5. The order of activity among the metals tested, beginning with the highest, is: palladium, platinum, cobalt, gold, with large differences in the order of magnitude of the activity. The activity of a number of other metals is too small to be discernible. The activity of gold is increased by surface oxidation, largely on account of increase of surface.

6. The results obtained are at variance with Sackur's conclusions with regard to the passivity of these metals and of hydrogen.

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ANALYTICAL WEIGHING.

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Introduction.

It appears that many chemists at the present time regard the use of long swings of the analytical balance as the best and most accurate method of weighing. Many recent text-books on quantitative analysis advocate this process, sometimes without even mentioning a simpler method, and the teaching of long swing weighing has evidently grown in favor in recent times.

While admitting that the use of long swings of the balance is capable of giving results that are accurate enough for ordinary purposes, the writer has absolutely no doubt that this practice is generally somewhat less accurate than the ordinary, simple method of using short swings. The very serious objection to the method of long swings, however, is that it is more difficult and much slower than the common method.

The object of this article, therefore, is to discuss methods of weighing, to present a plea for the general use in teaching and in practice of the simple, easy and accurate process of weighing with short oscillations of the balance, and for the abandonment of long swing practice, which evidently involves a great waste of time and labor, with no gain, but probably some loss, in accuracy.

The advocates of long swing weighing usually recommend the finding of a "zero-point" of the empty balance—a point not coincident with the zero of the graduated scale—in connection with each weighing, thus largely increasing the burden of labor in their otherwise cumbersome process. It is believed that this practice should be given up, no matter what method of weighing is employed, in favor of using the apparent zero of the balance as the basis of weighing, according to the old and reliable custom; for it is certain that when we weigh by difference, as we almost invariably do, the point of equilibrium of the empty balance is of no consequence, provided that the adjustment does not change between two weighings required to find a difference.

Long Swing Weighing.

Since the analytical balance, when near equilibrium, does not readily give long swings, those who employ extensive oscillations usually obtain them either by fanning one of the pans, by temporarily applying the rider, by suitably manipulating the pan-arresters or by using a point of equilibrium at a considerable distance from the center of the graduated scale.

The last of these devices is adopted in a well known text-book[1] which does not even mention the use of short swings. The directions given in this book for weighing a crucible are copied here as a striking example of how weighing should not be done:

"In making a weighing one should always accustom himself to note the observations methodically, as follows:

Assume that a platinum crucible is to be weighed.

	Zero-point.		I. Point of rest with load of 12.052 gms.		II. Point of rest with load of 12.053 gms.	
	Left.	Right.	Left.	Right.	Left.	Right.
	4.2	17.6	5.8	18.7	3.5	15.8
	4.6	17.1	6.2	18.3	3.8	15.4
	5.1	.....	6.6	.....	4.2	.....
Sum =	13.9	34.7	18.6	37.0	11.5	31.2
Mean =	4.63	17.35	6.2	18.5	3.83	15.60
		4.63	....	6.2	....	3.83
Sum of both means =		21.98	....	24.7	.....	19.43
Mean =		10.99	....	12.35	.....	9.71

Sensitiveness = 12.35 — 9.71 = 2.64 scale divisions.

12.35 —10.99 = 1.36 scale divisions.

1.36 : 2.64 = 0.5 mgm.

Weight of crucible = 12.052 + 0.0005 = 12.0525 gms."

Fifteen observations of swings, much book-keeping, 9 calculations of mean values, 2 subtractions and finally a division and an addition are required here to finish weighing a crucible after getting within one milligram of the result. It would seem that gravimetric analysis would often be regarded as an unattractive occupation by students obliged to do all this and to repeat the performance after igniting a precipitate in the crucible. By the use of short swings in connection with the center of the balance, it would be easy to finish such a weighing, just as accurately, in about 15 to 30 seconds, by making 2 or 3 trials with the rider.

After all the labor recommended by Treadwell the result is expressed only to the nearest tenth of a milligram, and it is safe to say that if another decimal figure were calculated in such a case it would probably have little or no significance. It is fully believed that the quick method is

[1] "Analytical Chemistry," by F. P. Treadwell. Translated by Hall.

rather more accurate than the enormously longer and more complicated one.

Treadwell shows the use of 3 readings on one side and 2 intermediate ones on the other side for finding each position of equilibrium, but it should be mentioned that some other advocates of long swings shorten the operation somewhat by employing 3 instead of 5 readings, while still others make the process longer by the use of 7 or more observations for each position.

An example of directions for using 7 readings in finding the "zero-point" is copied here from a very recent book by George McPhail Smith.[1]

	Left.		Right.	
	—6.8		+4.7	
	—6.6		+4.5	
	—6.4		+4.3	
	—6.3			
Average:	—6 5	Average:	+4.5	Zero-point = — 1.0

It may be remarked that, if it should ever be desirable to find such a zero-point when weighing by difference, it could be much more easily done by using short swings. For, with the point of equilibrium at —1.0, a careful release would cause the needle to travel, after its first excursion, from —2.0 to 0, or it might show slight variations from this, such as $-2^1/_4$ to $+^1/_4$ or $-1^3/_4$ to $-^1/_4$, etc. A glance at these swings would show their middle point with accuracy, and the observation could be repeated upon succeeding swings as often as desired.

De Konink[2] has gone so far as to recommend as many as 15 or 17 observations for each careful weighing with long swings, on the grounds that it is difficult to make the readings accurately and that numerous observations diminish the error. The writer does not believe that this exceedingly laborious plan is as accurate as careful short swing weighing.

The use of long swings appears to be an old process, for a description of it in 1864, in practically its present form, has been noticed.[3] Its use may have been fully justified with primitive balances not provided with riders and with the tendency to give very long swings, but its application to modern analytical balances is believed to be a very different matter.

Short Swing Weighing.

There are some variations in the practice of those who do not finish their weighings by the use of long swings and indirect calculations, but

[1] "Quantitative Chemical Analysis," New York, 1919, p. 11.

[2] "Chemie Analytique," Liége, 1894.

[3] "Handwörterbuch," by Liebig, Poggendorff and Wöhler, Fehling's Edition, Vol. 9, p. 493.

weigh quickly and directly by bringing the rider to the proper point and observing it.

Substances are almost always weighed by difference in crucibles, weighing tubes or other containers, with the use of the same apparent condition of equilibrium for any two weighings required to find a difference, and without any particular regard for the actual condition of the empty balance, provided that this remains constant. Of course, when substances are weighed directly upon the pan, as in the case of gold and silver assaying, it is necessary to have the empty balance carefully adjusted.

The swings generally used are so short that their retardation is inappreciable in a single movement, and hence the middle point corresponds with the point of equilibrium. They may thus vary from a maximum total length of about 4 divisions of the graduated scales of our American balances down to the shortest ones that are distinctly visible. The writer prefers very short swings, from $^1/_2$ to 2 divisions in total length, for final observations, because their retardation is inappreciable even after several repetitions, and because the central points of such short swings can be very accurately found by observations. However, this preference for rather short swings does not involve th erecommendation that the natural swings of the balance should not be generally used, nor that anyone should employ swings that are too short to be easily and clearly observed without the suspicion that the motion may have stopped.

It is the most common practice, and the one preferred by the writer on the grounds of convenience and accuracy, to employ the center of the pointer-scale as the final middle point of the swing in finding equilibrium. Sometimes, however, a point of reference slightly distant from the center is employed, especially with assay balances, some of which may not swing at all when released in perfect equilibrium with the center, but not necessarily with our analytical balances, which seldom fail to give a sufficient swing, no matter how carefully they are released.

The writer has been informed by his former colleague, Professor Bahney, that the device of employing a single, outward swing, from the center to a definite point, about three divisions away, as the final indication of equilibrium, is very extensively used with assay balances, and, further, that this plan, following his own suggestion, has been applied exclusively and satisfactorily to analytical balances in a very large technical laboratory. Practically the same device, under the name of the "Single Deflection Method," has been described just recently by Brinton,[1] who states that it is an old process of unknown origin (it appears probable that it came from the assayers), and who has found that it gives excellent results, but has some limitations on account of the unsuitable release of certain balances. This method appears to be a very good one, especially

[1] This Journal, 41, 1151 (1919).

for rapid technical weighing, but it is probably not quite as accurate as the use of short swings across the center, because it is possible for the release of the pans to impart a slight impulse to the balance and thus slightly shorten or lengthen the single outward swing.

It is customary to put weights upon the balance systematically by the trial of loads that are nearly midway between excesses and deficiencies, but as soon as the pointer, when carefully released, does not swing beyond the limits of the scale, the weighing may be finished very quickly by observing the extent of this outward excursion and thus finding, from the known sensitiveness of the balance, the exact, or almost exact, point at which the rider must be placed. Not more than one or two further trials are then usually needed to finish the weighing. Occasionally the excursions of the pointer, just referred to, are very long ones, and it may be remarked that this is the only kind of long swing observation that is approved of in this article.

Analytical balances are frequently so adjusted that their sensitiveness amounts to a swing of 5 divisions for one milligram, corresponding to $^1/_2$ division for 0.1 mg. With this condition of delicacy, therefore, a swing that varies less than $^1/_4$ division on the two sides of the center shows that the nearest tenth of a milligram has been found, and, since this is the usual limit of accuracy desired, the weighing is then finished.

It is not worth while to attempt to push the accuracy of ordinary analytical weighing beyond the limit just mentioned, either by reading the short swings with greater accuracy or by adjusting the balances to greater delicacy, because weighing to the nearest tenth of a milligram is usually the most accurate feature of an analytical process, and also because the balance is likely to display erratic behavior when extreme refinement is attempted, on account of changes of temperature, jarring or other causes.

Even in ordinary weighing, the greatest precautions should be taken in regard to temperature, for unless everything that it weighed is at precisely the temperature of the balance the errors may amount even to milligrams. The rapid increase in weight of a slightly warm object as it stands upon the balance is sometimes incorrectly attributed to hygroscopic behavior. The writer has heard the complaint that the asbestos in a Gooch crucible was hygroscopic, when the crucible had been weighed before it was quite cold.

Those who require weighing of the greatest accuracy, for atomic weight determinations or other purposes, must take the greatest precautions, such as the employment of a highly sensitive balance, making corrections for the buoyancy of the air, and making allowances for the errors in the sets of weights used. Such refinements, however, are usually out of the question in ordinary analytical work, because such work usually lacks the accuracy in other respects that would make such corrections reasonable, and the ordinary busy analyst cannot afford the time and labor for unessential things. All careful analysts, however, should be sure that their weights are good ones, and, if particular care is desired, sets of assay weights from one gram down can be procured, the errors in which are entirely inappreciable on an analytical balance. An assay balance is very suitable for testing such weights. As the weights above one gram are frequently inaccurate, it is best, in careful work, to use them merely as counterpoises, without changing them when weighing by difference.

Short swing weighing, with certain modifications, is very extensively employed with satisfactory results, and some of the most important works on quantitative analysis do not mention the method of long swings. Fresenius (1875) describes the point of equilibrium as the place where the needle will come to rest after swinging. Adolphe Carnot (1898) says that the equilibrium of the balance is indicated by the pointer oscillating equal distances on each side and finally stopping at zero. Neither Fresenius nor Carnot say definitely that we should wait for the pointer actually to stop, and it would evidently be more convenient to observe the middle point of short swings. Clowes and Coleman (1914) state that consecutive swings to the right and left must finally be equal in extent. It is evident in the last case that the swings, in order to be equal, must be short ones.

Arguments Against Long Swings.

There can be no doubt that these swings are used in the belief that they increase the accuracy of weighing, but there appears to be absolutely no theoretical or practical ground for this belief, for the following reasons:

1. A long swing shows no greater variation than a short one for the same difference in weight. The variation is an absolute distance, which is not proportional to, nor increased by, the length of the swing, because the balance acts as a pendulum and, except for retardation, the pointer must swing equal distances on each side of the point of rest. For example, if the point of equilibrium is at +0.2 the pointer should swing from 0 to +0.4 and from —0.5 to +0.9, and were it not for retardation, it would swing from —5.0 to +5.4, from —10.2 to +10.6, etc., where, in every case, the excursion is 0.4 greater on one side than the other, with equal distances from the point +0.2. There is no doubt that the difference, 0.4, could be more readily observed from the short swings, 0 to 0.4 and —0.5 to +0.9, than from the long ones in which retardation prevents direct observation.

2. The retardation of long swings is such that their middle points do not coincide with their points of equilibrium, so that the latter must be found indirectly by calculation. Since the retardation is practically proportional to the length of the swings, it becomes inappreciable in a single, moderately short swing, or even in several shorter ones, so that the middle points of these correspond to their points of equilibrium, and the latter can be found very easily and accurately by direct observation.

There is no doubt that the direct, accurate observation is better than the indirect calculation.

3. Long swings cannot be read as accurately as short ones, because the more rapidly moving pointer in the first case allows less time for the careful observation of the end-point, and also because the parallax due to unsymmetrical positions of the observer's eye is much more likely to affect the reading of long swings than of short ones. Furthermore, the observation of very short swings across the center requires only the direct comparison of the two distances on each side, and this comparison can be made with great ease and accuracy. For instance, a swing from +0.2 to —0.3 could be readily seen to be unsymmetrical with the center, and the observation would be repeated and confirmed upon a number of succeeding vibrations, whereas this variation of 0.1 division could hardly be determined with certainty with long swings on account of the difficulty of reading them accurately, and because of the complication of retardation. It should be mentioned that a variation of 0.2 division in the swing indicates a difference of less than 0.1 mg. as balances are commonly adjusted; hence with an adjustment as sensitive as this a variation of 0.1 division, just discussed, or one even twice as great, could be disregarded in ordinary weighing.

4. There is no advantage, as far as diminishing the probable error is concerned, in the finding of the mean values of several observations that is practiced in long-swing weighing; for when short swings are employed the final result is observed at once, and this can be compared with subsequent swings which are usually identical and confirmatory. In order to obtain similar comparison and confirmation, it appears that the long-swing operator should repeat the whole of his observations and calculations a number of times, and compare the series of results thus obtained.

5. The calculation of the point of equilibrium from long-swing readings is mathematically inexact, because the retardation diminishes with the extent of the swings, while the means of the readings on each side are used in the calculation. It is admitted that the error thus introduced is ordinarily inappreciable, but this would not be the case with a balance adjusted to unusual sensitiveness, or carrying a very bulky object, so that the retardation amounted to a rather large proportion of each swing. For example, supposing the retardation of each swing to be $^1/_4$ of the distance from its starting point to the center, the latter being the point of equilibrium, the long-swing readings to be expected might be +10.0, —7.5, +5.6, —4.2 and +3.2, which give by calculation the point of equilibrium +0.4 instead of the correct point, 0. On the other hand, short swings $^1/_{20}$ the length of the others would give the readings +0.5, —0.4, +0.3, —0.2, and +0.2, which would indicate the true point by calculation, or more simply by observation.

6. There is more probability of making accidental errors in weighing with long swings than with short ones, for the reason that there are numerous different readings to be made and recorded in the long-swing operation, any one of which if incorrectly found will affect the result, whereas in short-swing weighing the observation merely consists in reading the position of the rider after making sure that the short swings are almost equal on each side of the center. Then there are chances for errors in the complicated long-swing calculations, and these are not required with short swings.

7. There is no reason to suppose that long swings are in any way more reliable than short ones. It might be imagined, perhaps, that an old balance with blunted knife-edges or grooved bearings, or both, would give better long swings than short ones, but experience with a great many balances, some of which had been used by students for many years, has not disclosed any such case, and if such a balance should be found it would seem best not to use it at all.

8. Some readings of long swings made by the writer have shown considerable irregularity, and it was suspected that the currents of air set up by the swinging were a source of error. However, more careful experiments carried out with an excellent Becker balance, and with the aid of a magnifying glass, showed that the suspicion was probably groundless, and that the previous irregularities had been caused by errors in reading the long swings. In one instance, a 4-inch watch glass, used on account of presenting a large surface for stirring the air, was counterpoised upon the balance, and the swings +0.3, —0.3, +0.3, —0.3, +0.3 and then +11.9, —11.4, +11.0, —10.5, +10.0 were obtained, giving the indicated middle points 0 and 0.02, respectively. In another experiment the empty balance was adjusted to equilibrium at the center, long swings were started and readings were made until the oscillations had died down to short ones. The first 5 readings were +12.0, —11.7, +11.3, —10.9, +10.6, indicating that zero-point precisely, then, after 96 very satisfactory readings that will not be recorded here, the following were obtained: +0.7, —0.7, +0.7, —0.7, +0.6, —0.6, +0.6, —0.6, +0.6, —0.6, +0.6, —0.5, etc. Both comparisons show excellent, and perhaps unexpectedly good results with the long swings, in the reading of which no high degree of accuracy can be claimed, but there is no indication of any advantage in the long swings over the short ones, and it is evident that the latter are much more convenient for reading and for finding the result.

Conclusion.

If the arguments presented here are sound, as they appear to be, it is certainly very remarkable that many chemists have considered it desirable to force the reluctant analytical balance, when close to equilibrium, to give long swings, in place of its natural short ones, in order to do a vast amount of useless work. The suspicion is unavoidable that the simple pendulum principle of the balance has been lost sight of in the entirely false expectation that the absolute variation of a swing would be increased by lengthening it. Possibly it has been supposed that short swings would be more likely to stop or to be erratic than long ones, but this is contrary to the very great amount of experience of those who use short swings, and it is contrary also to the precepts of high authorities, such as Fresenius and Carnot, already alluded to in this article. There is little doubt that many have merely followed the example of others in adopting this astonishing practice, without due consideration of the matter, and perhaps the mathematical and physical aspects of the method, or possibly its spectacular features, have had some influence in leading to its adoption.

It is to be hoped that all recommendations of long-swing weighing will soon disappear from our text-books of quantitative analysis, so that our future workers in chemistry may not be in danger of being burdened with a preposterously laborious method.

The writer is indebted to his colleague, Dr. John Zeleny, Professor of Physics, who has kindly examined the arguments presented in this article and has approved of its main conclusions in regard to long and short swings of the balance.

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[Contribution from the T. Jefferson Coolidge, Jr. Chemical Laboratory of Harvard College.]

THE AQUEOUS PRESSURE OF SOME HYDRATED CRYSTALS. OXALIC ACID, STRONTIUM CHLORIDE AND SODIUM SULFATE.

By Gregory Paul Baxter and John Ernest Lansing.

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Information concerning the aqueous pressure of hydrated crystals is in an unsatisfactory state, partly because the different methods used have not yielded concordant results, and partly because no systematic attempt has been made to cover the ground thoroughly, so that data in this field are meagre. Yet, a knowledge of aqueous pressure of crystals is often desirable, for either theoretical or practical purposes, such as the determination of conditions under which hydrated crystals are stable. The present investigation was undertaken chiefly for the purpose of perfecting a reliable method of measuring aqueous pressures of crystals, although the data obtained may possess some intrinsic value.

The "air current" or "transference" method which was chosen, has frequently been employed for the purpose in the past, but as the results