

As to s , it is obvious that s is zero when σ_A and σ_B have such values that the molecules involved are far apart. We might further assume that s has the value unity (*i. e.*, reaction is sure to occur) when the values of σ_A and σ_B are such that the molecules have certain minimum energy contents and such that they have come into contact in the sense of the kinetic theory. Hypotheses of this type have led to useful considerations in the hands of Trautz and W. C. M. Lewis.¹ Any really satisfying solution of the problem, however, would necessitate much more information than we now have as to the nature of the functional relationships of the type

$$E_A = E_A(\sigma_A)$$

connecting the energy of a molecule with its coördinates and momenta. Such information will become available as our knowledge of atomic structure increases, and this is a field where great advances may be expected in the near future. As to the functional relationships of the type $a_A = a_A(T)$, these can be obtained with the help of Equation 25 as soon as the nature of the relationships $E_A = E_A(\sigma_A)$ is known.

In conclusion, although the considerations of this paper have dealt solely with reactions in dilute gases, the general nature of their extension to concentrated gases, non-gaseous systems, and even non-homogeneous systems, will be evident even if exact mathematical treatments are not now possible.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE.]

THE STANDARDIZATION OF WEIGHTS.

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In order that the student beginning quantitative analysis should acquire, at the very first, a thorough manipulative knowledge of the balance, it has been our custom to provide, as a first exercise, the standardization of his box of weights. This has proved in the past an excellent method of accomplishing the result indicated and in addition he has obtained a knowledge of the relative values of his weights.

During the progress of such a standardization, from the fractional denominations to the 50 g. weight, any error, however slight, is multiplied until at the end a not inconsiderable but factitious correction is accumulated. Richards, in his excellent and well known contribution,² has given us a method of redistributing this error according to the relative values of the weights. This method of calculation is now in general use.

¹ *Loc. cit.*

² THIS JOURNAL, 22, 144 (1900).

The present paper suggests a slight modification now being followed by students in the Amherst College laboratory, consisting of the introduction of checks at fixed intervals in the progress of the work.

Three considerations have influenced the authors to this result. In the first place, a system of checks by converting the long process into a series of short exercises, makes it possible to use single hours—an advantage when the student's time is not so continuous as one could wish.

The second consideration is the fact that the method of redistribution overlooks the possibility of compensation of errors occurring more often in the extended process, so that a 10 g. weight (*e. g.*) upon which there should be no correction might be assigned by the redistribution a positive or negative "correction" to which it is not entitled.

The last point is a pedagogic one, namely that the division of the long process into separate exercises results in a simplification, so that this method has been found in the past few years much easier for the student to understand than any of the older methods.

In this modification, the essential thing is the use of a small box of auxiliary weights, standardized by the Bureau of Standards, and used only for checking. Our box of standards, marked "S," contains 5 weights—100 mg., 1 g., 5 g., 50 g. and 500 g.—of which only the first 4 are called into use in standardizing the ordinary box of weights. The class, after 2, or at most 3, weeks has completed its use of the little box of standards and shortly after this these 5 weights are sent to Washington for restandardization. The charges for this are very small.

By consulting the accompanying chart, which gives the series of weighings from 100 mg. to 1 g., it will be seen that each group of weighings (Col. I) corresponds to the tare maintained upon the right-hand balance pan during the weighings of that group. In Col. II are found the weights used successively on the left-hand balance pan. Differences found between weights in the same group are expressed in milligrams (by dividing the differences in "centers"—Col. IV—by the sensitivity) as given in Col. V; and from these the true values of the weights are found by algebraic addition, as given in Col. VI.

The work begins by placing a 100 mg. tare on the right-hand pan and the 100 mg. Bureau of Standards weight on the left-hand pan and finding the center of oscillation. Since the value of this weight (marked "S") is known, the center thus found is used as the unit for comparison in the next 3 weighings, (*b*), (*c*) and (*d*). A 200 mg. weight, as tare, is then placed on the right-hand pan and Group II is carried through in the same way. At the end of Group IV, a second standard weight is reached—the one g. weight of the Bureau, and here it is desirable to break the progress of the successive weighings long enough to check the final weighing,

which contains all accumulated errors, against the new standard weight. In the illustration, this amounts to $+0.79$ mg.

CHART I.

Name B.....		Balance No. I.....			S = 2.1.....	
I.	II.	III.	IV.	V.	VI.	VII.
Group.	Denominations.	Centers.	Diff's.	Mg.	Values.	Corr. values.
I.	(a) 100 mg. (S).....	+1.15	100,10	100,10
	(b) 100'.....	+1.05	+0.10	-0.05	100,05	99,96
	(c) 100'.....	+1.01	-0.14	-0.07	100,03	99,94
	(d) 50 + 20 + 10' + 10' + R.....	+1.05	-0.10	-0.05	100,05	99,96
II.	(a) 100 (S) + 100'.....	-0.25	200,15	200,06
	(b) 200.....	-0.02	+0.23	+0.11	200,26	200,08
III.	(a) 200 + 100' + 100" + 100(S).....	-0.67	500,44	500,09
	(b) 500.....	-0.73	-0.06	-0.03	500,41	500,01
IV.	(a) III (a) + III (b).....	+0.70	1,000,85	1,000,06
	(b) 1 g. (S).....	+0.45	-0.25	-0.12	1,000,73	999,94
Check: True value, 1 g. (S) =					0.999,94	999,94
					Error =	+0,79

On passing on to that portion of the standardization which runs from one g. to 5 g., as given on the succeeding Chart II (furnished to the student, but not shown here) this error is automatically discarded, for here the work begins by making the "center" found for the standard one g. the new unit of reference for all weighings of Chart II. The weighings of this chart may be checked in the same way at the end, against the third standard weight which is the 5 g. weight, of the Bureau. Chart III, which completes the work up to 50 g., is covered in a similar manner.

Returning now to Chart I, it will be evident that it would be possible to distribute the total error by subtracting from the value given in Column VI aliquots of the total positive error, or by adding, in case the error is negative. The correction for each 100 mg. will be $\frac{1}{9}$ of the total error (*i. e.*, 0.088 mg. in the illustration) rather than $\frac{1}{10}$, since the standard 100 mg. weight does not share in this distribution. The result of this process is exhibited in Column VII.

The illustration chosen shows a portion of the work of a student finding a rather large final error. This has been selected in order that the process of redistribution as shown in Column VII may be made clearer. By careful checking the final error should be less than 0.1 mg.

Charts II and III have not been presented in this paper, since they are arranged in the same way as Chart I. The sequence of weighings and the method of checking is essentially the same.

It may be unnecessary to add that there is no advantage claimed for the use of standards, as absolute. It will be apparent, however, that in a system of checks it is necessary to use standards. The

theoretical objective is, of course, solely to have the weights accurately compared *inter se*. But there is also the desideratum, when the exercise is given to students who are using the balance for the first time, that the method should appeal to them as simple and easy to grasp.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

HYDROLYSIS OF ZIRCONYL CHLORIDE AND SULFATE AT ZERO AND TWENTY DEGREES.

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The hydrolysis of zirconyl chloride has been measured at room and higher temperatures by Ruer¹ and a partial table given by Ruer and Levin² for zirconyl sulfate at room temperature. It was thought desirable to repeat these for varying dilutions and to determine both the progress and extent of hydrolysis. To throw further light, if possible, upon the reaction, experiments were carried out with a precipitant, iodic acid, which forms a practically insoluble compound with a portion of the combined zirconyl radical and carries down with it the fully hydrolyzed zirconyl hydroxide. At least this is one explanation of its action.

The 2 stable salts, zirconyl chloride and zirconium sulfate, were chosen for the purposes of the investigation. The latter is readily hydrolyzed to the zirconyl sulfate on the addition of water. These salts were freshly prepared and their purity carefully tested. The hydrolysis depends upon 3 factors—concentration, temperature, and time. In these experiments the temperature was held constant and separate series were carried out for each degree of dilution.

The apparatus used in making the conductivity measurements consisted of a modification of the Arrhenius conductivity cell, a Wheatstone bridge, and a small induction coil with telephone receiver. The measurements were made with 0.2, 0.1 and 0.01 *M* solutions for the sulfate and chloride. Readings were taken at 5-minute intervals when the hydrolysis was fairly rapid, and at increasing intervals as it slowed down. The first reading was taken immediately after solution. At the expiration of 3 or 4 hours the changes were so slight that the readings were stopped, since it was difficult to maintain the constant temperature for many hours or days. The relative conductivity is given in reciprocal ohms.

It will be noticed that at both 0° and 20°, and especially at the higher concentration, there is a brief period of temperature adjustment. This

¹ Ruer, *Z. anorg. Chem.*, **43**, 282 (1905).

² Ruer and Levin, *ibid.*, **46**, 449 (1905).