# IX. *On the Microrheometer.*

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[Plate 35.]

The examination of the phenomena of the flow of liquids through capillary tubes, as well as the discovery of the fact that chemical composition influenced the rate of flow, were the work of M. Poiseiulle,* who, in the paper referred to, gave the results of an extended series of carefully conducted experiments, illustrating the laws regulating the rate of flow as affected by the length and diameter of the tube, the pressure acting upon the liquid, and also, within a certain range, by the temperature. His work was carefully examined, in an experimental manner, by a commission of chemists and physicists, and found to be very exact. The formula for the rate of flow which he found was—

$$Q=1836\cdot724(1+0\cdot0336793T+0\cdot0002209936T^2)\frac{HD^4}{L}$$

where—

$Q$ = quantity of liquid passed.
$T$ = temperature in centigrade degrees.
$H$ = pressure on liquid, measured by mercury column.
$D$ = diameter of tube.
$L$ = length of tube.

Poiseiulle pointed out that these results are different from those obtained by other investigators, but the results of others had been obtained by using tubes of much greater diameter, so that the laws regulating the flow of liquids through capillary tubes are different from those relating to wide tubes. The most characteristic law relating to capillary tubes appears to be that the rate of flow varies directly as the pressure; and as it is also the readiest method of testing a tube, I shall only use the

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* "Recherches Expérimentales sur le Mouvement des Liquids dans les Tubes de très-petits Diamètres," 'Annales de Chimie et de Physique' [3], t. vii., p. 50.

term "capillary" for tubes which adhere to this law. POISEIULLE was intending to apply his studies to the action of various substances when in the capillary vessels in the living body, and hence he examined such bodies as alcohol, blood, and various saline solutions. On examining the rate of flow of various mixtures of alcohol and water, it was found that a mixture of about equal quantities of alcohol and water required about three times as much time for passage as either pure alcohol or pure water. The mixture corresponded to a hexhydrate of alcohol, so that, in this case, POISEIULLE discovered a chemical compound by purely physical means. Some results were obtained by dissolving various salts in water, and finding the rates of flow of the solutions; but as there appeared to be no connexion between the combining weights and the rates, POISEIULLE could offer no explanation of the numbers. One thing can be gathered from POISEIULLE's work—that the flow of a liquid through a capillary tube is very seldom comparable with its physiological action in the veins. It was not for many years after this that any attention was paid to the subject, till GRAHAM,[*] in 1861, noticing the existence of the hydrate of alcohol discovered by POISEIULLE, made some experiments to find whether any hydrates of acids could be discovered by this method; and his researches showed that several acids took up water by three molecules at a time, each addition being shown by a further retardation, but always fainter than the previous one. This addition to the work of POISEIULLE showed that the capillary tube might become an important instrument in the hands of the chemist. Lately,[†] M. AUG. GUÉROUT has presented several papers on the subject to the Academy of Sciences, Paris, giving an account of some experiments on the rate of flow of various alcohols, in which he shows that the rate decreases while the molecular volume increases, but not in any definite proportion. GUÉROUT, however, overlooks the most important factor in this kind of investigation, namely, the temperature. He experiments with all his alcohols at the same temperature, while there is a difference of 60° between the boiling points. Now in such a substance as water, a difference of 60° means that the flow is three times as great at the high as at the low temperature, so that some of the alcohols which by GUÉROUT's method seemed to offer the greatest retardation, may really, if compared under just conditions, have the least friction. As regards liquids, it would appear from the researches of KOPP that in order to obtain chemical deductions from their physical examination they must be examined when their vapour tensions are equal, as then they exist under somewhat comparable conditions as to mobility and expansion. GUÉROUT has also in the second of these papers determined the effect of variation of temperature on the rate of flow, and comes to the conclusion that the rate for water varies by a constant factor whose value is 1·025. The experiments were, however, done within a very narrow range, viz.: 10° to 17°; and GUÉROUT seems to have been ignorant of the fact that his countryman, POISEIULLE, carefully determined this some forty years earlier, and

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[*] Phil. Trans., 1861, page 373.

[†] 'Compt. Rend.,' lxxix., 1201; lxxxi., 1025.

arrived at a different result. GRAHAM also published a table from 0° to 70°, but GUÉROUT does not appear to be cognisant of GRAHAM'S work. According to GUÉROUT, the curve representing the effect of temperature would be a straight line, whereas both POISEIULLE and GRAHAM'S numbers correspond with a curve. This shall be considered further on.

About four years ago it occurred to me that as all the work hitherto done with the capillary tube had not fairly tried its usefulness (either by reason of not considering temperature, or of using percentage instead of normal solutions), a fuller investigation of the subject might yield important results. The term "normal solutions" is used in the sense which chemists attach to it, namely, solutions in which the molecular weight of the compound in grammes is dissolved in a litre of water—or, shortly, grammes equivalent per litre. Where this could not be obtained owing to the insolubility of the salt, the strongest possible solution was taken, and its proportional effect calculated. In using the tube of POISEIULLE, which was also used by GRAHAM and GUÉROUT, I found a good deal of inconvenience. The apparatus consists of a tube bent at right angles, the horizontal lower portion being the capillary, and the vertical part consisting of the measuring bulb and tube for applying pressure. The whole was immersed in the liquid whose rate was required, and alternate suction and pressure applied to fill and empty the bulb. This requires so much of the liquid to be experimented upon that I modified the apparatus, as shown in Plate 35, fig. 1, by placing a receiving bulb at the other end of the capillary. But even this had its disadvantages, as the pressure-tube had to be placed alternately at each end, and this disturbance sometimes caused dust to fall into the bulb and choke the tube. It had, however, this advantage over POISEIULLE'S tube—that liquids like bromine could be experimented upon. After working some time with that form, I finally decided to adopt the form of apparatus shown in Plate 35, fig. 2. It consists of a capillary tube at the bottom, attached to which are two bulbs, one for the purpose of measurement and the other as a receiver. Two tubes pass up from these bulbs and end in Y-pieces. One of the Y-tubes from each tube is connected with an inverted Y-tube, and each is also provided with a clip or stop-cock. One of the inverted Y-pieces is connected with the pressure chamber, while the other is left open to the air. By this arrangement the pressure can be turned on to either side, and moreover the apparatus can be filled with any gas other than air. To introduce the liquid to be experimented upon, it is only necessary to undo the connexion of one of the Y-tubes on the measuring bulb side, and run in sufficient liquid. A thermometer is placed between the two bulbs, and its bulb is situated at the mean point of the whole system, thus registering the average temperature of the experiment. In the cases of some mixtures it was found that after some time they deposited a slight sediment which choked the tube. To obviate this another form was devised, as at Plate 35, fig. 3, where the receiving bulb is at the lower end, so that the liquid may be allowed to settle here for some time, and the upper portion forced up into the bulb free from any solid matter.

In his earlier experiments upon gases, GRAHAM gave to the passage of gases through capillary tubes the name "transpiration," which expresses admirably what is meant; but when he came to work with liquids he still used the term "transpiration," although the laws relating to liquids were quite different from those relating to gases; and as the term "transpiration" is not translatable into other languages, being already in use (as in French, for "perspiration"), I have decided to abandon the title, and substitute for it "microrheosis" (μικρός and ῥέω), and to call the instruments above described "microrheometers." The microrheosis of a liquid, then, is the time taken for the passage of a certain volume of liquid through a tube of such dimensions that the rate of flow varies as the pressure, the standard of comparison being in the meantime water.

It appeared probable at the outset that the friction in the microrheometer might be due, in a great measure, to the cohesion of the liquid; and this led me to seek for a method of determining the cohesion of all liquids (which has been published elsewhere),* but I soon found that the two phenomena were not comparable—in fact, the cohesion had almost no effect in retarding the flow. I need not quote the work here, as there will be plenty of proof further on to show the real cause of the retardation. In this paper I shall confine myself to the work I have done on saline solutions, and on the substance (water) in which the salts are dissolved. The tube and measuring bulb with which these experiments were done had the following dimensions. The capillary tube had an average diameter of 0·0938 millim., and deviated only ·002 from a circle. Its length was 21 millims., while the capacity of the glass bulb was 4·0530 cub. centims. Both bulb and tube were made of soda glass, whose expansion had been determined by weighing with mercury at different temperatures, with the following results:—

| | | |
|---|---|---|
| Coefficient from | 0° to 50° . . . | ·0000252 per degree. |
| „ „ | 50° to 100° . . . | ·0000259 „ |

In these experiments the temperature was measured by a thermometer, graduated to tenths of a degree, which had been compared with a standard. The pressure of the air in the chamber was at first regulated by an air-pump, but I found that I could regulate it much more accurately by blowing with the mouth; and this method was generally used when the pressure was not over 1 metre. In the apparatus shown in Plate 35, fig. 2, it will be seen that during one-half of the duration of the flow the liquid in the bulb from which it is flowing will be at a higher level than that in the other bulb, thus adding to the pressure; but as during the latter half of the flow it is below the level, the one effect neutralizes the other. The pressure was measured by a water-gauge, and the temperature of the water in the column noted, and when it differed from 15° a correction was made either way. In using fig. 3, Plate 35, the pressure was altered to take into account the difference in the level of the two bulbs.

At a temperature of 20°, and under a pressure of 1 metre of water, it was found that it took 131·3″ to empty the bulb as an average of the following 10 expe-

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* Trans. Roy. Soc. Edin., vol. xxviii., p. 697.

riments. The time was marked by a stop-watch, the bulb being filled to above the mark, and the watch started when the level of the fluid passed the upper mark, and again stopped as it passed the under mark—

$$131{\cdot}2+131{\cdot}3+131{\cdot}2+131{\cdot}2+131{\cdot}4+131{\cdot}4+131{\cdot}3+131{\cdot}3+131{\cdot}4+131{\cdot}2'' \div 10 = 131{\cdot}29''.$$

It will be seen that this method gives very concordant results, the deviation in these experiments being only $\frac{1}{10}$th of a second, and that most likely due to personal causes. The pressure was then halved—that is, only half a metre of water was used—when the following times were obtained :—

$$263{\cdot}0+262{\cdot}9+262{\cdot}8+263{\cdot}1+263{\cdot}2+263{\cdot}1+263{\cdot}1+262{\cdot}9+263{\cdot}0+263{\cdot}1'' \div 10 = 263{\cdot}02''.$$

As this number is nearly double the former result, the tube may be said to have been capillary, according to the above definition of that term.

The probable error of the mean of the above experiments, calculated by the formula

$$\cdot 6745 \sqrt{\frac{\Sigma\epsilon^2}{n(n-1)}},$$

amounts to ·060″ in the first series, and ·256″ in the second. It appeared that before going into the examination of complex organic bodies, it would be better to attempt to gain some knowledge of the causes of the phenomena presented by the microrheosis of liquids, by thoroughly examining one liquid, to be used as a standard and as a menstruum, and then examining a series of comparable inorganic salts about whose constitution a good deal is already known, dissolved in the standard menstruum. Water was the liquid chosen.

Poiseiulle had noticed that as the temperature rose the rate of passage increased, and at first thought that the loss of density was one of the causes of this; but on examining water at temperatures below 4° he found that the retardation increased very rapidly, whereas the density decreased. Graham also determined the rates for water at different temperatures, but offered no remarks on the phenomena presented. As neither of these investigators determined the rate above 70°, I undertook another examination from 0° to 100°. The temperature was regulated by a large glass water-bath, as shown in Plate 35, fig. 2; and at least 10 experiments were done at each temperature. As a pressure chamber, a large glass reservoir of about 20 litres capacity was used, placed very close to the microrheometer, and connected therewith with tubes of pure caoutchouc (such as toy balloons are made of), of only $\frac{1}{8}$th inch bore. By this arrangement no leakage occurred, and a very slight addition to the air in the reservoir was required after reversing the order of the stop-cocks. The reason for using glass as a reservoir was because it is not nearly so sensitive to slight variations of temperature as copper (used by Poiseiulle), and one has always time to regulate the pressure, even when the temperature of the laboratory is quickly rising or falling.

The following table represents the result of experiments upon water. Each number is the mean of 10 experiments, the probable error from 0° to 60° being under ·2″, and from 60° to 100° under ·4″ :—

| Temperature. | Time. | Temperature. | Time. |
|---|---|---|---|
| ° | ″ | ° | ″ |
| 0 | 235·0 | 30 | 106·0 |
| 1 | 220·8 | 35 | 96·8 |
| 2 | 211·7 | 40 | 88·7 |
| 3 | 205·0 | 45 | 81·8 |
| 4 | 198·5 | 50 | 75·5 |
| 5 | 192·5 | 60 | 65·0 |
| 6 | 187·1 | 70 | 57·5 |
| 7 | 181·0 | 80 | 49·8 |
| 10 | 167·2 | 85 | 47·1 |
| 15 | 146·0 | 90 | 45·5 |
| 20 | 131·3 | 95 | 44·3 |
| 25 | 115·5 | 100 | 43·8 |

It becomes plainly apparent from this table, as well as from curve No. I., that the retardation increases very rapidly as the temperature approaches the freezing point; but we know that the contraction of water as the temperature falls ceases at 4°, and below that becomes negative. It thus appears probable that we have two separate forces at work which act in the same direction in retarding the rate of flow in the microrheometer, but which act in opposite directions in the case of the thermal expansion of water, the one being due to the vibrations we call heat, and the other being due to the gradual arrangement of the water particles to form crystals of ice. The thermal force is much greater if we have regard to the space between 0° and 100°, but we know that water remains liquid below 0° if undisturbed, and could we cool it till its density were as low as ice the crystallic force would then be enormously greater than the thermic. An attempt was made to trace the microrheometrical curve below 0°, but the motion of the water through the tube always caused freezing. Below is a formula shorter than POISEIULLE'S, which agrees with the curve pretty well. Let $\theta=$ temp. C°. and T= time, then $\theta+6{\cdot}36=158{\cdot}93({\cdot}98618)^{T}$, which gives—

| Temperature. | Found. | Calculated. |
|---|---|---|
| ° | ″ | ″ |
| 0 | 235 | 231 |
| 1 | 220·8 | 220·6 |
| 2 | 211·7 | 211·6 |
| 4 | 198·5 | 196·2 |
| 10 | 167·2 | 163·4 |
| 20 | 131·3 | 130·0 |
| 40 | 88·7 | 88·4 |
| 50 | 75·5 | 74·5 |
| 60 | 65·0 | 62·7 |
| 80 | 49·8 | 43·8 |

It is quite evident, on examining the microrheometrical table, that the crystallic force has a retarding action, but what proportion of the retardation it causes could only be determined by examining several liquids and comparing the numbers so obtained with their thermal expansion curves.

Having obtained some knowledge of the menstruum in which the salts were to be dissolved, an examination of the following salts was then commenced. As some of the substances to be examined were only slightly soluble and could not be made of normal strength, the effect of the amount of salt present was first investigated. Pure dry sodium chloride was used for this purpose, and three solutions made up—I. normal, II. half normal, III. quarter normal. The times taken for these three solutions at 20° and under 1 metre of water-pressure were—

| | | Probable error of mean. |
|---|---|---|
| | " | " |
| I. | 140·5 | 0·26 |
| II. | 135·9 | 0·20 |
| III. | 133·6 | 0·22 |
| Water. | 131·3 | 0·06 |

Calling water zero, here we have an exact series in which the retardation increases in the same ratio as the salt present. No. III. retards by 2·3″, No. II. by 4·6″, and No. I. by 9·2″; the time is doubled in each case and so is the salt. The same law was found to hold good for the following salts—

Potassic nitrate,
,, chloride,
,, sulphate,
Sodic nitrate,
,, sulphate.

From this law it follows that any body, however slight may be its solubility, may be compared with salts which are soluble enough to form normal solutions.

To find whether or not the microrheosis is affected by the crystalline form of the salt, the following substances were examined:—

| Formula. | Crystalline form. |
|---|---|
| $KCl$ | Cubic. |
| $NaCl$ | Cubic. |
| $KNO_3$ | Trimetric. |
| $K_2SO_4$ | Trimetric. |

The salts were dissolved to form normal* solutions, and examined at what I will call the standard temperature and pressure, viz.: 20° and 1 metre. The following are the rates:—

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* By normal solutions I mean normal as to the metal, thus $K_2SO_4$ is halved in order to render it comparable with $KCl$, &c.

| Salts. | Rates. | Probable error of mean. |
|---|---|---|
| | ″ | ″ |
| KCl | 129 | 0·08 |
| NaCl | 140·5 | 0·14 |
| $KNO_3$ | 126·4 | 0·06 |
| $\frac{1}{2}K_2SO_4$ | 143·6 | 0·25 |
| Water | 131·3 | 0·06 |

A single glance at these numbers is sufficient to show that the crystalline form has no recognisable effect on the rate. We find two cubic salts, potassium and sodium chloride, acting in opposite directions, the one accelerating the flow by 2·3″ and the other retarding by 9·2″. These it is true are salts of different metals, but below we have potassic nitrate and sulphate both trimetric, and yet they diverge more widely than the two first, the nitrate accelerating the flow by 4·9″, and the sulphate retarding by 12·3″. Solubility, too, does not account for it, because sodic chloride is more soluble than potassic nitrate, and yet it retards while the nitre accelerates, and potassic sulphate is less soluble than sodic chloride, and retards more than it. In fact, some series go one way and some directly opposite; thus in the case of barium, strontium, and calcium the latter flows least rapidly, and at the same time is most soluble, while in the case of the chloride, bromide, and iodide of potassium the first is both least soluble and flows slowest; so that we see that neither the crystalline form nor the solubility of a salt materially affect the microrheosis of its solution; nor can the specific volume affect it, as we know that isomorphous compounds have equal specific volumes. It appeared then that the phenomena of microrheosis could only be affected by the mass or energy of the salt in solution. It may be as well here to explain that as normal solutions are used, mass is synonymous with "atomic weight," "equivalent proportion," or such other term, and that when the energy of the salt is spoken of it means the amount of work which can be obtained from it by successive combinations till it is degraded to such a state that no more work or energy can be obtained from it, which state I describe as "exhausted." The question is, Does each metal change its value when uniting with a acid, or does each metal and each acid radicle have a value of its own which is constant? To determine this four compounds were chosen, namely, the chlorides and nitrates of potassium and sodium (three of which were already known) and their values found—

| Salts. | Time. | Probable error of mean. | Difference $H_2O = 0$. | |
|---|---|---|---|---|
| | ″ | | | |
| $KNO_3$ | 126·4 | .. | −4·9 | |
| $KCl_1$ | 129·0 | .. | −2·3 | +4·3 |
| NaCl | 140·5 | .. | +9·2 | +4·3 |
| $NaNO_3$ | 137·9 | 0·10 | +6·6 | |
| Water | 131·3 | .. | 0 | |

When the time taken is less than water I have used a minus sign, although this may require to be changed at a future time, but I thought that if we only consider time at first it saves confusion, hence I use the above arrangement. It will be seen from the above table that each metal and metalloid or acid radicle has a value of its own, because it does not matter which way the compounds be written, the result is the same; whether we take $KNO_3+NaCl$ or $KCl+NaNO_3$, we get a retardation of 4·3″. Thus on mixing the solutions we get as an average of 10 experiments—

| Salts. | Time. | Difference. | Probable error of mean. |
|---|---|---|---|
| | ″ | ″ | ″ |
| $KNO_3+NaCl$ | 133·45 | +2·15 | 0·08 |
| $KCl+NaNO_3$ | 133·45 | +2·15 | 0·10 |
| Water | 131·3 | .. | .. |

or as the solutions by being mixed are diluted to half strength, on doubling the value we get 4·3″ as before calculated. A series of solutions were then made up and their values determined. The following table gives the results, the numbers given being the average of 10 experiments. The time was determined by a stop-watch which beat fifths of seconds, and I found, after having conducted over 500 experiments, that my personal error was reduced from 0·6 of a second to 0·3, that being the general average of the greater bulk of the work. Each number is the mean of 10 experiments.

| Salts. | Time. | Probable error of mean. | Difference. |
|---|---|---|---|
| | ″ | ″ | ″ |
| Water | 131·3 | .. | 0 |
| Potassic nitrate | 126·4 | 0·06 | − 4·9 |
| „ chloride | 129·0 | 0·08 | − 2·3 |
| „ bromide | 126·4 | 0·15 | − 4·9 |
| „ iodide | 123·9 | 0·10 | − 7·4 |
| „ sulphate | 143·6 | 0·25 | +12·3 |
| Sodic nitrate | 137·9 | 0·10 | + 6·6 |
| „ chloride | 140·7 | 0·14 | + 9·4 |
| „ iodide | 135·7 | 0·06 | + 4·1 |
| „ sulphate | 155·3 | 0·10 | +24·0 |
| Ammonic nitrate | 125·5 | 0·08 | − 5·8 |
| „ chloride | 128·1 | 0·14 | − 3·2 |
| „ sulphate | 142·5 | 0·12 | +11·2 |
| Magnesic nitrate | 155·0 | 0·12 | +23·7 |
| „ chloride | 157·3 | 0·26 | +26·0 |
| „ sulphate | 171·9 | 0·30 | +40·6 |
| Baric nitrate | 141·4 | 0·14 | +10·1 |
| „ chloride | 144·0 | 0·15 | +12·7 |
| Strontic nitrate | 143·2 | 0·00 | +11·9 |
| „ chloride | 145·8 | 0·07 | +14·5 |
| Calcic nitrate | 145·0 | 0·10 | +13·7 |
| „ chloride | 147·6 | 0·05 | +16·3 |
| „ sulphate | 152·2 | 1·48 | +30·9 |
| Cupric nitrate | 150·2 | 0·12 | +18·9 |
| „ chloride | 152·9 | 0·00 | +21·6 |
| „ sulphate | 167·4 | 0·20 | +36·1 |

| Acids. | Time. | Probable error of mean. | Difference. |
|---|---|---|---|
| | ″ | ″ | ″ |
| Nitric acid | 131·4 | 0·11 | + 0·1 |
| Hydrochloric acid | 136·3 | 0·23 | + 5·0 |
| Sulphuric acid | 141·8 | 0·07 | 10·5 |

Now leaving out the acids, which have evidently a special action on water (for a reason given further on), if we take the difference between the nitrate and chloride of any metal we find it has a constant value. The same holds good for the difference between chloride and sulphate or between the various salts of any two metals. Thus we find a constant value for chlorine and the acid radicles as well as for the individual metals, and these values are extremely constant, as will be seen from the subjoined table. There are a few cases in which there would appear to be a slight divergence, but these are in hydrated salts, and the reason is easily found. The following table gives the differences :—

| | Metals. | ″ |
|---|---|---|
| Difference between $\frac{1}{2}N_2O_5$ and Cl in | Potassium | 2·7 |
| | Sodium | 2·6 |
| | Ammonium | 2·6 |
| | Magnesium | 2·3 |
| | Barium | 2·6 |
| | Strontium | 2·6 |
| | Calcium | 2·6 |
| | Copper | 2·7 |

| | | |
|---|---|---|
| Difference between Cl and $\frac{1}{2}SO_3$ in | Potassium | 14·6 |
| | Sodium | 14·8 |
| | Ammonium | 14·4 |
| | Magnesium | 14·6 |
| | Calcium | 14·6 |
| | Copper | 14·5 |

The total difference between the extremes of the three inorganic acids is an average of 17·2″.

The difference between chloride and bromide in the potassium salts is 2·6″, and between bromide and iodide 2·5″; the total difference between the chloride and iodide in both potassium and sodium salts being 5·1″. Two facts are brought out by these numbers : first, that the bodies containing the greatest amount of energy offer the least resistance in the tube—for instance, nitrates all flow fastest, and sulphates, which are fully exhausted compounds, flow slowest ; the second fact is that the greater the mass the less resistance does it offer. We see this in the cases of the chlorides, bromides, and iodides, the last having the highest combining weight, and hence the greatest chemical mass, flow much easier than either of the others. Let us now examine the metals.

Potassium offers the least resistance of the metals (we will not consider ammonium a metal just now), and we will call it zero. Taking all the salts into consideration, we have the following differences :—

| Metals. | Differences.<br>″ |
|---|---|
| Potassium | 0 |
| Sodium | +11·6 |
| Barium | +15·0 |
| Strontium | +16·8 |
| Calcium | +18·6 |
| Copper | +23·8 |
| Magnesium | +28·6 |

Here the second of the above laws comes out very clearly: the greater the chemical mass the less the retardation. In the series of barium, strontium, and calcium, which are analogous metals, this comes out with numerical exactness.

The difference between the metalloids in combination also illustrates these laws. The following table will exhibit this :—

| | ″ |
|---|---|
| Difference between Cl and Br in K salts | 2·6 |
| „ „ Br and I in „ | 2·5 |
| | 5·1 |
| Difference between Cl and I in Na salt | 5·1 |

Here the greater mass of iodine causes the salt to pass much more easily through the microrheometer. We must not forget, however, that the heat of formation of those salts varies very much, and not only has the chloride the lowest mass but it has evolved most energy in its formation. In considering the relation between mass and energy, we had perhaps better look at two series, such as the following :—

| Elements. | Equivalents. | Differences. | Rates. | Differences. |
|---|---|---|---|---|
| Iodine | 127 | 0 | −7·4 | 0 |
| Bromine | 80 | 47 | −4·9 | 2·5 |
| Chlorine | 35·5 | 44·5 | −2·3 | 2·6 |
| Barium | 137 | 0 | 10·1 | 0 |
| Strontium | 87·6 | 49·4 | 11·9 | 1·8 |
| Calcium | 40 | 47·6 | 13·7 | 1·8 |

Now it will be seen that although the masses of the metallic bodies are considerably greater than those of the metalloids, and their differences are greater, yet the effect in the microrheometer is much less.

Again, looking at the rates of the three inorganic acids, it seems clear that water has a special reaction for each acid, as the rates are not removed from each other by the same differences as when metallic solutions are employed, thus—

| Acid. | Rates. | Differences. |
|---|---|---|
| | ″ | ″ |
| $HNO_3$ | 131·4 | + 0·1 |
| $HCl$ | 136·3 | + 5·0 |
| $\frac{1}{2}H_2SO_4$ | 141·8 | +10·5 |
| Water | 131·3 | |

At first thought, we would expect that the acids being salts of the monatomic metal hydrogen, and so exactly comparable with potassium and sodium salts, would show the same microrheometrical reactions; but when we consider, in the first place, the very weak saturative power of hydrogen (as a base), and also that the salt of hydrogen is dissolved in its own oxide, we see that it is probable that the results will not agree with those of a strong monatomic base like potassium. The relation of the acids require a much fuller investigation, as it has lately been shown that acid which has been allowed to stand for some time does not evolve so much heat on saturation with an alkali as acid which has been freshly prepared. Hence on further investigation the above rates may require alteration.

Lastly, as to mixtures. A large number of mixtures have been done, and as they all give exactly the calculated number, only one example need be quoted here by way of illustration. A solution was made up by mixing equal parts of the following normal solutions:—

$$KNO_3,\ K_2SO_4,\ NaNO_3,\ NaCl.$$

Each salt, therefore, exerted only one-fourth of its influence, which gives by calculation a rate of

$$\frac{-4·9}{4}+\frac{+12·3}{4}+\frac{+6·6}{4}+\frac{+9·4}{4}+131·3=136·9''.$$

| | Probable error of mean. | |
|---|---|---|
| Average of 10 experiments | 0·06″ | 136·85″. |

Of course, as each metal and each acid has a value of its own, it does not matter how they are distributed, thus affording further conclusive proof that neither solubility, crystalline form, nor specific volume have any effect upon the microrheosis of a salt.

From the above facts we see that the microrheometer, not merely dealing with the superficial qualities of chemical matter, but bringing to light the fundamental relations of mass and energy, is likely to become the centre of a new branch of the science. My next work will consist of an examination of liquid bodies whose thermal relations are known, so as to find a fundamental relation between the energy expended by elements in forming a certain mass of substance, and the retardation offered by such substances in the microrheometer.

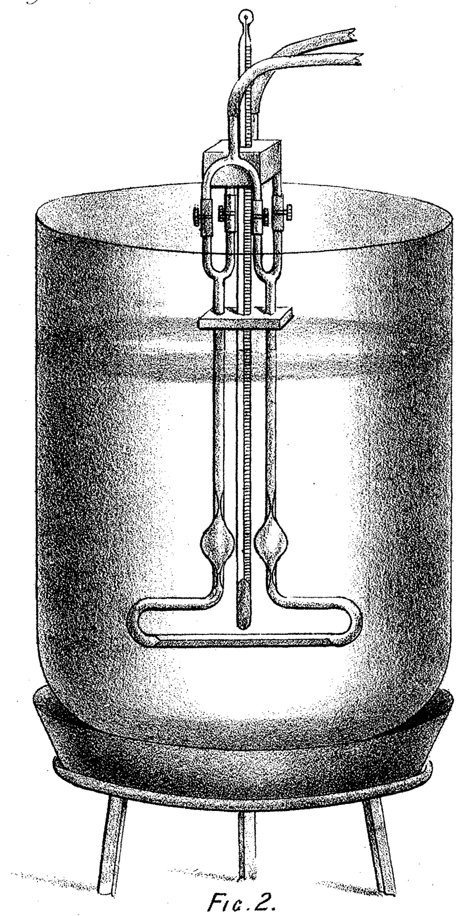

Fig. 2.

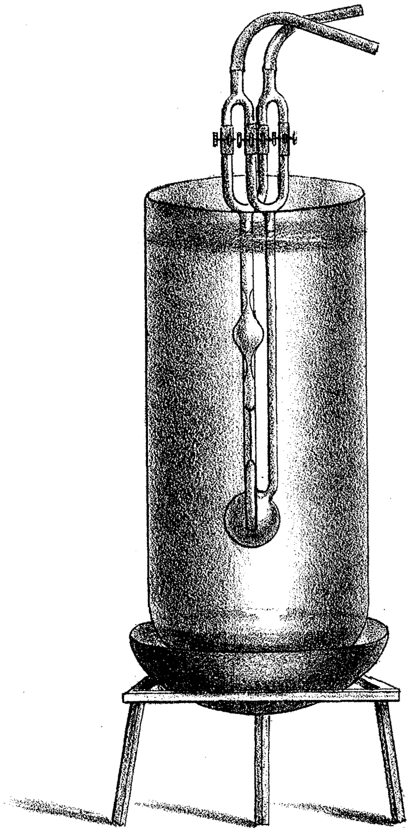

Fig. 3.

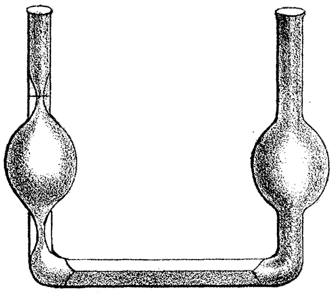

Fig. 1.

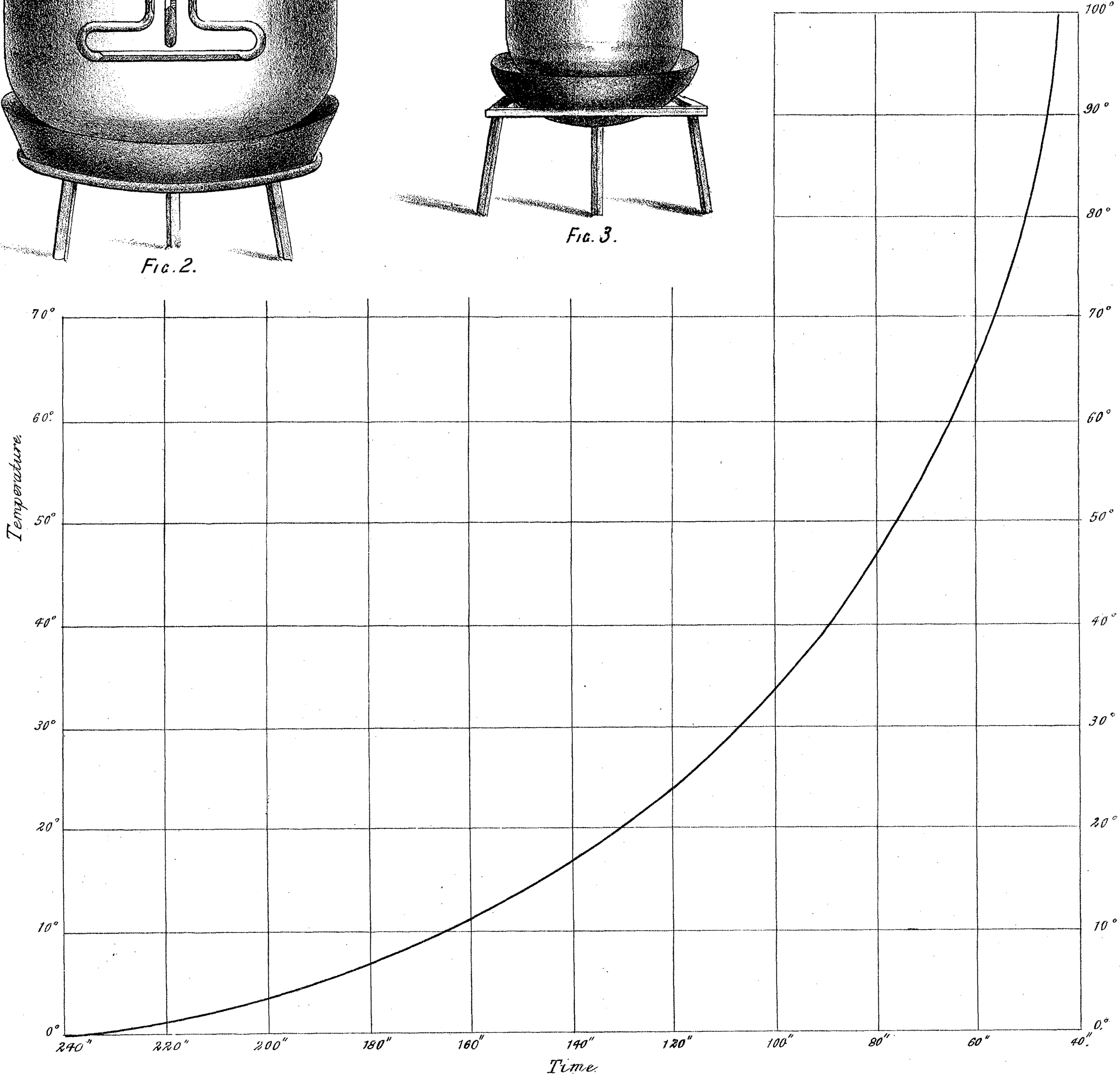

Fig. 4.

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