body which will set free or absorb heat according as  $a$  is greater or less than  $x$ .

§ 13. Accordingly I made a pound or two of a sodium amalgam of such a strength as to be solid at the atmospheric temperature. This was beaten up in an iron mortar as it cooled. Putting some of this into a porcelain crucible, plunging it into water containing a few drops of hydrochloric acid, and collecting the hydrogen, it was found that after a day or two, if the amalgam was occasionally stirred, all evolution of hydrogen ceased ; the volumes, reduced to dry hydrogen at  $0^\circ$  C. and 760 millim., were  $\left\{ \begin{smallmatrix} 156 \\ 128 \end{smallmatrix} \right\}$  cub. centim. The mercury, after drying, was found to weigh  $\left\{ \begin{smallmatrix} 15\cdot1096 \\ 13\cdot7841 \end{smallmatrix} \right\}$ . This gives the percentage of the amalgam, which I shall call *Am* amalgam :—

Hg.....	98·2	97·97	98·08
Na .....	1·8	2·03	1·92
	<hr/>	<hr/>	<hr/>
	100·0	100·00	100·00 (mean)

The ideal amalgam would perhaps be one of such a composition that heat would neither be set free nor absorbed on

further mixing with mercury. But such an ideal condition could only be ideal in its beginning, and, I think, disturbances due to this cause are insensible in comparison with other sources of error. The above amalgam, when stirred with mercury, may reduce its temperature as much as  $5^{\circ}\text{C}$ .

I am informed that sodium may contain a large quantity of hydrogen. I am not called on to discuss the experiments (not my own) upon which this rests; but I think that any considerable quantity would be expelled on amalgamation. Perhaps the glow or blush to be described immediately and in § 14 is due to the escape of residual hydrogen at the released tension-surface of the mercury.

The first experiment in regard to the diffusion of sodium out of this amalgam into mercury was of course a qualitative one. A U-tube (fig. 2, Pl. XV.) was made of glass tube of  $\frac{1}{2}$  inch internal diameter—the one limb, A, being about 3 inches and the other, B, about  $2\frac{1}{2}$  inches long, reckoned from the inner bend *a*. This was fastened into a massive fusible metal foot to give stability. The U-tube was dried perfectly under the ordinary air-condition, and received pure dry mercury, which stood in both limbs at a height of about  $2\frac{2}{3}$  inches (reckoned from *a*). The whole was placed in a flat-bottomed vessel *g* containing a little melted paraffin, and then upon an immovable slab, to which it was stuck by a few drops of paraffin. The vessel *g* then received water slightly acidulated with HCl so as to cover the mercury in the shorter limb, and reach about  $\frac{1}{4}$  inch above the edge of the glass tube on that side. A test-tube filled with similarly acidulated water was inverted over the shorter limb. Upon the surface of the mercury in A about 15 grams of the amalgam *Am* was placed; this was covered with petroleum, and the tube was plugged with cotton-wool.

Immediately after introducing the sodium amalgam a kind of frosted appearance is seen on the immediately lower parts of the mercury and glass surface in A. This appearance, which is a blush of bubbles, creeps downwards with strange rapidity, reaching the bend, say  $2\frac{4}{10}$  inches, in a quarter of an hour.

In about 30 hours, bubbles of hydrogen appear at the surface of the mercury in B and collect in the pneumatic tube. Such evolution continues sensible for about a month. After two months such evolution ceased, the contents were emptied

out, thereby being of course mixed, and no further evolution of hydrogen could be detected.

Such a method of experimentation is, however, far from quantitative, because when the sodium has diffused down through A as far as  $a$ , it will, being lighter than mercury, rise through B and cause whirls.

The ideal condition of such diffusion would be of course similar to the ideal condition of heat- or electrical transference, where one may have a given potential at one end of the column, and a given lower one, fancifully called zero, at the other.

Perhaps this condition is to be attained with the greatest practical completeness by the simple *long* vertical column.

§ 14. Three glass burettes were made, about a foot in length and an inch in internal diameter. They were drawn out sharply at the bottom into capillary tubes, upon which pressure-taps were fixed in the ordinary way. These were nearly filled with pure mercury. A little of the mercury was allowed to run through so as to fill the capillary and caoutchouc tube.

Upon a tube so prepared and filled, about 15 grams of the amalgam *Am* were placed. The amalgam was thereupon covered liberally with petroleum; and the top of the tube was slightly corked. Instantly clouds of minute bubbles began to make their appearance between the mercury and the glass. In half an hour the whole column appeared frosted (see § 13). On drawing off a measure, say  $\frac{1}{3}$  of the whole, from the bottom after two or three hours, no appreciable amount of hydrogen was to be got from it.

Accordingly the tube was reemptied, cleaned, dried, and refilled. The amalgam (*Am*) was then allowed to rest upon the top for 14 days and nights in an undisturbed and steady place, where the temperature ranged from  $13^{\circ}$  to  $18^{\circ}$  C. At the end of this time the amalgam was drawn off. The drawing off was effected as follows:—A little block of paraffin was hollowed so as to have a smooth cavity of the capacity of about  $\frac{1}{3}$  of the tube in fig. 3. The edge was ground flat, and a flat slab of paraffin served as a cover. The amalgam was drawn into this very slowly so as to stand above the edge; the slab being then pressed down, a unit volume was entrapped. This being transferred to a porcelain capsule, the few drops of

overflow were returned to unit measure, which was again filled up, and so on. The six lowest measures (each about  $\frac{1}{13}$ ) did not show a trace of hydrogen. The seven higher ones evolved hydrogen in the quantities shown in the following table, in which the actual weights of the mercury are reduced to 100, the cub. centim. of hydrogen being recalculated and reduced to dry hydrogen at  $0^{\circ}$  C. and 760 millim. It appears that in 14 days the sodium had penetrated down a little more than halfway, say 7 inches, in quantity appreciable.

I put now these results in such a form that they may be, as far as possible, immediately comparable with the results obtained by other metals. They come out as follows :—

Per cent. Na.	Hg.	Na.
·0035.....	100 and	·0035
·0178.....	„ „	·0178
·0665.....	„ „	·0666
·1769.....	„ „	·1772
·2034 .....	„ „	·2038
·2295.....	„ „	·230
·2414.....	„ „	·242

§ 15. A potassium amalgam prepared in a similar manner was found, when analyzed as in § 13, to have the composition 1·34 per cent. of K. About the same quantity of this was put into the same tube as had been used for the Na, under, as far as possible, the same conditions.

Reducing the evolved H to 0 and 760, as before, it was found that the 13 volumes of the column (all of which were nearly equal except the last, which, instead of about 84–82 grams of mercury, only held about 52, for this was the drainage from the amalgam), had the composition :—

Per cent. of K.
0·00082
·0038
·0146
·0331
·1185
·2061
·2811
·3490

As to the comparison between Na and K, we need only contemplate the potential-difference between 1.92 and 1.34 respectively.

With regard to the frosted appearance mentioned in §§13, 14, it can scarcely be doubted that the minute bubbles which compose it are hydrogen, due to the film of water or vapour on the glass. But while this appearance travels at the rate of at least one foot an hour, there is no sensible quantity of Na to be found at even a lesser depth after fourteen days. The effect must therefore be a surface-effect, and be of the same order as the effect described in § 8, where the mercury-slab expands when touched by sodium amalgam, on account of metals spreading almost instantaneously over its surface and enfeebling its skin. The condition actually set up in the mercury column is probably this:—A minute film of sodium spreads downwards between the mercury and the glass: this decomposes the water on the glass, and so clothes the glass with a film of minute hydrogen bubbles, and the mercury surface with a film of caustic soda, which latter is in absolute contact with the mercury surface. It is a question whether the sodium film is less than, equal to, or more than sufficient to decompose the water—probably more. At all events it is so minute as not to exhibit itself in any chemical reaction. The spectroscopic reaction here has no significance.

The curves Na and K, Plate XVI., which represent these experiments graphically, are not directly comparable with the curves Sn, Pb, and Zn (§ 17) in the same plate, because in the case of Na and K, for reasons given in § 11, it was found necessary to start with an amalgam, and indeed with one containing only about 2 per cent. of sodium. The time in the case of the Na and K amalgams was also a little less than half that occupied in the diffusion of Zn, Pb, and Sn.

§ 16. The rapid penetration of zinc by mercury suggested the question whether, when an amalgam of an alkaline metal was presented to zinc, the mercury would penetrate the zinc and carry the alkaline metal with it. Accordingly the above potassium amalgam was introduced into a hollow cylinder of cast zinc, 17 millim. internal, and 21 millim. external diameter (thickness 2 millim.), 45 millim. external height, 35 millim. internal height (10 millim. thickness of bottom). The

amalgam was scraped upon the zinc so as to ensure contact, and then covered with petroleum. The zinc cylinder was thereupon corked up and the cork covered with paraffin. It was placed in a beaker of distilled water and covered with a tube of water according to fig. 4, Plate XV. After two months' standing at a uniform temperature of about  $15^{\circ}$ , scarcely a pin's-head volume of gas had collected in the top of the tube. Abundance of the semiflocculent fine oxyhydro-carbonate had collected on the zinc and at the bottom of the beaker. That part on the zinc was rubbed off the zinc with an ivory blade, and, together with the sediment in the beaker, dissolved in hydrochloric acid overneutralized with ammonia and sulphide of ammonium. After separation of the Zn, no trace of K could be found. No potassium had found its way through the zinc. Perhaps a more remarkable fact still is this, that on scraping about a gram of the solid metal from the outside of the zinc cylinder, not a trace of mercury could be found in it. Not only, therefore, did the alkaline metal fail to follow the mercury into the zinc, but it prevented the mercury from entering the zinc. Compare this with § 18, where the cylinder of zinc is literally "slaked" by the mercury.

§ 17. Cylinders of zinc, lead, and tin were cast, an inch and a quarter long and  $\frac{7}{8}$  inch in diameter. These were floated on the mercury contained in the tubes described in § 14. The quantity of the mercury in each tube was such that it stood at the same height, reckoning from the bottom of each cylinder. The burettes had been previously lashed to massive stands, cork buffers being interposed between the tubes and the stands. The three were placed side by side on a slab let into the wall, and were protected as much as possible by cloths from sudden changes of temperature. The mean temperature was  $15^{\circ}$  C. The experiments lasted a month, and the extreme range of temperature was from  $13^{\circ}$  C. to  $17^{\circ} \cdot 5$  C.

At the end of the month (31 days) the mercury was run off from the bottom very slowly and discontinuously into the paraffin vessel described in § 14; so that, with the exception of the top quantities, the volumes of the successive portions were very nearly the same. With regard to the top quantities, it is clear that, since the metals float at different depths in the mercury, the surfaces of contact are not the same in the

several cases ; and therefore these top, or richest, amalgams can scarcely be compared. Again, the shape of the bottom of the tube with its capillary &c. puts the lowest or poorest out of court. But as the contents of the lower, irregular part of the tube is not more than a third of the volume of the unit measure, it is only the very lowest amalgam that need be rejected.

In each case there were twelve full unit vessels drawn off, and in each case a fraction of a thirteenth, which last contained the drainage from the metal.

Through the kindness of Dr. Hodgkinson a number of these amalgams were analyzed in the chemical laboratory by Messrs. Adie, Gahan, and Grange, to whom I am therefore indebted. These three gentlemen analyzed the zinc, lead, and tin amalgams respectively. The metals were determined in the following manners :—

*Lead*.—The amalgam dissolved in nitric acid and evaporated with sulphuric acid, and the residue either ignited directly or after washing with dilute alcohol (as sulphate of lead).

*Tin*.—The amalgam dissolved in nitric acid, evaporated to dryness, and ignited (as metastannic acid).

*Zinc*.—( $\alpha$ ) By dissolving in nitric acid, evaporating to dryness, and igniting ; or ( $\beta$ ) by separating the mercury as sulphide and the zinc as sulphide, and igniting (both as oxide of zinc).

§ 18. In Table I. the results of such determinations are given, so that the proportion of the errors of analysis may be compared with the true diffusion in each, and the difference of diffusion in the three cases.

At the end of the experiment the cylinders of tin and lead presented nothing remarkable in appearance. On standing a couple of months the upper part of the lead cylinder has become as hard as zinc, though there is no sensible deformation. The zinc cylinder swelled considerably in the tube ; and when left to itself afterwards, though drained from the mercury, it continued to swell and crack, and ultimately fell to pieces like a “lime-light” lime-cylinder when slaked. Two cones with their apices towards the centre of the cylinder were formed at top and bottom ; the cracking otherwise was for the most part in radial planes.



In Plate XVI. the percentages of metal in the several amalgams of the three metals are given graphically, and without founding-off or other interpolation. The abscissæ reckoned from the left are distances from the bottom ; the ordinates are the corresponding percentages of the respective metals.

TABLE I.

	Zinc. Per cent.	Lead. Per cent.	Tin. Per cent.
1 (bottom). ....	$\left\{ \begin{array}{l} 0.061 \\ 0.062 \end{array} \right\}$ 0.063	$\left\{ \begin{array}{l} 0.188 \\ 0.204 \end{array} \right\}$ 0.196	$\left\{ \begin{array}{l} 0.13 \\ 0.21 \\ 0.174 \end{array} \right\}$ 0.171
2. ....	$\left\{ \begin{array}{l} 0.076 \\ 0.080 \end{array} \right\}$ 0.078		
3. ....	.....	$\left\{ \begin{array}{l} 0.243 \\ 0.225 \end{array} \right\}$ 0.234	$\left\{ \begin{array}{l} 0.28 \\ 0.30 \end{array} \right\}$ 0.29
4. ....	$\left\{ \begin{array}{l} 0.126 \\ 0.117 \end{array} \right\}$ 0.122		
5. ....	.....	$\left\{ \begin{array}{l} 0.303 \\ 0.274 \end{array} \right\}$ 0.289	$\left\{ \begin{array}{l} 0.38 \\ 0.41 \end{array} \right\}$ 0.40
6. ....	$\left\{ \begin{array}{l} 0.214 \\ 0.183 \end{array} \right\}$ 0.199		
7. ....	.....	$\left\{ \begin{array}{l} 0.402 \\ 0.403 \end{array} \right\}$ 0.403	$\left\{ \begin{array}{l} 0.63 \\ 0.62 \end{array} \right\}$ 0.63
8. ....	$\left\{ \begin{array}{l} 0.254 \\ 0.266 \end{array} \right\}$ 0.260		
9. ....	$\left\{ \begin{array}{l} 0.337 \\ 0.338 \\ 0.325 \end{array} \right\}$ 0.333	$\left\{ \begin{array}{l} 0.609 \\ 0.646 \end{array} \right\}$ 0.628	$\left\{ \begin{array}{l} 0.99 \\ 1.01 \end{array} \right\}$ 1.00
10. ....	$\left\{ \begin{array}{l} 0.408 \\ 0.365 \end{array} \right\}$ 0.387		
11. ....	$\left\{ \begin{array}{l} 0.468 \\ 0.454 \end{array} \right\}$ 0.461	$\left\{ \begin{array}{l} 1.03 \\ 0.94 \end{array} \right\}$ 0.99	$\left\{ \begin{array}{l} 1.68 \\ 1.41 \\ 1.25 \end{array} \right\}$ 1.45
12. ....	$\left\{ \begin{array}{l} 0.573 \\ 0.569 \end{array} \right\}$ 0.571		
13 (top). ....	$\left\{ \begin{array}{l} 0.618 \\ 0.735 \end{array} \right\}$ 0.677	$\left\{ \begin{array}{l} 1.38 \\ 1.47 \end{array} \right\}$ 1.43	$\left\{ \begin{array}{l} 1.86 \\ 1.87 \\ 1.76 \end{array} \right\}$ 1.83

§ 19. It appears accordingly that the three metals lead, tin, and zinc, all of which and all of whose amalgams are

lighter than mercury, diffuse downwards through this latter metal in such a fashion that they appear, after a month's interval, in appreciable quantity at a depth of a foot beneath the surface when the temperature is about  $16^{\circ}$ – $17^{\circ}$  C. With regard to this latter point, as to temperature, I suppose that mercury is so good a conductor of heat that the influence of convection-currents is at least as inconsiderable as in the experiments which have been performed for determining the diffusion of soluble salts in water. It is scarcely worth while amusing oneself by dividing these diffusion *percentages* by the so-called "atomic weights" of the metals. A more serious consideration might be the result of the division of the diffused weight by the specific gravity of the metal. Comparing the numbers of the group Sn, Pb, and Zn with one another, we may remember that the metals are all cast, and therefore so far indefinite in structure. This may be especially the case with zinc, which cracks and thereby allows the mercury to rise by capillarity and so enrich itself, and generally set up conditions of amalgamation which I do not care to trace, for I do not see my way through.

As to the comparison of the alkaline group with the Sn, Pb, Zn groups, such comparison must be vague, for the reason that the K and Na are employed as amalgams (as though one would study the diffusion of nitre into water by employing a solution of nitre containing only 2 per cent. of the anhydrous salt); whereas the Sn, Pb, and Zn are used with what was supposed to be a sufficient supply of pure 100-per-cent. metal. But this imperfection of these conditions is manifest if we remember that while the solid metal melts and dissolves downwards, the liquid mercury rises. Accordingly there is, after the first instant of contact, supposing the metals diffuse, no constant metallo-motive force in the same place.

§ 20. I conclude therefore that the general curve of amalgamation, and therefore of alloyage, and therefore perhaps of elementary atomic and molecular diffusion generally, is of the kind shown in fig. 5, Pl. XV. In the case of Na almost the complete curve was obtained; whereas in the case of Zn the point of contriflexure had not been reached. The very fact that the K and Na curves are more complete in this fashion than the Pb, Zn, and Sn, prove to my mind that K and

Na have a far greater diffusive energy than the heavier metals examined. And although in this case the percentage of metal actually found at a given depth was in all cases much less than the percentages of the heavier metals, it will be borne in mind that, while the latter were pure and had acted for thirty-one days, the former were amalgams containing less than 2 per cent. of the metal. Comparing K with Na, I do not think we can draw any conclusion beyond the rather negative one, that the superior diffusive faculty which seems to be the property of K salts in regard to water does not evidence itself, if it exist, when that metal and sodium are compared in respect to their diffusion in mercury. I am far from asserting that such preeminence may not exist; but I do not think that it is here made conspicuous.

My friend Prof. Chandler Roberts has for a long time been engaged in studying the diffusion of melted metals, and the matter has been a subject of frequent conversation between us. I await with great interest the details of his experiments. The relative dates of our publication have no relation to the dates of our experiments.

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### XL. *On a new Insulating Support.*

By Professor SILVANUS P. THOMPSON, B.A., D.Sc.\*

[Plate XVII.]

INSULATING supports consisting of rods rising through the necks of glass jars containing concentrated sulphuric acid, for the purpose of absorbing moisture which otherwise would condense upon the glass, appear to have been first introduced in practice by Sir William Thomson†. Similar devices have been more recently designed by Mascart‡, by Professor Clifton§, and by Professors Ayrton and Perry. The apparatus of Mascart differs only from the original design of Sir W.

\* Read December 8, 1883.

† Proc. Roy. Soc. June 1867, and 'Reprint of Papers on Electrostatics and Magnetism,' p. 322. See also the figure given on page 14 of Maxwell's 'Elementary Treatise on Electricity.'

‡ *Journal de Physique*, t. vii. p. 217 (1878); 'Nature,' xviii. p. 44 (1878); see also Wiedemann's *Electricität*, Bd. i. p. 16.

§ Proc. Roy. Soc. No. 182, p. 300 (1877).