
On the Apparent Change in Weight during Chemical Reaction

J. J. Manley

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VIII. *On the Apparent Change in Weight during Chemical Reaction.*By J. J. MANLEY, *Hon. M.A. Oxon., Daubeny Curator, Magdalen College, Oxford.**Communicated by Prof. J. H. POYNTING, F.R.S.*

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(1) *Introductory.*—During the year 1890 the late Prof. LANDOLT inaugurated his prolonged researches upon the apparent alteration in the total mass of chemically reacting substances. From the time of its inception until it was brought to a conclusion in 1907, the experimental work was freely varied both as regards the conditions and the nature of the chemical reactions involved. The methods and precautions adopted, together with the final results obtained, are to be found embodied and set forth in detail in LANDOLT'S important memoir, “Über die Erhaltung der Masse bei Chemischen Umsetzungen.”*

* ‘Königl. Akademie der Wissenschaften,’ Berlin, 1910.

Before proceeding to deal with my own investigations in this field of research, it may not be inappropriate first very briefly to recall the chief features of LANDOLT'S work and conclusions.

From LANDOLT'S memoir we find that in all some 15 different chemical reactions were used; these were, for very obvious reasons, brought about within hermetically-sealed vessels. Convenient methods were adopted for ensuring a very slow mixing of the reacting bodies, the period allowed for this purpose varying from two to four days, and therefore the heat evolved during the chemical transformation was so dissipated that no very perceptible rise in the temperature of the vessels and their contents occurred. By following this plan it was hoped that all measurable temporary changes in the volumes of the reaction vessels would be avoided.

In connection with the weighings, devices were introduced for securing as nearly as possible a truly symmetrical disposition of the combined masses of the suspended vessels, their contents and carriers, about the vertical lines passing through the terminal knife-edges of the balance. The relative weights of the reaction vessel and its compensating counterpoise were determined according to the method advocated by GAUSS. The oscillations of the balance beam were observed with the aid of a telescope placed at a distance of 3 metres from the balance; and from the same distance (3 metres), by means of suitable apparatus, the balance was both loaded and the positions of the contents of the pans interchanged. LANDOLT effected most of his final weighings at a temperature approximating 19° C.; this temperature was, for convenience, selected as a standard one, and if at the time of weighing the temperature deviated from the standard value, then from a knowledge of the temperature coefficient of the balance it was possible to calculate the value which the observed resting-point of the beam would possess at 19° C.

It appears that the balance prior to the majority of the weighings was duly fatigued, but whether the necessary fatigue was designedly imposed or was merely the outcome of accidental convenience it is difficult to say.

The fully corrected final values derived from the whole of LANDOLT'S most trustworthy observations are tabulated on pp. 153-4 of his memoir. From those values we find the minimum apparent change in mass during any one chemical reaction to be ± 001 mgr., and the two maxima $+021$ mgr. and -038 mgr. respectively. Of the 48 final values, 23 show an apparent *increase* in weight and the remaining 25 an apparent *decrease*. The mean positive difference deduced from all the tabulated results we find to be $= 009$ mgr., and the mean negative difference $= 015$ mgr.

Combining the whole 48 corrected values, we obtain as a final result an apparent decrease in weight $= 006$ mgr.

Now LANDOLT estimated his possible experimental error to be approximately $= \pm 03$ mgr.; in his memoir he also expresses the opinion that ± 03 mgr. represents the present attainable degree of accuracy in weighing; it will therefore be observed that

both the probable error and the limit of accuracy in weighing, as estimated by LANDOLT, are just five times as large as the final value for the apparent decrease in weight during chemical reaction. The only legitimate conclusion that could be drawn was that which LANDOLT himself drew, namely, that if there occurs any real change in the total mass of reacting substances, then in the cases investigated any such change is less than ± 1 in 10,000,000 parts. This then was LANDOLT'S final verdict after much tedious and highly refined work conducted with patience, skill and resourcefulness, during the lengthy period of 17 years.

For the sake of brevity and to avoid repetition, certain other very important points connected with LANDOLT'S investigations are considered in later portions of this paper; their influence upon the final result is also discussed.

In concluding these introductory remarks, we may observe that a number of experiments bearing upon the apparent want of strict constancy of mass have been conducted by HEYDWEILER.* The reactions chosen were carried out along the lines set down by LANDOLT; but HEYDWEILER'S estimated possible experimental error was larger than LANDOLT'S, being = ± 0.4 mgr.; therefore for the purpose which we have in view further comment is unnecessary.

In an earlier communication to the Royal Society, the present author suggested that the differences in weight recorded by LANDOLT were in all probability due, at least in part, to the presence of slight and unsuspected disturbing factors within the balance beam itself. In the belief that this was the correct view, in June, 1910, one of LANDOLT'S experiments was repeated under circumstances still more favourable than those which obtained during the German chemist's investigations. As the conditions, precautions and refinements which are absolutely indispensable when weighings of the highest order of accuracy are to be undertaken have been described and discussed in two former communications, the author would beg to refer any reader seeking information upon those points to his two other papers.†

We now proceed to describe—

- (a) The manner in which the various experiments were conducted;
- (b) Some additional refinements which were introduced for securing a still higher degree of accuracy in the weighing of counterpoised glass vessels; and
- (c) The final results obtained by the several methods and their bearing upon LANDOLT'S work and conclusions.

(2) *The Balance*.—The balance used in this research was one which has already been fully described.‡ We may, however, repeat that the chief features of the instrument are as follows:—The beam is cantilever in type; its length is 14 cm., and the maximum load for which the balance was built = 200 gr. The beam is cut out from solid, hard-rolled phosphor-bronze plate; the terminal knife-edge blocks are

* A. HEYDWEILER, 'Ann. d. Physik.' (4), vol. V., 1901, p. 394.

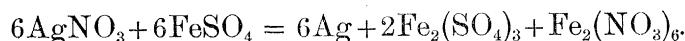
† 'Phil. Trans.,' A, vol. 210, pp. 387-415; 'Roy. Soc. Proc.,' A, vol. 86, 1912, pp. 591-600.

‡ 'Phil. Trans.,' A, vol. 210, p. 407.

secured in positions which fall within the outer struts of the beam. The practically perfect rigidity of such a beam is proved by the fact that the sensibility of the instrument remains, so far as can be demonstrated by actual experiment, quite constant for all loads varying from 0–200 gr. The knife-edge blocks and the planes they engage are of agate; beam, pans and stirrups are highly gilt. The beam is enclosed by one of the author's protecting inner cases which effectively excludes all disturbances which would otherwise be produced within the beam during the time the ordinary case is open for the loading and unloading of the pans, &c. By means of a platinum wire bolometer placed within the beam case, we were at any time able to test the air temperature in the immediate neighbourhood of the extremities of the beam; the bolometer was capable of detecting temperature differences so small as $1/10,000^{\circ}$ C. The actual temperatures of both the interior and exterior of the beam case were noted by means of delicate mercury-in-glass thermometers; with these instruments we were able to read to $1/100^{\circ}$ C. The sensibility, S , of the balance, was set moderately high; it was equal to 45 scale divisions per 1 mgr. and was kept unchanged throughout.

(3) *The Reacting Substances.*—In commencing this investigation some little difficulty was felt in selecting a reaction likely to be the most suitable and convenient for the object in view. Of the 15 chemical reactions chosen by the original investigator, a well defined apparent decrease in the total mass of the reacting substances was usually obtained by means of ferrous sulphate and silver sulphate; and this was particularly the case during the earlier experiments. In two other series of experiments, silver nitrate was substituted for silver sulphate, the second body being, as before, ferrous sulphate. For the one series the final result was +0.003 mgr., and for the other –0.003 mgr.; the mean final value was therefore = 0. Our choice ultimately fell upon the latter reaction, which in LANDOLT's hands had, from the standpoint of the present-day theory of the strict conservancy of the total masses of reacting bodies, led to the most satisfactory conclusions.

LANDOLT states the reaction which takes place between silver nitrate and ferrous sulphate in the form of the equation



He, however, remarks, that the reaction is not complete. In the sequel it will be shown that this conclusion is correct. It will also be shown that had LANDOLT experimented more freely and extensively with silver nitrate and ferrous sulphate the degree of concordance observed by him would, in all probability, have been considerably modified.

(4) *The Reaction Vessels and their Preliminary Treatment.*—For the first series of experiments, the form chosen for the reaction vessels was that largely adopted by LANDOLT; it is best described as an inverted **U**, the two limbs of which were cylindrical bulbs, each having a capacity of about 70 c.c. Two such vessels were

prepared and used together in every experiment. Each limb of a reaction vessel was charged, the one with a convenient quantity of concentrated silver nitrate solution, and the other with an equivalent amount of solution of pure re-crystallized ferrous sulphate. The charges were introduced, as in LANDOLT'S own experiments, through side tubes, t_1 , t_2 (fig. 1). After the vessels had been charged they were weighed, and the weights of the two vessels and their contents were almost equalised by adding distilled water to the lighter one. Then the vessels were allowed to stand side by side for some hours, after which the side tubes were hermetically sealed by the blowpipe. The external volumes of the charged and sealed vessels were now separately measured by the hydrostatic method, and to the one having the smaller volume was added a sealed auxiliary bulb, the volume of which had been adjusted by trial, until it was as nearly as possible equal to the difference in the volumes of the two vessels. One of the side tubes of the vessel having the larger volume was then opened, and water introduced to compensate the weight of the auxiliary bulb of the other vessel; the tube was then re-sealed. The vessels were next immersed in fairly concentrated nitric acid for ten days; after being removed from the acid, they were continuously washed with water for some hours; and then finally wiped with a fine linen cloth and placed under a glass cover until required for use. Proceeding in the manner described, we obtained two charged reaction vessels having as nearly as possible a common volume and therefore an almost equal air displacement; and as their weights differed but slightly, the vessels when suspended from the arms of the balance almost exactly counterpoised each other.

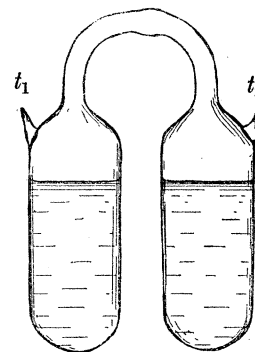


Fig. 1.

(5) *Of the Manner in which Weighings were Conducted. Series I.*—At the outset it was desired to discover the degree of approximation that might be attained when LANDOLT'S determinations were compared with my own; the first series of experiments were therefore planned and conducted on the same general lines as those laid down by LANDOLT, but with the addition of the distinctly more favourable conditions which accrue from the use of a protected balance beam. Here it may also be stated that throughout this research all weighings were carried out in a darkened room, the one window of which faces N.E. The ivory scale of the balance was, at the time of weighing, brightly illuminated by a convergent beam of yellow light; for this purpose a large lens was placed in front of a 6-litre flask filled with a dilute solution of potassium chromate solution in which a carbon filament lamp was placed centrally.

On July 11, 1910, the prepared and charged vessels which have been described in the preceding section were momentarily immersed in distilled water and then wiped with old fine linen, care being taken to avoid contact between the vessels and the hand; they were then suspended from the balance by means of attached platinum wire loops. As vessel A was a little heavier than vessel B, the necessary weights were

added to B to establish equilibrium; the beam was then duly fatigued, and the differential bolometer placed within the beam case read; if the reading = 0, then, with the aid of a reading-telescope, a first set of observations of the oscillating pointer was taken, and the temperature of the air surrounding the beam noted; after this, the bolometer was again read; if the difference between the first and second bolometer readings did not exceed $1/5,000^{\circ}$ C., then, and then only, was the set of observations retained for calculating the resting-point, R.P., of the beam.

July 18, 1910.

TABLE I.

Vessel A in left pan.					Vessel A in right pan.				
Observations.	Pointer readings.	Observations.	Pointer readings.	R.Ps.	Observations.	Pointer readings.	Observations.	Pointer readings.	R.Ps.
No. 1	164	No. 2	68	115·5	No. 1	152	No. 2	28	89·3
" 3	162	" 4	71	116·0	" 3	149	" 4	31	·5
" 5	160	" 6	72	115·5	" 5	147	" 6	33	·3
" 7	158	" 8	74	·5	" 7	144	" 8	37	·5
" 9	156	" 10	76	·5	" 9	140	" 10	39	·0
" 11	154	" 12	78	·5	" 11	138	" 12	42	·8
" 13	152				" 13	137			
			Mean =	115·6				Mean =	89·4
Temperature of { before observation = $17^{\circ}\cdot40$ C. beam case { after ,, = $17^{\circ}\cdot40$,,					Temperature of { before observation = $18^{\circ}\cdot42$ C. beam case { after ,, = $18^{\circ}\cdot44$,,				
Mean R.P. reduced for 18° C. = $114\cdot2$. (1).					Mean R.P. reduced for 18° C. = $90\cdot4$. (2).				
Other reduced R.Ps. similarly { = $115\cdot1$. (3). obtained during the same { = $114\cdot7$. (5).					Other reduced R.Ps. similarly { = $90\cdot8$. (4). obtained during the same { = $90\cdot5$. (6).				
Taking the sensibility of the balance = 45, we find from (1) and (2) the difference in the weights of the two vessels to be									
$\frac{114\cdot2 - 90\cdot4}{2 \times 45} = 0\cdot264 \text{ mgr.}$									

Using convenient lifters, the positions of the vessels A and B were now interchanged and the beam again fatigued; observing the precautions and same method of procedure as before, new data were obtained for calculating the R.P. In general, the data secured both before and after reversing the positions of the two vessels enabled us to make six independent calculations of the R.P. The average value deduced from each set of six R.Ps. was then, by means of the temperature coefficient of the balance,

reduced for a standard temperature of 18° C. We now possessed all the information necessary for a first determination of the difference in the weights of vessels A and B.

Leaving the positions of the vessels unchanged and the beam free to swing, we, somewhat later, effected, by the methods of reversal and vibration described above, a second determination of the apparent difference in the weights of A and B. Following this plan, we usually obtained during the course of a day from 2 to 3 complete and perfectly independent comparisons of the relative masses of A and B. From these completed determinations, a mean difference value for the whole day was deduced. With the object of removing any possible ambiguity, the actual data together with the final results secured during one day are set out in Table I. on p. 232.

Similarly, by using every possible combination of the two sets of reduced R.Ps., we obtain the differences tabulated below :—

TABLE II.

From experiments (1) and (2), A = B + 0·264	mgr.	- 004	Differences from the final mean value.
” ” (1) ” (4) ” = ”	·260	- 008	
” ” (1) ” (6) ” = ”	·263	- 005	
” ” (3) ” (2) ” = ”	·274	+ 004	
” ” (3) ” (4) ” = ”	·270	+ 002	
” ” (3) ” (6) ” = ”	·273	+ 005	
” ” (5) ” (2) ” = ”	·270	+ 002	
” ” (5) ” (4) ” = ”	·266	- 002	
” ” (5) ” (6) ” = ”	·269	+ 001	
Final mean differences found on July 18 = 0268		± 004	

This table shows the maximum variations from the final mean value for the day to be approximately = ± 007 mgr. ; and as the vessel and its contents weighed 127 gr. we observe that in this case, which is one of the most concordant of the whole series, the mean value was liable to a fluctuation the order of which was about 1 in 17,000,000 parts.

Proceeding according to the plan just explained and indicated in Tables I. and II., we obtained the 9 daily final mean differences in the weights of A and B set forth in Table III. ; the maximum variations to which the several mean values were subject, and also the corresponding degrees of accuracy attained are likewise stated. There were in all 169 weighings of A against B before reversal, and 173 after.

At 10.30 a.m. on July 25, the contents of A were mixed ; 7 hours later the first of the new series of weighings was commenced and continued at intervals during the succeeding 5 days, after which the observations ceased. The daily final mean values for the difference in the weights of A and B were the following :—

	July 25,	26,	27,	28,	29,	30.	
Differences in milligrammes =	0·37,	·28,	·22,	·35,	·37,	·36.	Mean = 025.

TABLE III.

Date.	Differences in the weights of A and B.	Maximum variations.	Approximate degree of accuracy.
July 14, 1910 . .	mgr. 0·265	mgr. ± ·033	± 1 in 3·8 millions
„ 15 „ . .	·338	·005	„ 25·4 „
„ 16 „ . .	·285	·016	„ 8·0 „
„ 18 „ . .	·268	·007	„ 17·0 „
„ 19 „ . .	·223	·009	„ 14·0 „
„ 20 „ . .	·260	·020	„ 6·4 „
„ 21 „ . .	·360	·038	„ 3·3 „
„ 22 „ . .	·350	·035	„ 3·6 „
„ 23 „ . .	·280	·042	„ 3·0 „
Mean . . .	·292	± ·023	± 1 in 9·4 millions

We may here mention that the maximum variations in the daily mean values, and also the degrees of accuracy indicated, were of the same order as those shown in Table III.

The final result of all the experiments of Series I. may now be stated thus:—

Before mixing the contents of A, the difference $A - B = +0\cdot292$ mgr.
 After „ „ „ „ „ „ $A - B = +\cdot325$ „
 Apparent change in mass = $+\cdot033$ „

It is curious that the apparent change in mass here shown is almost exactly equal to the limit given by LANDOLT for accurate weighing.

Series II.—After the observations and experiments which have been dealt with in the immediately preceding section had been completed, various circumstances arose which for a time prevented me from continuing this research; but in April, 1911, opportunity was again afforded for resuming the work.

Adopting, with slight modifications, the method of procedure followed in Series I., the weight of A in terms of B was again determined, the number of independent values obtained being 36. The final mean value deduced from the whole of the observations for the difference in the weights of the two vessels and their contents was

$$A - B = +0\cdot026 \text{ mgr.}$$

In this set, the maximum and minimum values found for the difference $A - B$ were respectively $+\cdot042$ mgr. and $+\cdot005$ mgr. Of the 36 determinations, 20 exhibited an average variation from the mean value = $+\cdot007$ mgr.; for the remaining 16 determinations the average variation was = $-\cdot008$ mgr.; for any one determination the average deviation from the final mean value may therefore be taken as approximately = $\pm\cdot008$ mgr.

After mixing the contents of B, 16 independent determinations of the difference, $A-B$, were made ; from these was calculated the final mean difference

$$A-B = +\cdot022 \text{ mgr.}$$

During this set of measurements the observed maximum and minimum values for the difference $A-B$ were respectively equal to $+\cdot049$ mgr. and $+\cdot003$ mgr. Of the 16 determinations, 9 showed an average deviation from the mean value = $+\cdot009$ mgr. ; for the remaining 7, the average deviation was = $-\cdot011$ mgr. ; the final mean variation may therefore be taken as = $\pm\cdot010$ mgr.

Concisely stated, the final conclusion reached by means of Series II. is,

Before mixing the contents of B,	the difference	$A-B = +\cdot026$	mgr.
After	„ „ „ „ „	$A-B = +\cdot022$	„
	Apparent change in mass	= $-\cdot004$	„

The apparent change here observed is of the order of about 1 in 32,000,000 parts. We now proceed to review, very briefly, the results yielded by the two series of experiments, and to indicate the probable causes and sources of the observed variations.

(6) *Of the Possible Errors associated with the Experiments of Series I. and II.*—In itself, and from a certain point of view, the final result secured by means of the experiments of Series II. was both excellent and gratifying. We may not, however, ignore the important fact, that this result is not in harmony with the final result obtained from Series I. As the two sets of measurements were effected under precisely similar conditions, the two final values are, so far as can be known, equally reliable. If we combine the two final values, then the apparent change in mass is equal to

$$\frac{1}{2}(\cdot033 - \cdot004) = \cdot015 \text{ mgr.}$$

Or, the apparent change in the whole weighed mass is equal to 1 in 8·5 million parts ; this degree of accuracy was frequently attained by LANDOLT and by him sometimes surpassed.

In our opinion it was now definitely established that the observed apparent changes in mass arise, not from any appreciable inherent or unallowed-for defects in the balance itself, but that the fluctuations were the natural outcome of certain unsuspected variables associated with the glass reaction vessels and their contents. It is believed that at least three such variables have been unwittingly allowed to creep, not only into my own experiments, but also into the majority of those of other observers. These three variables may be generated by—

- (α) Very small yet sufficiently distinct, irregular and unequal convection currents in the air near the balance pans.
- (β) Slight differences in the total external areas of the two vessels.

(γ) A want of strict equality in the temperature of the contents of the two vessels.*

We now proceed to a more detailed consideration of each of the above-named variables; we shall also attempt to show how the errors incidental to each may be either overcome or eliminated.

(6) *a. Of certain Irregularities produced by Air Streams.*—From the law of uniform decay, we know that the path of a vibrating pendulum will shorten by nearly equal steps during each successive vibration; and therefore in a series of observations of the extreme positions of an oscillating balance pointer, we expect to find the same law operative; in practice, however, we frequently get not *uniform* but well marked *irregular* decay.

On a former occasion† I was able to show that the temperature of the air within an ordinary balance case is seldom or never either constant or uniform. Any differences in temperature, however small, tend to set up a more or less complicated and ever-changing system of convection currents; and these currents produce certain effects upon any object that is being weighed. If the volume of the object be considerable, then by using the most refined methods available for weighing, the existence of the air streams should be rendered evident by corresponding irregularities in the successive differences in a series of pointer readings. That such irregularities are not only theoretical possibilities, but also insistent realities, may be seen by referring to the columns headed “pointer readings” in Table I, p. 232. In the first of those columns of “pointer readings” the successive differences have a common value, namely 2; it is suggested that the equality of the differences is due (*a*) to the absence of appreciable air streams, or (*b*) to the presence of two practically equal air streams acting in opposition, and therefore mutually compensating each other’s effects. In the third and fourth columns of “pointer readings” (Table I.) we observe that successive differences, instead of possessing a common value, range in value from 1 to 4. Any or all of these variations might well be brought about by—

- (1) A single air stream acting upon one pan only;
- (2) Two or more air streams acting in unison upon both pans;
- (3) Differential effects produced by opposition air streams.

Probably, however, they were sometimes due to one cause and sometimes to another—for it is difficult to see how an ever-changing temperature, such as the one the existence of which I was able to prove upon a former occasion, could possibly give rise to perfectly steady and uni-directional air streams.

* There is also a possibility that during sudden changes in the temperature of the room, the balance shelf may undergo a minute but perceptible warping and thus temporarily tilt the balance case and so introduce a fourth variable. As this point has been dealt with in the ‘Roy. Soc. Proc.’ A, vol. 86, p. 598, we do not further allude to it here.

† ‘Phil. Trans.’ A, vol. 210, p. 405.

Granting, then, the existence of air streams which vary both in direction and intensity as proven, the question which now confronted us was: How can these air streams be best suppressed, or their effects neutralised? As it appeared impossible to institute any simple or convenient scheme for neutralising the disturbances, an attempt was made to eliminate their cause.

As a result of earlier experiments, it was known that a delicate bolometer placed within an ordinary balance case almost invariably reveals the existence of continuous fluctuations in the temperature of the contained air. In general, the fluctuations assume the form of minute and somewhat irregular oscillations about some mean temperature. Such disturbances occurring in the vicinity of the beam may be reduced to a vanishing point by the simple expedient of enclosing the whole beam with a small additional inner case. With these facts before us, it was concluded that the difficulties arising from the presence of air streams might be successfully met by completely enclosing the pans and stirrups by means of shells having a very high conductivity for heat. Theoretically, the following very distinct advantages are gained by the use of such shells, more particularly if the exterior surfaces are polished and the interior coated with carbon :—

- (1) The effective volume of the disturbed air is very greatly reduced ;
- (2) A shell having a high conductivity for heat may, when placed within a balance case, be regarded as possessing throughout a strictly uniform temperature ; in consequence of this, combined with the fact that the inner or carbon skin has the power of rapidly absorbing and radiating heat energy, the contained air will also acquire the same uniform temperature ;
- (3) Radiant energy falling upon the outer polished surface of the shell will be almost entirely reflected ; the insignificant fraction that may enter will be incapable of producing any appreciable disturbing effects in the air enclosed by the shell.

All these advantages were effectually secured in the following way :—

Four half cylinders of stout sheet copper were prepared, the diameters of two being made a trifle less than the diameters of the other two. Using two half-cylinders, one of each size, a complete closed cylinder could at any time be formed by so placing the two portions that the vertical edges of the wider half slightly overlapped and just gripped the two corresponding edges of the narrower one. The height of the compound cylinders was as nearly as possible equal to the vertical distance between the upper surface of the base of the ordinary balance case, and the lower surface of the aluminium base-plate of the auxiliary beam case above. Before being used their inner surfaces were coated with Indian ink and their outer surfaces rough polished with fine sand-paper. The device was now tested. First, the reaction vessels were re-wiped and again suspended from the arms of the balance ; then the

two pans, together with their contents, were enclosed by means of the copper cylinders. Taking all the usual precautions numerous determinations of the R.P. were now made; in any one series the observed rate of decay in the amplitude of the vibrations was, with very few exceptions, almost perfectly uniform, and even in the exceptional cases, the deviations from uniformity were so small as to become negligible. The conclusion was therefore drawn that this device amply fulfils the functions for which it was designed.

The success which attended the introduction of the enveloping cylinders is primarily attributed to the fact that the fluctuations in the temperature of the air within an ordinary balance case are so extremely small; so minute are they that all ordinary attempts to discover their existence must necessarily end in failure. We desire to emphasise the importance of this fact: for we believe that in the presence of abnormally large fluctuations, measures even more stringent than those adopted here might be required for maintaining perfect uniformity in the temperature of the air within the cylinders. It is only by preventing *all* fluctuations in the temperature of the air immediately surrounding the pans and stirrups that we can hope to completely suppress disturbing air streams. We do not, of course, assert that the disturbing effects of air streams were *completely* neutralised, but we are convinced that their magnitude was so far reduced that, for all present practical purposes, the assumption of a zero value was permissible.

(6) β_1 . *Of certain Errors producible by Differences in the Areas of two Reaction Vessels.*—In the immediately preceding section is given a method whereby small air streams flowing in the vicinity of the balance pans may be suppressed; and in the same section it is also stated that under the new conditions a very concordant set of values for the reduced R.P. may generally be obtained from *any one series* of pointer readings. It was, however, found that the mean R.P., deduced from one series of observations, frequently deviated very slightly from the mean R.P. value calculated from another series; slightly differing values were obtained not only from day to day, but sometimes also from hour to hour during the same day. After many tentative experiments, the conviction was borne in upon us that the deviations were, in all probability, due to corresponding variations in the amount of moisture condensed upon the surfaces of the reaction vessels.

LANDOLT and others have laid great stress upon the fact that the *volumes* of the two vessels used in any given experiment were adjusted by trial until they were not appreciably different; any difference that might exist between the two was removed by adding to the one possessing the smaller volume a suitable length of sealed glass *tubing*. Now, if nothing more than a cursory thought is bestowed upon the matter, it may easily be unconsciously assumed that as the two vessels are almost, though not quite, equal in volume and very similar in form, their superficial areas are, for all practical purposes, identical. An analysis of the actual facts may lead, as will be seen, to a very different conclusion. We would draw attention to several very important

and interesting points. Let us consider the following three cases and the possible attendant errors :—

- (1) The two vessels have identical forms but *decidedly* different volumes ;
- (2) The two vessels are identical in form but possess *slightly* different volumes ;
- (3) The two vessels are precisely equal in volume, but whilst the form of the one is truly *spherical* that of the other is slightly *ellipsoidal*.

Case 1.—In one of my own experiments (*vide infra*) the difference in the volumes of the two vessels was found to be = 8 c.c. It was decided to equalise the volumes by adding to the vessel possessing the smaller volume a spherical glass bulb. Accordingly a bulb was formed and its diameter repeatedly altered until it was found to be 2·47 instead of the exact value 2·48 cm. demanded by theory. Neglecting the attached thin stem and hook, we find the external area of an 8 c.c. sphere to be = 19·2 sq. cm. The volumes of the two reaction vessels were respectively 145·2 c.c. and 137·2 c.c. ; and assuming the vessels are truly spherical in form, we find that the corresponding external areas are 133·6 sq. cm. and 128·7 sq. cm. On adding the volume-compensating sphere to the smaller vessel, the respective and opposed external areas of the two become 133·6 sq. cm. and $128·7 + 19·2 = 147·9$ sq. cm. The difference in the areas is therefore = 14·3 sq. cm. Had LANDOLT'S plan been followed the air displacement of the two vessels would have been equalised by using a cylinder of the required volume prepared from a glass tube. Let the cylinder having $V = 8$ c.c. be made from tubing (*a*) 2 cm., and (*b*) 1 cm. in diameter. In the former case the length of the cylinder will be 2·55 cm. and in the latter 10·20 cm. The external area of the shorter cylinder will be = 22·3 sq. cm., whilst that of the longer one will be = 33·6 sq. cm. The superficial areas of the two cylinders will therefore exceed that of a sphere of the same volume by approximately 3 sq. cm. and 14 sq. cm. respectively. Or, the ratios of the opposed areas of the two reaction vessels will be changed from $147·9/133·6$ to the respective values of $151/133·6$ and $162·3/133·6$.

Case 2.—This case also may best be illustrated by means of the actual data acquired in a particular experiment. For the sake of brevity we term the two reaction vessels X and Y. For X, $V_1 = 145·15$ c.c., and for Y, $V_2 = 143·56$ c.c. ; and therefore $V_1 - V_2 = 1·59$ c.c. The volume of the compensating sphere used was found to be 1·68 c.c. instead of the required exact value 1·59 c.c. ; its external area therefore equalled 6·8 sq. cm. Regarding X and Y as spheres we find their respective superficial areas to be 133·5 sq. cm. and 132·6 sq. cm. ; therefore the total external area of Y plus that of the volume-compensating sphere = 139·4 sq. cm. ; and the ultimate difference in the areas of X and Y is equal to 5·9 sq. cm.

If the volume compensator be formed from tubing having a diameter of 1 cm., we find that its external area will be = 8·3 sq. cm. ; the final ratio of the surfaces of X and Y exposed to the influence of the air will therefore = $140·9/133·5$.

Case 3.—In this case it is assumed that the two reaction vessels have strictly equal

volumes; also, that whilst the one is a true sphere, the form of the other is ellipsoidal. It follows, therefore, that although the volumes are identical the superficial areas of the two vessels will be somewhat different.

I desire to express my indebtedness to Mr. H. HILTON, formerly Fellow of Magdalen College, Oxford, for his kindness in determining for me the changes that occur in the superficial area of a prolate spheroid as the ratio of the major and minor axes is varied within the limits 1 : 1 and 1 : 0·667. Mr. HILTON's results are here given in tabulated form :—

Ratio of axes of prolate spheroid of volume = 200 c.c. } = 1	0·95	0·90	0·80	0·75	0·667
Surface of spheroid in square centimetres } = 165·39	165·48	165·71	166·79	167·71	169·93

From the above data it follows that when the ratio of the axes is 1 : 0·765, the superficial area of the spheroid is greater than that of a sphere of the same volume by 2 sq. cm. Very similar changes are found for corresponding oblate spheroids.

(6) β_2 . *Of the Weight of a Water Skin on the Surface of Jena Glass.*—Having satisfied ourselves that the superficial areas of two vessels of similar form and equalised volumes may differ considerably, the next obvious and important step in our enquiry was to determine, as accurately as possible, the weight of water vapour that might condense upon a glass surface. It is well known that glass is hygroscopic, and that different varieties of glass exhibit distinctly different hygroscopic properties. In all the final experiments described in this paper, vessels of Jena glass only were used; we therefore confine our attention to that particular glass and its comportment towards aqueous vapour.

By repeated trials we at last obtained a suitable and almost perfectly spherical bulb of Jena glass; the attached tube, which was short and of small diameter, was drawn out and bent round so as to form a small hook, the tip of which was sealed before the blowpipe. A small stool bridged one of the balance pans and upon it was placed a cylinder containing a little distilled water. The glass sphere was then, by means of a fine silver wire, suspended from the balance and placed within the cylinder and as near the water as circumstances permitted. Observing the usual precautions for refined weighing, the apparent weight of the sphere was repeatedly determined; when its weight was found to remain constant the water was removed from the cylinder and a similar volume of concentrated sulphuric acid introduced. After the lapse of some considerable time the apparent weight of the sphere was repeatedly re-determined. The barometer was read and reduced for temperature, and the temperature of the balance case noted at intervals; finally, the mean diameter of the glass sphere was measured and the corresponding external area calculated. We now possessed all the

data necessary for estimating, with the aid of certain tables, the total weight of the invisible water skin (as it may be appropriately termed) that had formed upon the sphere during the time it was suspended in air saturated with aqueous vapour; presumably this skin had been removed when the final weighings over sulphuric acid were effected. The data, together with the final result, are set forth below:—

$$\text{Jena glass sphere} \left\{ \begin{array}{l} \text{Diameter} = 3.0 \text{ cm.} \\ \text{External area} = 28.4 \text{ sq. cm.} \\ \text{Volume} = 14.1 \text{ c.c. (Taken} = 14 \text{ c.c.)} \\ \text{(Apparent weight in damp air)} - \text{(apparent weight in dry air)} = 0.118 \text{ mgr.} \end{array} \right.$$

Reduced barometer = 753 mm. = P.

Mean absolute temperature in balance case = 295°.

Pressure of water vapour at 295° A = 20 mm. of mercury = p.

Weight of I.L. of dry air at 753 mm. and 295° A = 1.185 gr.

“ “ moist “ “ “ $\frac{P - .38p}{760} \times \frac{273}{295} = 1.179$ “

Therefore 14 c.c. dry air at 753 mm. and 22° C. weigh .016590 gr.

and 14 “ moist “ “ “ “ .016506 “

Loss of buoyancy for sphere = difference = .000084 gr.

The increase in the apparent weight of the sphere is due to the joint effects of two causes acting in the same direction—

- (1) a decrease in the density of the air owing to the presence of aqueous vapour; and
- (2) the formation of a water skin upon the sphere.

The weight of the water skin will therefore be equal to $0.118 - .084 = .034$ mgr. From this we find the weight of the water skin upon 1 sq. cm. to be equal to $.034/28.4 = .0012$ mgr.; and this we accept as the maximum value obtainable under the conditions of pressure and temperature that existed during the determination.* In practice, the maximum density for the water skin would very seldom be realised. In connection with some of the experiments carried out during the summer of the year 1910, a hygrometer was set up quite close to the balance case. The mean air temperature for some days was approximately equal to 19° C., and the mean reading for the wet bulb thermometer for the same period was approximately 16°·5 C.; the truth will therefore be closely approached if we assume the mean weight of the water skin per 1 sq. cm. of the glass to be equal to .001 mgr. instead of .0012 mgr. as found above. Accepting the smaller value, we find the respective weights of the water skins that

* IHMORI, experimenting with boiled-out Jena glass, found that the water skin varied within the limits .035 and .068 mgr. per 100 sq. cm., or a mean approximately = .0005 mgr. per 1 sq. cm. (Quoted in LANDOLT'S memoir.)

may be formed upon the several volume-compensators discussed in Cases 1 and 2 (pp. 239 and 240) to be as follows :—

<i>Case 1.</i> —Spherical compensator.		Water skin	= '014 mgr.
	Short cylindrical compensator.	Water skin.	= '017 „
	Long „ „ „ „		= '029 „
<i>Case 2.</i> —Spherical compensator.		Water skin	= '006 „
	Cylindrical „ „ „		= '007 „

It is almost superfluous to point out that the density of the water skin will be subject to fluctuations ; it is, in fact, a variable dependent upon three others ; namely, the pressure, temperature, and hygrometric state of the adjacent air.

The difficulties and uncertainties associated with the variations in the weight of a water skin were, it is believed, successfully met and overcome by the simple device which we now describe.

(6) β_3 . *Of the Methods used for the Removal of Water Skins.*—Some observers may be considerably surprised to learn that anyone should attempt to weigh accurately glass vessels without previously drying the air within the balance case in the usual manner. This departure from a time-honoured, orthodox, and, as we shall try to show, sometimes worse than useless custom, was, on our part, of deliberate design.

Let us consider the actual facts. As ordinarily practised, the air within a balance case is dried by means of such substances as solid calcium chloride, sticks of caustic potash or soda, phosphorus pentoxide, or by concentrated sulphuric acid contained in shallow vessels placed upon the bottom of the case. Any of the substances named will lap up the moisture in the lowest layers of air with great avidity ; but as the density of air increases with the removal of moisture, and as an attempt is usually made to maintain the temperature of the balance both uniform and steady, it will be necessary to depend almost exclusively upon the inter-diffusion of the dry and damp air for completing the removal of the moisture. Remembering the law governing the rate of the diffusion of one gas into another, and that usually for our present purpose we may take the ratio of the densities of ordinary and of dried air as 1/1'005, it will be at once apparent that such a process is both lengthy and inconvenient.

Again, whenever the shutter of the balance case is lifted the greater portion of the dried air will be lost ; this loss can only be replenished by the further expenditure of valuable time. The introduction of some form of stirrer for mixing the air during the initial process of drying would frequently be objectionable ; for a stirrer in motion would create a suction in places and so dust, otherwise harmlessly reposing in out of the way crevices, would be drawn into the air and in part be subsequently deposited upon the balance pans and upon the objects placed upon them. But a still further objection to the use of the ordinary method of drying the air may be given.

In the course of some preliminary experiments with desiccating reagents, a distinctive

odour frequently manifested itself when solid caustic soda was used; and it was suspected that the odour indicated the presence in the air of minute particles of the more or less hydrated reagent. Our suspicions were tested in the following way:— Two clean porcelain dishes, each $4\frac{1}{2}$ inches in diameter, were taken; the one was charged with short sticks of caustic soda, and the other with a little “conductivity” water which was then tinted with methyl orange; the two dishes were placed side by side and covered with a large bell-jar. After the lapse of several hours the bell-jar was removed and held in a horizontal position; a Bunsen flame was then introduced; the flame was at once tinged faintly but perceptibly yellow, thus showing the presence of soda particles. It was next observed that the colour of the methyl orange was markedly yellow, thus indicating the presence of free alkali; we therefore proceeded to titrate the alkaline solution with N/100 HCl, and found that between 4 c.c. and 5 c.c. of the acid were required for the neutralisation of the absorbed alkali; from this it follows that the amount of caustic soda present in the water was equal to nearly 0.2 mgr.* Acid was then added until the colour of the indicator was decidedly pink and the dishes were again covered with the bell-jar. After some considerable time it was found that the excess of acid had been neutralised, the methyl orange having re-assumed a bright yellow tint. From these observations we conclude that the moisture in the air is so powerfully attracted by the drying reagent that a perceptible rebound from the absorbing surface follows. Although no experiments were made, it appears reasonable to conclude that similar phenomena would attend the use of other desiccating bodies.

In concluding this brief criticism of existing methods, we desire to remark upon some possible inaccuracies that may follow the use of sulphuric acid as a desiccating reagent.

On exposure to air concentrated acid quickly becomes diluted over its surface; as dilution proceeds the acid develops an appreciable vapour tension; it therefore follows that surfaces exposed in the vicinity of the acid will first lose their water skins and so become lighter; then, with prolonged exposure, they will acquire acid skins. I myself have frequently noted an increase in the weight of a porcelain crucible over-dried (if I may use the term) in this way.†

Seeing then that the usual method for drying the air can but lead in the direction of uncertain values it was abandoned for the following plan which proved both convenient and highly satisfactory.

* This experiment has recently been repeated. The volume of N/100 acid required for neutralising the alkali absorbed by the water in the dish = 1.5 c.c., or $\frac{1}{3}$ the amount required in the experiment described above.

† The following evidence tends to confirm the accuracy of the views expressed above. The upper portions of the interiors of 18 Scheibler desiccators, which had been in constant use for 8 weeks (some being used much more frequently than others), were examined by wiping them with wet blue litmus paper; in 12 cases a distinct acid reaction was obtained.

A large glass jar, *J* (fig. 2), was fitted so as to form a blower, the exit tube of a water pump being made to enter through a side tubulure near the bottom; the desired air pressure, p , was provided by suitably proportioning the length of stem of the funnel *F*. By duly regulating the working of the pump the jar was kept full of air; any air entering in excess of that actually drawn off through the tap *t* escaped with the water through the funnel. The bulb of the funnel should be large, and it must communicate freely with the external air, otherwise the attached waste pipe comports itself as a water pump and so greatly interferes with the uniform delivery of air through *t*. On stopping the supply of water, that which still remains in the jar automatically syphons off through the pump and its air tube; consequently the apparatus is always ready for immediate use. On leaving the jar by way of the tap *t*, the air is by means of two other taps, situated beyond the first, divided into two equal streams, each of which is then driven through a Drechsel wash-bottle charged with concentrated sulphuric acid; the acid serves a two-fold purpose: it removes the greater portion of the contained moisture and also indicates the rate at which the air is passing. As the partially dried air emerges from the wash-bottles, each stream enters its own set of 3 purifying tubes; the first half of each set is packed with small fragments of soda-lime and the second half with similar pieces of calcium chloride;

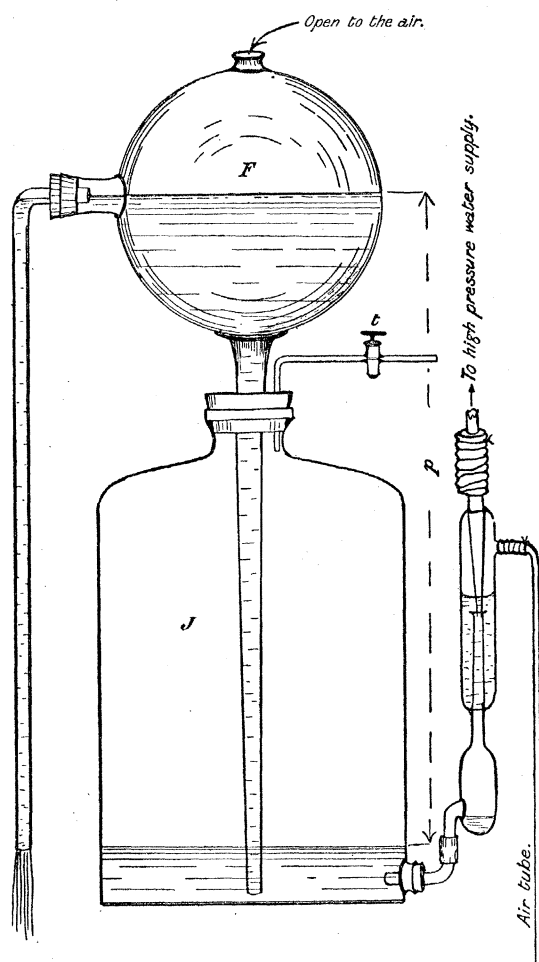


Fig. 2.

finally, the air is allowed to filter through plugs of glass wool and is then conducted by glass tubing through one side of the balance case to the interior of the copper cylinders which surround the pans and stirrups. The glass air-tubes were passed through niches cut in the upper edges of the cylinders, their free ends being bent so that the air streams were delivered centrally and downwards.

The apparatus just described enabled us to subject any objects, the masses of which we desired to subsequently compare, to a very perfect washing with air freed from carbon dioxide, moisture and dust; in fact, we were now, for the first time, in a position to weigh an object under well-defined and easily re-producible conditions. The efficacy of the newly devised method was now put to the test; for this purpose another pair

of reaction vessels was made and charged as in the earlier experiments, and their volumes equalised as before. After the usual preliminary cleaning and wiping, the vessels were suspended from the balance, the necessary small weight added to one of the pans and the beam fatigued. During the first series of determinations which were then undertaken, the weighings were conducted in the presence of the ordinary air; but the second and third series of weighings were effected in the presence of dried and purified air only. In using the purified air, the streams were allowed to flow continuously until just before the actual weighing was commenced when they were temporarily arrested by closing the tap *t*. The first and third series of determinations each extended over a period of 7·5 hours; the second series occupied a period of 5·5 hours. The final results obtained are given below :—

TABLE IV.

Date.	Experiments.	Air used.	R.Ps. reduced for 22° C.				Number of determinations.
			Mean.	Maximum.	Minimum.	Maximum difference.	
August 21, 1911	Series 1	Ordinary	106·1	108·3	105·1	3·2	15 sets of 3
„ 22 „	„ 2	Purified	104·8	105·3	104·1	1·2	11 „ 3
„ 23 „	„ 3	„	104·7	105·3	104·2	1·1	7 „ 3

In connection with the above table two points may be noted. (*a*) In Series 1, the mean value for the reduced R.P. is 1·3 greater than the corresponding value deduced from Series 2 and 3; it is believed that this difference is due to a probable want of equality in the areas of the two vessels. Our data showed that the reaction vessel, to which a small volume compensator had been attached, suffered the loss of weight indicated by the change in the R.P.; this is, as we have already shown, exactly what we should expect; for, generally speaking, we find that the volume compensator causes the area of the compensated vessel to exceed the area of its companion. (*b*) Notwithstanding the very considerable additional refinements that had now been introduced, there still remained some residual disturbing factor, the magnitude of which was approximately represented by the extreme variations in the R.P., observable in Series 2 and 3. Doubtless a portion of the small variation was due to unavoidable experimental error; but at least another portion was probably due to a cause which we shall now proceed to discuss in the next section.

(6) *γ*. *Of Errors Arising from Slight Variations in the Temperature of the Contents of a Vessel.*—Coming now to a brief consideration of the influence exercised by the third variable (*γ*, p. 236), we note that some workers have been somewhat perplexed and exercised in their minds as to what material constitutes the most appropriate substance for wiping glass vessels that are to be weighed; some advocate the use of silk, others are in favour of the use of old and fine linen, others again

recommend a preliminary immersion of the vessel in distilled water. Various observers have found that the apparent weight of a vessel which has been wiped with silk is somewhat changed if re-wiped with linen, and *vice versa*. Certain experiments which we have made with the view of elucidating the cause of the admitted and observed differences, suggest that the apparent change in weight is intimately bound up both with the *manner* in which the vessel is finally prepared for weighing and with the *nature* of the substance used for wiping. A typical case which is simpler than but equivalent to one of my own experiments will make this clear. The selected case is that of a glass sphere having a capacity of 150 c.c. and filled with water. The operation of wiping and the attendant rise in the temperature of the vessel and its contents will, in general, effect—

- (1) Slight variations in the weight of the water skin ;
- (2) A very small alteration in the air-displacing power of the vessel ; and
- (3) A decrease in the buoyant properties of the surrounding air.

Passing over the first-named variable which we have already fully discussed, and ignoring yet another associated with possible minute changes in the weight of an air skin as distinguished from one of water, we observe that a glass sphere having a volume $V = 150$ c.c. at some temperature t° C., and a cubic coefficient of expansion $= \cdot 00003$, will at $t+1^\circ$ C. assume the approximate volume of $150\cdot 005$ c.c. ; $\cdot 005$ c.c. of air weighs something like $1/170$ mgr. The great majority of workers would, by following the methods usually adopted for accurate weighing, quite fail to detect so small a change with any degree of certainty ; and therefore, for our present purpose, the variation may be treated as an insignificant factor which calls for no further comment.

In considering the effects which may be produced by the last of three variables named above, we would first note that when the buoyancy of the air is to be allowed for, a thermometer is placed in some convenient position within the balance case and read at the time the object is weighed ; the density of the air at the observed temperature is then taken into account and the proper correction applied. For very many cases this way of treating the problem in hand is doubtless sufficiently accurate and calls for little or no criticism. Yet it must be admitted that a close examination of the actual facts will show that such a plan must not infrequently lead to the adoption of an inaccurate correcting value for the buoyancy. To obtain a rigorously true correcting value, the temperature of the air should be taken, not as is often done *anywhere* within the balance case, but at a point *infinitely near* the object weighed ; for, unless the temperature of the air which is in close contact with the object upon the balance pan be accurately known, it will be impossible to assign to the correcting factor a precise value. The following remarks will, it is hoped, render evident the nature of the error that may be introduced by pursuing the usual instead of the ideal method.

Let the temperature of a sphere having $V = 150$ c.c. be $0^{\circ}\cdot 1$ C. greater than the mean temperature of the air within the balance case; we shall commit no serious error if we assume that the enveloping shell of air which is in close contact with and therefore readily warmed by the walls of the vessel is likewise $0^{\circ}\cdot 1$ C. greater than the mean temperature of the general body of air; for theory shows that such a shell of warmer air, though thin, will be appreciable and fairly well defined. Taking the weights of 1 c.c. of dry air under $p = 760$ mm., and at the respective temperatures of $15^{\circ}\cdot 0$ C. and $15^{\circ}\cdot 1$ C. as ω_1 and ω_2 mgr., we find the difference $\omega_1 - \omega_2 = \cdot 0005$ mgr.; the corresponding difference for 150 c.c. (the volume of the sphere) is therefore $= \cdot 075$ mgr. Under the conditions which existed during our final experiments it was estimated that the smallest change in weight that could be detected with certainty equalled $\cdot 002$ mgr.; and therefore $\cdot 075$ mgr. would, comparatively speaking, produce a very marked effect upon the R.P. value.

In order to discover how far the temperature might be affected during the process of wiping, we introduced into a reaction flask, containing 150 c.c. of water, a thermometer graduated in $\frac{1}{10}^{\circ}$ C.; holding the flask by the upper end of the neck the contents were shaken and the temperature noted. A doubled silk or linen handkerchief was then employed in the usual manner and the flask wiped for the space of half a minute preparatory, as it were, to weighing, and the temperature again noted; this experiment was repeated a number of times both with the silk and the linen; in each case the results were surprisingly concordant. With silk the mean rise in the temperature was $0^{\circ}\cdot 15$ C. and with linen $0^{\circ}\cdot 25$ C. These experiments, therefore, show the correctness of the more or less prevailing idea that for the purpose of wiping glass vessels silk is superior to linen, the superiority being with reference to the resultant temperature changes and, according to our measurements, in the ratio of 25/15.

If we assume an otherwise strictly constant temperature within the balance case and apply the Stefan-Boltzman law of cooling, it becomes evident that a very considerable period must elapse before it will be possible to weigh correctly the slightly warmed vessel and its contents. If the above line of argument followed for the assumed difference of $0^{\circ}\cdot 1$ C. be extended so as to include the results obtained in the experiments upon the effects produced during wiping, it is found that the apparent increase in the weight of the vessel due to this cause alone is respectively $0\cdot 113$ and $0\cdot 188$ mgr.; in practice, however, other effects such as those arising from the action of convection currents would modify and lessen these values. So far as I am aware, little or no attention has hitherto been given to the possible effects following *very slight* differences in the temperature of a vessel and the general body of air surrounding it; for our present purpose the influence exercised by even minute differences in the temperature of the air and that of the vessel may become highly important and must not be neglected.

Having reviewed and indicated the sources and approximate magnitudes of at least

some of the errors associated with the operations of refined weighing, we now proceed to give as brief an account as may be of the results obtained during the final experiments connected with this present research.

(7) *Of the Final Experiments Conducted with Silver Nitrate and Ferrous Sulphate Solutions.*—During the earlier part of this research use was made, as already stated, of inverted U-shaped vessels; but according to our experience such vessels are not so free from sundry inconveniences as we could wish for. It was therefore decided to substitute for those vessels others of a more or less globular form; and in order that the surfaces, volumes, and figures of the two vessels might be as nearly as possible identical, recently purchased Kjeldahl flasks of Jena glass were chosen. The two flasks were then repeatedly softened in a blowpipe flame and re-blown until by trial it was found that they were in all essential respects very similar; it is believed that the repeated softening in the flame also ensured, as no other treatment could have done, a very close similarity in the nature of the surfaces of the flasks.

With the object of separating the two reacting bodies, another flask of convenient volume was blown within each of the two Jena glass vessels. The silver nitrate solutions were introduced into the small inner flasks, and the equivalent weights of ferrous sulphate solutions into the outer and larger vessels; the necks of the outer vessels were then softened, thickened, and drawn out in the form of capillary tubes; these when cold were re-heated and bent hookwise and their tips sealed in the flame. The volumes of the vessels were next measured hydrostatically, and to the one possessing the smaller volume was added the necessary spherical compensator having $V = 1.59$ c.c. The sealed tip of the lightest vessel was now removed and distilled water introduced until the weights of the two vessels, together with their contents, were almost exactly equal; the tip was then re-sealed. After subjecting the vessels to the usual preliminary and extended cleaning with (*a*) nitric acid, (*b*) potash, and (*c*) water, and finally wiping, the weighings were commenced and conducted under the newer conditions which have been outlined and discussed in the immediately preceding sections.

In planning the final experiments it was decided that the operations of weighing should be simplified as far as might be consistent with the conditions demanded for the high degree of accuracy to which we hoped to attain; the method of double or reversed weighing was therefore, in our opinion, with advantage discarded, for in this present enquiry a knowledge of the absolute weights of the reacting bodies is inconsequent. The question which we were endeavouring to answer was an apparently remarkably simple one, namely, Does the total mass of two or more interacting bodies undergo any appreciable change during chemical reaction? Now LANDOLT had already shown that if such changes take place they must be so small that there would result but a very slight displacement in the R.P. of a balance adjusted to a high degree of sensibility; in fact, so slight was any possible displacement likely to be that for the final comparison it would be quite unnecessary even to change the position of the rider upon the beam.

From the results obtained during the wiping of a charged flask (*vide supra*), it was inferred that the less frequently we repeated the operation of wiping the reaction vessels, the greater would be the reliability of final results drawn from a whole series of experiments. Again, the oftener the balance case is opened the greater will be the risk incurred from falling dust, varying temperature, and moisture effects; and with oft-repeated reversals we incur the further danger due to possible minute alterations in weight brought about by the friction between the hooks of the reaction vessels and those of the balance stirrups.

Further, we were convinced that the elaborate precautions taken by LANDOLT for centering the masses under comparison upon the balance pan were unnecessary. Modern precision balances are so constructed that masses placed in their pans or suspended from the hooks above are automatically centred; but in order to remove, as far as our own balance was concerned, any doubt that might arise on this point, a number of experiments carried out with the aid of the inverted **U**-tubes conclusively showed that the contained liquid might be either equally or otherwise divided between the two limbs of the vessel without producing any perceptible change in the apparent weight of the whole.

After the two Jena glass reaction vessels, henceforth termed X and Y, had been similarly wiped, they were suspended from the hooks of the balance stirrups and equipoised with the aid of a small weight and the rider; the balance pans and their contents were next completely enclosed by the copper cylinders (p. 237), and the tubes delivering dry and purified air, placed *in situ*. The shutter of the balance case having been closed the beam was released and fatigued for a prolonged period; the actual weighing was then commenced and continued at intervals during successive days. For every determination of the relative weights, five pointer readings were taken for deducing the R.P. and the temperature of the balance beam noted. By means of the temperature coefficient of the balance, the various R.Ps. were then reduced for a standard temperature of 16° C. The streams of purified air were always arrested during the time of the actual weighing, but allowed to flow freely at all other times.

From September 28 to October 2, preliminary weighings only were undertaken; for it follows from the theoretical considerations which have already been given that it would be quite useless to attempt thus early to discover the true relative weights of the two vessels and their contents. The results obtained during the preliminary weighings served chiefly to indicate the cessation of temperature fluctuations within the contents of the vessels which had, of necessity, been so freely handled. As may be seen from Table V., p. 250, in which the summarised results are set forth, the fluctuations as represented by the variations in the R.P. gradually die away and ultimately become quite small.

From the above evidence it was concluded that the vessels and their contents had, on October 2, assumed an almost truly normal state; but it was thought to be safer to wait yet another day before beginning a final comparison of the weights of the two.

TABLE V.

Date.	Number of determinations.	Reduced R.P. values.				
		Maximum.	Minimum.	Differences.	Variation in weight.	Mean.
September 28, 1911	21	108·7	105·0	3·7	mgr. ·082	106·8
” 30 ”	12	111·5	109·8	1·7	·032	110·7
October 2 ”	6	107·0	106·6	·4	·009	106·8

On the morning of October 3, the vessels were in succession removed from the balance and held by a suitably designed lifter whilst they were very lightly and quickly re-dusted with silk; the operation was so effected that there was practically no risk of producing an appreciable rise in the temperature of their contents. Before the vessels were re-introduced the balance pans were also re-dusted and the whole apparatus arranged as before. The weighings were commenced an hour after the beam had been released and repeated at moderately short intervals throughout the day. Three independent determinations of the R.P. were made upon each occasion, and each of these was calculated as in the preliminary experiments from 5 observations of the extreme positions of the pointer; the mean value of the 3 determinations was accepted as the true one, and this was then reduced as before for the standard temperature of 16° C.

Proceeding in this manner we obtained in the course of 9 hours 20 groups of 3 R.P. values; from these again were calculated 20 mean values, from which a final mean value for the relative weights of X and Y, before mixing the contents of either, was deduced. An actual example will serve to illustrate the method of procedure adopted—

Example.

Group.	Time.	R.Ps.				Temperature.	R.P. at 16° C.
No. 1	11.10 a.m.	119·6	119·4	119·3	119·4	10·8	106·9

The chief points of interest associated with the 20 groups of determinations may be conveniently set forth as follows :—

The Final Mean value deduced for the R.P. = 107·0. Of the 20 mean values obtained during the day the maximum value equalled 107·3 and the minimum value 106·5; 10 of the 20 mean values were greater than the final mean and 7 were smaller; the remaining 3 values were equal to the final mean. The mean + difference was

(still in terms of the R.P.) = 0.15, and the mean — difference = 0.16. We therefore obtain a close approximation to the truth by taking as a final mean R.P. = 107.0 \pm 0.15. With a sensibility, *S*, of the balance = 45, we find that the variation \pm 0.15 in the R.P. = 15/450 = \pm .003 mgr. As the total mass in either pan was approximately equal to 127 gr., the variation \pm .003 is equivalent to 1 in 42.3 millions.

(8) *After mixing the Contents of X.*—On the following day (October 4) two additional groups of 3 R.P. determinations were obtained; their mean values at 16° C. were respectively equal to 107.0 and 107.1; the accuracy of the value of the R.P. given above was thus confirmed.

The contents of X were now rapidly mixed and the vessel replaced. Observing the usual precautions, the relative weights of X and Y were frequently determined during an ensuing period of 6 hours. The first comparison showed that the value of the R.P. had increased from 107 to 122.4; but when the weighings were brought to a conclusion for the day the value had fallen to 107.8; it was observed that the decline was fairly uniform throughout the 6-hour period. The comparisons were continued on October 5 and 6 and very fully repeated on October 10. Briefly the results were as follows:—

TABLE VI.

Date.	R.P. values at 16° C.				Number of determinations.
	Maximum.	Minimum.	Differences.	Means.	
October 4, 1911 . .	122.4	107.8	14.6	115.8	14
„ 5 „ . .	110.7	106.1	4.6	108.3	14
„ 6 „ . .	111.1	95.6	15.5	104.9	8
„ 10 „ . .	109.2	107.2	2.0	108.2	60

The final result obtained from the series of determinations on October 10 shows that the R.P. value had increased from 107.0 before mixing the contents of X, to 108.2 after mixing; the difference 1.2 is equivalent to an apparent *increase* in the weight of X of .027 mgr.

(9) *After mixing the Contents of Y.*—As the variations in the apparent weight of X and its contents showed immediately after mixing some degree of uniformity, it was decided so to conduct the weighings, after mixing the contents of Y, that it would be possible to determine in this case the actual rate with which the decrease in the apparent weight proceeded. Accordingly, the solutions in Y were quickly mixed, both X and Y were then wiped and replaced in the balance, and the usual preparations completed for weighing. The first weighing was made 20 minutes after the reacting bodies had been mixed; other weighings followed at known intervals, which though at first brief, became more extended as the experiment progressed. In this way there

were obtained between the hours of 10 a.m. and 8.30 p.m. 19 independent R.P. values. The weighings were continued during the three succeeding days. The results obtained during the four days over which this experiment extended are given in a very condensed form in the following table :—

TABLE VII.

Date.	R.Ps. reduced for 16° C.				Number of determinations.
	Maximum.	Minimum.	Differences.	Means.	
October 11, 1911. . .	110·0	91·6	18·4	102·8	19
„ 12 „ . . .	109·7	108·4	1·3	108·9	45
„ 13 „ . . .	109·8	109·1	·7	109·6	18
„ 14 „ . . .	112·2	109·6	2·6	111·1	12

The results obtained during October 11–14 inclusive are represented graphically and in a more detailed manner by Curve No. 2 (fig. 3). Curve No. 1 exhibits the small variations observed in the relative weights of X and Y before the contents of either were mixed, and at the same time indicates not only the degree of accuracy attained under the improved conditions introduced for weighing glass vessels, but also serves the useful purpose of a standard with which the other curves may be compared. The several curves are formed by plotting the differences in the apparent weights of X and Y against the times when those differences were measured.

Curve No. 2 presents two interesting features, the most arresting of these being the well defined undulations in the first portion. The slope of the axis of the undulations, though at first steep, becomes with lapse of time, less pronounced; finally the undulations die away and the further apparent changes in weight are from that time onward best represented as an approximately straight line curve having a direction which tends to become horizontal. The mean path of the whole graph suggested to our minds a very strong resemblance to a cooling curve; we were thus led to suspect the existence of some simple relationship between the decreasing temperature of the recently mixed contents of X and the changes in the apparent weight of the same. We therefore decided to measure the rate of cooling for X and its contents under conditions similar to those which obtained during the weighings. With this object in view, another vessel, similar in all essential respects to X, was charged with solutions of silver nitrate and ferrous sulphate, the quantities used being the same as those employed in our LANDOLT experiment. A thermometer graduated to 0°·1 C. was introduced and read; the two solutions were then mixed, and the thermometer again read; the increase in the temperature equalled 4°·8 C. and this was therefore the range of temperature for which the rate of cooling had to be determined. In carrying

out the cooling experiment, the vessel, loosely corked and fitted with a thermometer placed centrally within, was first warmed and the temperature of its contents raised about 6° C. above that of the surrounding air ; it was next placed upon a light three-point support of fire clay and surrounded with one of the copper cylinders from the balance case ; this done, the top of the cylinder was covered with a tin-foil lid through which the stem of the thermometer projected ; finally, one of the tubes leading from the air-purifying apparatus was passed downwards and just through the tin-foil lid, and the whole covered with a large glass dome. The time required for the vessel and its contents to cool from 21° C. to $16^{\circ}\cdot 2$ C. was then determined, a chronometer being for this purpose read for each fall of $0^{\circ}\cdot 5$ C. until the temperature had sunk to $16^{\circ}\cdot 5$ C. ; as the rate of cooling had then become very slow, chronometer readings were recorded for three succeeding temperature steps each of $0^{\circ}\cdot 1$ C.

For this experiment we purposely chose a day when the weather was dull and the air fairly still ; under those conditions the temperature of our balance room is remarkably constant ; in this present instance the variations kept within the limits $15^{\circ}\cdot 2$ C. and $15^{\circ}\cdot 4$ C. during the 6 hours the experiment lasted. The results derived from this experiment were now set forth in the form of a curve (No. 3) of dimensions corresponding to those chosen for Curve No. 2 ; we were thus enabled to institute a direct comparison between the two.

Superposing the cooling and decrease in weight curves, it is found that the former very approximately coincides with the axis of the undulations of the latter ; this very approximate coincidence appears to persist and improve until finally the two curves merge into one and so become indistinguishably the same. The portion $\alpha\beta$ of the change in weight curve was obtained by extrapolating, and the point marked γ indicates the result obtained during our final weighing in this portion of our experiment.

The results we have just given and briefly discussed afford strong confirmatory evidence of the correctness of the theory already advanced, and which indicates that for a body of some considerable volume the apparent mass, as determined within a very restricted air space free from convection currents, must appreciably increase when the temperature of the body is raised, and decrease when the temperature is allowed to fall.

With regard to the undulations which appear in the first portion of the Curve No. 2, it must be confessed that we are not yet in possession of sufficient data to be able to definitely assign a cause from which they may arise ; we may, however, state that the results of several experiments led to the conclusion that the undulations will be inappreciable unless the temperature of the charged vessel which is being weighed exceeds that of the air by 1° C. or more. The more or less harmonic form of the undulations suggest two possibilities : (1) for a given temperature difference, periodic oscillations may be set up in the air shell which encloses the warm vessel, (2) the transference of the heat energy from the interior to the bounding surface of the

cooling liquid proceeds not in one perfectly and steadily decreasing flow, as might at first be expected, but in the form of a surging stream. It is hoped that further experimental evidence will reveal that which is now obscure.

We now briefly refer to the results set forth in Tables VI. and VII. Comparing the corresponding data of the two tables, very distinct differences are at once apparent; but that which claims our immediate attention is the want of agreement between the two final results; the first of these indicates an apparent *increase* in weight = '027 mgr., and the second an apparent *decrease* = '067 mgr. As these apparent changes in weight constitute, relatively speaking, large discrepancies of a wholly contradictory character, we began to suspect that the marked irregularities were due to the presence of some hitherto unlooked for variable; but before deciding upon any other course, additional comparisons of X and Y were effected at intervals for some days longer; the large fluctuations in the relative weights showed that it would be useless to further prolong experiments in this direction. Curve No. 4 (fig. 3) represents some of the irregular results obtained from the additional weighings.

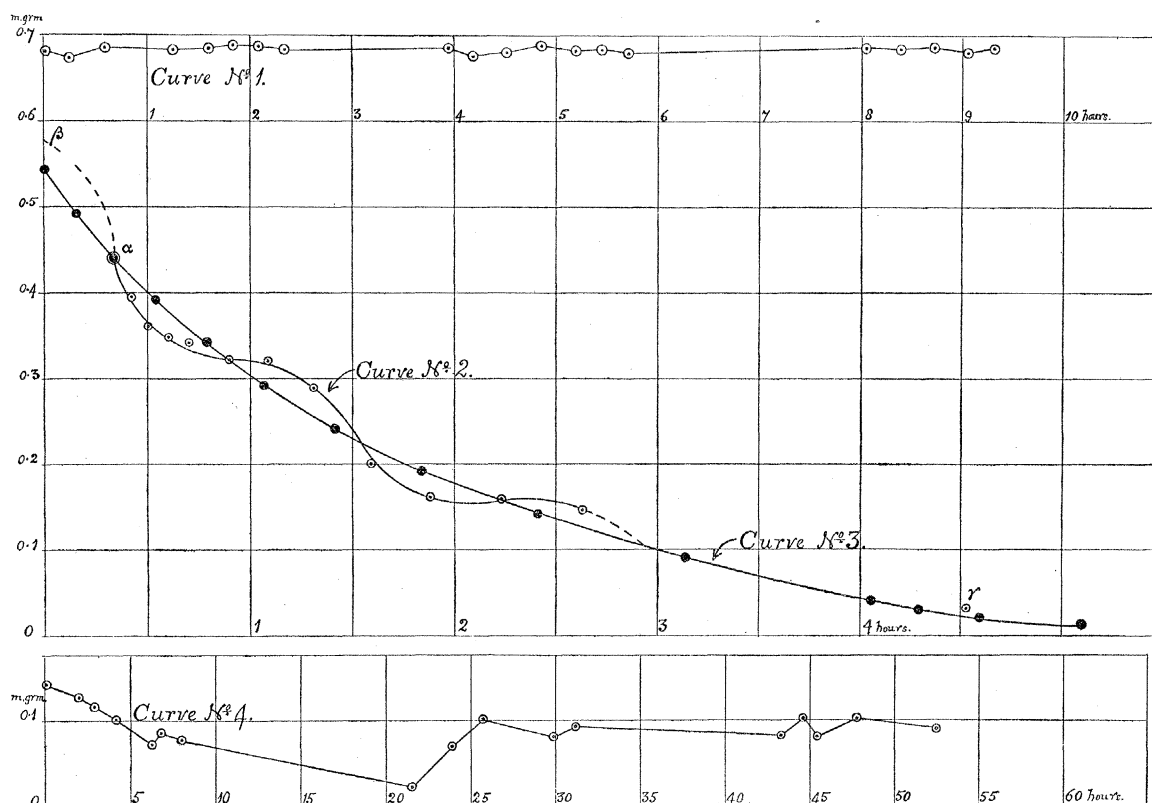


Fig. 3.

At this period of the investigation we obtained a clue so valuable that we were enabled to perceive the probable cause of the frequent changes in the relative weights of X, Y and their contents. During an earlier experiment, not previously mentioned,

whilst the contained solutions were being mixed a fine crack was developed across the lower portion of a sealed reaction vessel; this crack rendered the vessel useless for the purpose for which it was designed. Following a habit we have of retaining for the time being anything connected with our work, the vessel was placed inside a beaker and set aside. At the end of about eight weeks it was discovered that the whole of the liquid had left the vessel and passed out into the beaker; seeing that the vessel was still intact, it was obvious that a considerable pressure had been generated within; in no other conceivable way was it possible to account for the ejection of the liquid.

An experiment was now devised to enable us to measure the growth in the pressure which follows the mixing of the two solutions. A flask was prepared and charged after the manner already described, but the capillary tube was made as uniform as possible and longer, and then bent so as to assume the form shown in fig. 4. A spot at the base of the capillary tube was softened before the blowpipe, and a short fine capillary tube, t , drawn out and left open; it was now possible to introduce a convenient quantity of mercury into the U-shaped limb; this done, the vessel was placed for some hours in a thermostat, maintained at a mean temperature of $29^{\circ}5$ C., and then hermetically sealed by fusing the tips of the capillary tubes t and t_1 ; the atmospheric pressure at the time of sealing was observed and recorded. Next, the solutions were mixed, the vessel replaced in the thermostat, and the sealed mercury manometer, m , read from time to time. During the first day the manometer remained unaffected, but at the expiration of the second day its indications showed that the pressure within had commenced to fall; the diminution in the pressure became more and more marked until the sixth day during which the change reached a maximum; from this time onward the pressure began to slowly return towards its original value, the increase during the four succeeding days being equal to 20 mm. of mercury.

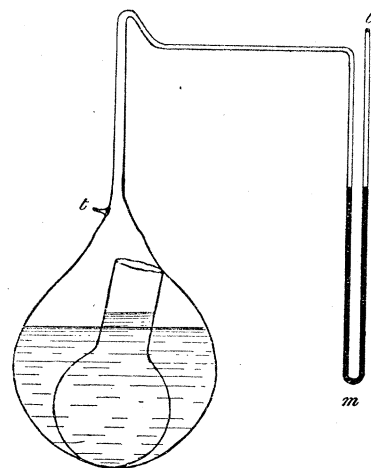


Fig. 4.

We next tried the effect of light upon the mixture, and in order to carry out this experiment the flask was removed from the thermostat, allowed to cool, and then placed together with a 25 candle-power "tantalum" lamp inside a bright tin box, the top of which was then covered with tin-foil. Switching on the lamp for short intervals only, the pressure was now observed to increase so rapidly that it was deemed wise to terminate the experiment at the end of an hour. The flask was then replaced in the thermostat and the new pressure measured; this pressure remained unaltered during the succeeding day, but 24 hours later it had still further increased. The experiment, which had by this time been proceeding for a fortnight, was now brought

to a conclusion by opening the tip of the manometer under mercury; when this was done, a considerable quantity of gas escaped from the reaction flask; the bulk of this was caught in a tube previously filled with mercury. An analysis showed that the gas consisted of nitrogen and nitric oxide, their volumes being approximately in the ratio of 1 : 2.

The determination of the cubic coefficient of expansion of the flask for pressure was next undertaken, in order that we might be in a position to calculate the changes in the apparent weight of the flask resulting from the related variations in the buoyancy of the air.

The pressure coefficient of expansion was measured with the aid of the apparatus represented in fig. 5. The flask, previously emptied and dried, was introduced into a small bell-jar and its neck passed up through a cork securely fixed in the mouth of the jar; the wide open end of the jar was then closed by means of a stout iron plate, *p*, which was attached with cement. The jar, together with the tube *t*, were next completely filled with air-free water, and, except when in use, the fine capillary jet in which the tube *t* terminates was kept immersed in water. In measuring the pressure coefficient, the water was removed from under the jet and a small weighed capsule substituted for it; air was then forced into the reaction vessel until the internal pressure was equal to 3 atmospheres, as indicated by the sealed mercury manometer *m*; as the pressure distended the flask, water was ejected through *t* into the capsule, which was then removed and again weighed. With slight modifications the contraction coefficient of the vessel was also determined. Both determinations were carried out several times and the results obtained were very concordant. It was thus found that an additional pressure of 1 atmosphere increased the

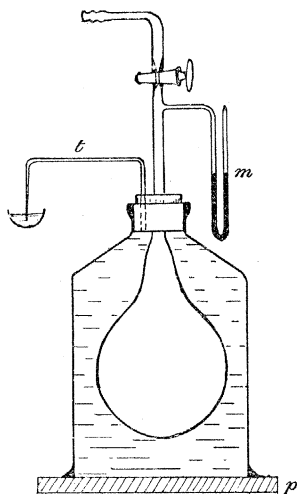


Fig. 5.

volume of the reaction vessel by an amount equal to $\cdot 02$ c.c. The weight of $\cdot 02$ c.c. of air may be taken = $\cdot 024$ mgr., and this is therefore the change produced in the buoyancy effects of the air upon the flask by a pressure = 760 mm. of mercury. We now give in Table VIII. which follows a summary of the results obtained during this branch of our inquiry.

The contents of Table VIII. are almost sufficiently self explanatory. It may be seen that on mixing the two reacting bodies, two hitherto absent variables the one dependent upon the other, were unknowingly introduced; there were prolonged, unsuspected and complicated chemical changes producing an irregular temperature and consequent loss in the buoyant properties of the air enveloping the reaction vessel; and as a necessary result of the chemical changes, a quantity of gas with its attendant pressure was generated within the vessel which, becoming distended, displaced additional air and was thus rendered more buoyant. The observed fluctuations in the

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TABLE VIII.

At the time of sealing the bulb the barometric reading = 744 mm.

Date.	Pressure within bulb.	Change in pressure.	Change in volume of bulb.	Equivalent change in weight.	
November 16, 1911 . .	744 mm.	± 0	± 0	± 0	
After heating {	" 17 " . .	744 "	± 0	± 0	± 0
	" 18 " . .	670 "	- 74 mm.	- .0015 c.c.	+ .002 mgr.
	" 19 " . .	Not read.			
	" 20 " . .	611 mm.	- 133 "	- .0026 "	+ .003 "
	" 21 " . .	578 "	- 166 "	- .0033 "	+ .004 "
	" 22 " . .	587 "	- 157 "	- .0031 "	+ .004 "
	" 23 " . .	587 "	- 157 "	- .0031 "	+ .004 "
	" 24 " . .	593 "	- 151 "	- .0030 "	+ .004 "
	" 25 " . .	598 "	- 146 "	- .0029 "	+ .004 "
	" 26 " . .	Not read.			
After exposure to light {	" 27 " . .	1594 mm.	+ 850 "	+ .0167 "	- .020 "
	" 28 " . .	1594 "	+ 850 "	+ .0167 "	- .020 "
	" 29 " . .	1674 "	+ 930 "	+ .0183 "	- .022 "

relative weights of the two vessels, X and Y, are therefore to be attributed to the sum of the two variables, one of which tends to increase, and the other to decrease the weight of either vessel. If the two variables have been, and still are, equally operative in both vessels, there will follow strictly equal opposition effects; as the sum of these = 0, the balance remains unaffected, and the presence of the variables remains unsuspected. In all probability this is just what happened in LANDOLT'S experiments with silver nitrate and ferrous sulphate. There is, however, one other possibility. Further experiments have proved that for the secondary reactions occurring, the period of induction may be very considerable; that is to say, the primary reaction may proceed to a point where a first chemical equilibrium may be established, and then no further appreciable changes follow before the whole experiment is completed. Viewed mathematically, we have but re-stated the case; in so far as the actual weighing is concerned, the results are precisely the same.

The mixture left in the flask after concluding the experiments with the tantalum lamp, proved on examination to be very acid. The clear liquid obtained on filtering, contained in addition to acids, ferrous, ferric, and silver salts; the undissolved portion which was somewhat yellow, contained metallic silver, silver nitrate and some salts of iron. We must now leave the chemical problem here presented to be more fully dealt with in some future communication; but from the remarks made, it will be abundantly evident that the chemical equation set forth on p. 230 gives but a very incomplete representation of the actual facts; that equation may indeed represent

more or less correctly, the initial stage of the whole reaction, but it is quite clear that other and perhaps somewhat involved and little understood chemical changes are induced some time later, the period varying greatly with the conditions of light, heat, &c.

Seeing then that a close study of one apparently simple chemical reaction led to such totally unexpected conclusions, and remembering that the nature of some of the other reactions made use of by LANDOLT cannot, in all probability, be simpler than that of the reaction which we have investigated somewhat imperfectly here, it would naturally appear that a more perfect knowledge of the chemical changes which were made use of by LANDOLT, combined with the application of the methods we have advocated and practised for refined weighing, would enable us to explain at least some of those obscure points which arise in LANDOLT'S memoir. We now pass to the consideration of one final experiment and the results which were obtained by its aid.

(10) *Of some Results obtained with Barium Chloride and Sodium Sulphate.*—With the object of securing additional and confirmatory evidence in support of the correctness of the views which we had now formed, a final experiment was devised and carried out.

It will be universally admitted that the reaction which follows the mixing of barium chloride and sodium sulphate solutions is, for all practical purposes, instantaneous and complete. We are not, however, aware that either this or other similarly rapid and complete reactions have been deliberately and systematically made use of by preceding investigators; but the results we have obtained and described force us to the inevitable conclusion that the only reactions we may legitimately make use of for our present purposes are just those in which the chemical changes terminate within a reasonably brief period; further, the products of the reaction must be of such a nature that the pressure within the vessel is not appreciably altered.

For the purpose of carrying out the final experiment two re-blown Jena glass vessels, similar to those used in the preceding experiments, were prepared; but as it was not intended to duplicate the experiment, one vessel only was supplied with an inner flask; the other vessel was used simply as a counterpoise. The reaction vessel was charged with equivalent quantities of almost saturated solutions of highly purified barium chloride and sodium sulphate, the latter being placed in the small inner flask; the counterpoise was charged with the proper weight of water; the reaction vessel and its counterpoise were then sealed, their volumes and weights determined and afterwards equalised; finally the vessels were cleaned. All these necessary operations were performed in the manner described on pp. 231 and 248. The subsequent weighings were conducted under precisely the same conditions and with the same precautions as those introduced and observed during the final experiments with silver nitrate and ferrous sulphate. The results obtained during the course of this experiment are summarised and set forth in the following table:—

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TABLE IX.

Date.	Number of determinations.	Reduced R.P. values.*					
		Mean values.	Number above mean.	Average difference from mean.	Number below mean.	Average difference from mean.	Number of zero differences.
BEFORE REACTION.							
December 30, 1911.	6 groups of 3	97.50	2 determinations	+ 0.30	4 determinations	- 0.15	0
January 1, 1912	6 " 3	.74	2 " "	+ .20	3 " "	- .12	1
" 3 "	6 " 3	.11	2 " "	+ .18	4 " "	- .09	0
" 4 "	6 " 3	.55	4 " "	+ .10	2 " "	- .19	0
	Final means . .	<u>97.48 = M₁</u>		<u>+ 0.20</u>		<u>- 0.14</u>	
					± 0.17		
AFTER REACTION.							
January 12, 1912	9 groups of 3	97.39	3 determinations	+ 0.26	6 determinations	- 0.36	0
" 13 "	12 " 3	.62	3 " "	+ .44	9 " "	- .33	0
	Final means . .	<u>97.51 = M₂</u>		<u>+ 0.35</u>		<u>- 0.35</u>	
					± 0.35		
Difference M ₂ - M ₁ = + .03 = .0007 mgr.							

* All these R.Ps. were corrected for changes in atmospheric pressure. The corrections were rendered necessary by the fact that the air displacements of the vessel and counterpoise were, through a small arithmetic error (discovered after the experiments had been concluded), not quite equalised. A variation in the barometric height = 10 mm. resulted in a change in the relative apparent weights = .002 mgr.

From the above tabulated results it may be seen that there were 72 5-point determinations of the relative weights of the reaction vessel and its counterpoise before effecting the chemical reaction, and 63 similar determinations after. The maximum variations observed amongst the several daily mean values (Column 3) were 0·63 before the reaction and 0·23 after; these variations in the R.P. correspond respectively to ·014 and ·005 mgr. The mean values of all the daily average differences in the R.P. (Columns 5 and 7) before the reaction are +0·20 and -0·14 respectively, or a final mean variation $\pm 0\cdot17$. After the reaction the corresponding values are respectively +0·35 and -0·35, or a final mean variation = $\pm 0\cdot35$. Expressing the two final means in the form of weight variations, we have for the first $\pm\cdot004$ mgr. and for the second $\pm\cdot008$ mgr. The increase in the average variation here shown, though in itself small, is, we believe, definite, and we think that it is quite possible that as a result of the chemical reaction some at present unknown minute disturbing factor has been introduced; further research may bring this to light.

Taking the final mean variation in the relative weights = $\pm\cdot006$ mgr., it appears that the additional refinements and precautions which we have introduced and described have resulted in raising the attainable degree of accuracy in weighing from the lower limit of $\pm\cdot03$ mgr. given by LANDOLT to one having just 1/5th of that value.

The weight of the reaction vessel and its contents may in round numbers be taken = 109 gr.; if, therefore, the difference $M_2 - M_1$ be taken = ·001 mgr., instead of the smaller difference ·0007 mgr. as found experimentally, the apparent increase in the total mass during the chemical reaction is of the order of 1 in 109,000,000 parts; but this, it may be observed, is 6 times smaller than the average variations exhibited throughout these final experiments.

Reviewing then the whole available evidence, we are led to conclude that this present research has tended but to confirm the truth of an almost universally accepted belief, that a given total mass is an unchanging and unchangeable quantity.

In conclusion, I desire to acknowledge my indebtedness to the Government Grant Committee of the Royal Society for the continued loan of certain apparatus which has considerably facilitated this research. My best thanks are due to Mr. R. T. GÜNTHER, Fellow of Magdalen College, and to Mr. N. V. SIDGWICK, Fellow of Lincoln College, Oxford, for the valuable assistance which both have rendered me. Lastly, I would express my appreciation of the kindness shown me by the Radcliffe Observer. In the absence of data afforded by Dr. RAMBAUT'S continuous barograph records it would have been difficult to apply certain minute but necessary corrections to the final R.P. values of the barium chloride and sodium sulphate experiments.
