it is taken into consideration, are given in the paper at his suggestion. The value of these minima is, however, practically of so small importance that the results hardly repay the extra trouble involved in the treatment of the equations. Moreover, it is practically almost impossible to insure a maximum produce with the amount of oxygen indicated by this calculation, which, of course, always presupposes perfectly air-tight chambers. I have, therefore, preferred to give the theoretically less accurate but practically probably better result, which has the advantage of easy computation. A similar treatment would indicate that for chambers working with brimstone (where no oxygen is consumed otherwise than for production of sulphurous acid in the hilus) the maximum of chamber space is obtained by making

$$S = \frac{2 \times 0.42}{3 \times 3} = 0.0933$$

or 9.33 per cent. of sulphurous acid in the inlet gas, corresponding to 8.14 per cent. oxygen at the outlet.

ERRATA.

JANUARY NUMBER.—Page 9, second column, line 7, read "magnitude of the order of the radius of the sphere of action," instead of "magnitude of the radius," etc.

FEBRUARY NUMBER.—Page 50, instead of Fig. 5 under the diagram on this page, read Fig. 6; page 51, instead of Fig. 6 under the diagram on this page, read Fig. 5; page 51, instead of Table 1, read Table 5.

Wednesday, February 15th, 1882.

ON A METHOD USUALLY EMPLOYED FOR ESTIMATING SODIUM HYDRATE IN PRESENCE OF CARBONATE, TOGETHER WITH OTHER OBSERVATIONS ARISING FROM THE RESULTS OBTAINED.

BY WATSON SMITH, F.C.S.

In the experiments by myself, in conjunction with Mr. W. T. Liddle, on an insoluble form of soda existing in "lime mud," or crude calcium carbonate, produced in the process of causticising sodium carbonate solutions ("Proc. Lit. and Phil. Soc. of Manchester," vol. xx., 2 and 5, 1880-1, pp. 20 and 58), it was shown that this insoluble sodium compound was most probably a double carbonate of sodium and calcium, and formed from the alteration or partial change (possibly loss of combined water) which had taken place in a certain quantity of originally-formed artificial Gay-Lussite,

existing in the liquors in the earlier stages of the process of causticising. The artificial Gay-Lussite was first prepared in the crystalline form by Fritzsche ("Journ. für Prakt. Chem." 93, 339). It had more than once occurred to me that under similar circumstances an insoluble compound would be formed with barium carbonate. The idea received further point when, a few months ago, my friend, Dr. J. Grossman, of St. Helens, told me he believed an insoluble compound of sodium hydrate with barium carbonate is formed, when the usual method for estimating sodium hydrate in presence of carbonate is employed, by adding barium chloride solution to one of the caustic carbonate, followed by filtration, and titration of the filtrate. His reasons were that he had observed certain losses of caustic to occur when the method was tested with known quantities of all the materials. Dr. Grossman made a few preliminary experiments, showing that there

was evidence of such losses in the general mode of operating, and this formed the starting-point of the present closer practical inquiry. A frequent mode of operating this process for the estimation of the causticity of the so-called caustic soda ashes, used by paper-makers for rag-bleaching, etc., is to dissolve a given weight of the ash in water, and to add barium chloride in excess, when the following general reaction occurs:—

In some cases now the whole is thrown on the filter, and washed well, the filtrate being tested with normal acid, the amount of barium hydrate equivalent to the quantity of originally-existing hydrate of sodium (caustic) in the filtrate being thus determined. In more exactly-performed experiments the ash is treated in a stoppered flask of known volume, with the barium chloride solution in excess; water is added up to the graduation mark, and, after stoppering, the whole is well shaken up. After settling awhile the flask is opened, and a quantity of the supernatant fluid, still more or less turbid, taken out and filtered. A known volume of the filtrate is titrated with normal acid, and the alkali, as caustic, thus determined. Now it is easily conceivable that in the former case, and looking at the equation quoted, the carbonic acid in the atmosphere of the laboratory will rapidly convert more or less of the barium hydrate formed into carbonate, whilst the filtration and washings are taking place. This, of course, represents a loss on the sodium hydrate. Again, the solution of barium hydrate which does run through the filter into the testing-dish or flask may also become slightly carbonated, and this barium carbonate, as soon as all hydrate is neutralised in the subsequent titration, will no longer show alkaline reaction. In the second case—the one where the graduated flask and pipette are used—we have contact with the atmosphere of the laboratory (1) in drawing up the supernatant fluid from the flask into the pipette; (2) allowing it to flow in a thin stream upon the filter; (3) in standing on the filter; and (4) in flowing through into the test-vessel, etc. Hence, in this case, one would *a priori* expect certain losses to occur. Waiting till the contents of the stoppered graduated flask have completely cleared involves considerable expenditure of time spent in waiting. And then, in pipetting a quantity of clear liquor directly to the test-dish or flask, and titrating at once, still some little loss may occur in exposing so large a surface of the solution to the air in (1) drawing up into the pipette, and then letting run into the flask or dish in a thin stream, any barium carbonate formed in the solution not showing an alkaline reaction. The method of allowing the shaken contents of the stoppered flask to stand and clear perfectly, and then pipetting directly to the test-dish, and immediately titrating, is accurate, but requires time. But the actual experiments shall now speak for themselves, and here I must mention that these experiments have been carefully made by Messrs. H. Glendinning and R. J. Gow, in the laboratory of The Owens College, each gentleman working independently. Our object, in the first place, was to discover if, in the course of experiment, employing the different modifications usually adopted of the method generally described and known, losses do actually appear, and, if so, to what they are due, and how they may be eliminated.

EXACT PRECIPITATION WITH BARIUM CHLORIDE.

A solution was made by Mr. Glendinning, containing 9.801 grms. of caustic soda (from the Magnesium Metal Company) in the litre. 100 c.c. of this solution were

placed in a half-litre flask, precipitated exactly with barium chloride solution (thus only realising No. (ii.) of the equation above), and water added to fill up to the mark. In this case, therefore, only the sodium carbonate present is changed by the barium chloride, the hydrate remaining unaltered. A quantity of the supernatant liquor was now filtered, 200c.c. taken, and these required 9.3c.c. of normal acid for neutralisation. Again, 100c.c. of the original caustic solution were placed in a half-litre flask, and 25c.c. of a 3 per cent. solution of sodium carbonate were added, and then barium chloride, but only to exact precipitation, and, finally, cold water, till the flask was filled up to the mark. 200c.c. of the filtered liquor required 9.3c.c. of normal acid. A precisely similar experiment was now made, filling up the flask, however, with hot water. On cooling, filling to the mark, and testing as before, 9.3c.c. normal acid were again required.

PRECIPITATION WITH EXCESS OF BARIUM CHLORIDE.

The experiments just described were now repeated, employing, however, considerable excesses of barium chloride in the precipitations. 100c.c. of the original caustic solution (9.861grms. to the litre) were precipitated, with excess of barium chloride, diluted to the half litre, and 100 c.c. of the filtrates were then found to require 4.3c.c. of normal acid. Assuming the first experiment, tried with exact precipitation, to represent the correct percentage of hydrate in the 9.861grms. of caustic taken, which will therefore be 94.32 per cent. NaOH, we find from the above experiment, where excess of barium chloride was employed, that the percentage indicated is 87.22 of NaOH, showing a deficit from the former experiment of 7.1, which we may call 7.1 per cent. loss. Another experiment, taking 100c.c. as before, gave 4.4c.c. normal acid required, i.e., 9.8c.c. for 200c.c. = 89.25 per cent. NaOH; and this deducted from what we assume as the correct percentage, 94.32 gives 5.07, which we will call 5.1 per cent. of loss.

EXACT PRECIPITATION WITH BARIUM CHLORIDE.

Mr. Gow's results quite coincide with the foregoing. A solution was first made containing 9.96grms. of pure caustic, made from sodium, exact precipitation with BaCl_2 in the litre. (200c.c. of this solution required 49.5c.c. of normal acid, whose coefficient for correction is 0.98. Hence, the caustic contains 97.4 per cent. of alkali, all reckoned as hydrate, or 75.5 per cent. Na_2O .) 100c.c. of the above solution were precipitated, in the half-litre flask, exactly, with barium chloride solution, and then filled up to the mark. 250c.c. of the filtered supernatant solution required 12c.c. of normal acid, showing that the caustic contains 94.46 per cent. of NaOH actually, making some assumption of absolute accuracy as in the case of Mr. Glendinning's experiments at the same stage. Another 100c.c. were now mixed with 25c.c. of a 3 per cent. sodium carbonate solution, in the half-litre flask, exactly precipitated with barium chloride, and the flask was filled up with cold water. 250c.c. of the filtered liquor required still 12c.c. of normal acid, indicating no loss in the process. Another 100c.c. treated exactly as above, only now filling up the flask with boiling water. On cooling, filling again to the exact mark, 250c.c. of the filtered liquor required still 12c.c. of acid.

PRECIPITATION WITH EXCESS OF BARIUM CHLORIDE.

Now, precisely similar experiments were made, using excess of barium chloride in precipitation, 100c.c. caustic solution precipitated with excess of

barium chloride diluted to half litre, portion of supernatant fluid filtered, and 100c.c. taken. These required 4.6c.c. normal acid, representing 90.52 per cent. NaOH in the caustic instead of 94.41, as before indicated, and hence a loss of 3.89 per cent. 100c.c. of the caustic solution in another experiment, when hot water was used, required 4.65c.c. of normal acid = 2.91 per cent. of loss.

CONCLUSIONS.

Hence, from the experiments given, it would (1) appear that when exact precipitation with barium chloride is adopted, so as only to realise (ii.) of the equation, accurate results may be obtained by this method. Of course, on filtering the caustic solution, containing more or less suspended barium carbonate (exact precipitation having been adopted with barium chloride), any caustic previously present in the samples operated upon will remain as NaOH; and when carbonic acid is absorbed from the atmosphere the sodium carbonate formed filters as readily as caustic, and is estimated in the after-titration as easily. (2) On the contrary, when excess of barium chloride is employed, all caustic soda present yields barium hydrate, and this if carbonated during filtration, as before, remains on the filter; if after filtration, it will not manifest alkaline reaction. Hence varying losses are shown to occur.

APPARENT LOSSES OF SODIUM HYDRATE WHEN USING AN EXCESS OF BARIUM CHLORIDE TO PRECIPITATE CARBONATE.

Per cent.	Per cent.	Per cent.	Per cent.
7.1	5.1	3.89	2.91

RETENTION OF ALKALI BY THE PRECIPITATED BARIUM CARBONATE.

It now occurred to me that it would be of interest to settle the question already referred to at the commencement of this paper, viz., "Is alkali retained in the insoluble form by the barium carbonate when a solution of sodium carbonate is precipitated with barium chloride?" It would appear, from the experiments given, that no retention of sodium hydrate occurs by precipitated barium carbonate, and the question is now to be settled, "Is sodium carbonate retained?" That a double compound of barium carbonate with sodium hydrate should be formed under any circumstances, seemed from the outset structurally unlikely; but it is by no means safe, under all circumstances, to argue merely from observations of symmetrical theoretical structure, based upon stringent rules of valency. The following experiments were made by Mr. H. Glendinning:—

1. A solution containing 30grms. of pure sodium carbonate and 3grms. of sodium hydrate per litre was prepared. Of this 50c.c. were taken, and barium chloride was added in excess. The precipitate formed was thrown upon the filter, and washed thoroughly with boiling water, until the filtrate no longer manifested any alkaline reaction. The precipitate of barium carbonate was then dissolved in dilute hydrochloric acid, precipitated with pure sulphuric acid, filtered, washed thoroughly, and the filtrate was evaporated to dryness, when a small residue remained, which was weighed. The weight was 0.0655grm., and the substance was found to be pure sodium sulphate. This means 3.26 per cent. Na_2CO_3 on the sodium carbonate in the solution of known strength very nearly. (The carbonate contained in the caustic as impurity was disregarded.)

2. Again, 0.88grm. of pure sodium carbonate was dissolved in water, and barium chloride added, as before. After filtration, and thorough washing with boiling water, the barium carbonate remaining on the

filter was dissolved in hydrochloric acid, and all barium precipitated by sulphuric acid. After filtering, and washing thoroughly, the filtrate with wash liquors was evaporated to dryness, and the residue was weighed. It amounted to 0.0645grm., and consisted of pure sodium sulphate. This would mean 5.46 per cent. Na_2CO_3 on the 0.88grm. of pure carbonate taken.

3. In another experiment 1grm. of the ignited sodium carbonate was dissolved in water, and treated exactly as before, a final residue of 0.112grm. of sodium sulphate being obtained, indicating a retention in the insoluble form by the barium carbonate of 0.0836grm. of Na_2CO_3 , which is 8.36 per cent. of the weight of carbonate taken (1grm.).

Mr. R. J. Gow's results were generally confirmatory of the preceding, obtained by Mr. H. Glendinning:—

1. A solution was operated upon containing 30grms. of sodium carbonate and 3grms. sodium hydrate, in the litre. 50c.c. of this gave a final residue of 0.058grm. of pure Na_2SO_4 , operating exactly as in the previously-described experiments. This represents 2.89 per cent. on the Na_2CO_3 taken. Again, 1grm. pure sodium carbonate was now dissolved, precipitated with barium chloride, etc., finally yielding a residue of 0.084grm. of Na_2SO_4 = 0.062grm. of Na_2CO_3 = 6.2 per cent. Na_2CO_3 on that taken. But this experiment was carried a step further, for not only was the filtrate evaporated and the residue weighed, but the barium sulphate left on the filter was also weighed = 2.094grms. This equals of BaCO_3 , 1.77grm. But 1grm. of Na_2CO_3 should precipitate a weight of barium carbonate equivalent to 2.19grms. BaSO_4 , the equivalent weight of barium carbonate being 1.858grm. Hence, the loss in barium carbonate between what should be and what is obtained, is $(1.858 - 1.770)\text{grm.} = 0.088\text{grm.}$; and this, of course, should equal the weight of sodium carbonate retained by the barium carbonate, or calculated as equivalent to the sodium sulphate found as the residue, on evaporating the filtrate. This weight is 0.062grm., and, making due allowances for experimental errors, it comes tolerably near the number 0.088 obtained by difference. The results may be thus tabulated:—

Weight of Na_2CO_3 taken = 1grm.	
BaCO_3 , which should be precipitated by the 1grm. of Na_2CO_3 = 1.858grm.	BaCO_3 calculated on BaSO_4 obtained, after washing out all Na_2SO_4 = 1.770grm.

$(1.858 - 1.770)\text{grm.}$, or difference due to Na_2CO_3 removed, including experimental errors = 0.088grm.

Direct weight of Na_2SO_4 , calculated to Na_2CO_3 , gives of this 0.062grm.

The above gives 6.2 per cent. Na_2CO_3 retained by the BaCO_3 in an insoluble form. This insoluble soda compound is, in all probability, the exact counterpart of that formed in the lime-mud, on causticising sodium carbonate solutions, the latter being derived from Gay-Lussite,

and the former possibly from a barium Gay-Lussite,

It would thus appear that not only is the insoluble compound a carbonate, but, moreover, that the presence of sodium hydrate seems to prevent, to some extent, the formation of the double compound; at any rate, in the case of both experimenters, where sodium hydrate was present a much smaller retention was the result. Thus:—

H. GLENDINNING'S RESULTS.

I.
Ratio of caustic to carbonate in the solution used = 0.0250/91.

Sodium carbonate retained = 3.25 per cent.

II.
Carbonate alone used.

Sodium carbonate retained = (a) 5.46 per cent.
= (b) 8.36 per cent.

R. J. GOW'S RESULTS.

I.
Ratio of caustic to carbonate in the solution used = 0.0250/91.

Sodium carbonate retained = 2.89 per cent.

II.
Carbonate alone used.

Sodium carbonate retained = (a) 6.20 per cent.
(b) —

INFLUENCE OF THE FACTS NOW PROVED ON CERTAIN QUANTITATIVE ANALYTICAL PROCESSES.

From the results now described, it became plain that certain errors must arise in any analytical processes in which barium carbonate is precipitated in presence of sodium carbonate, if special precautions be not taken, and this led me to look around amongst such methods, to see if any are described in which the error referred to might creep in. A good example of the effect of ignorance of the above fact is furnished in the case in which the old method of operating was often applied for determining caustic soda in ash, by filtration from the precipitate produced by the addition of barium chloride in excess, and washing with boiling water, followed by titration of the filtrate and washings. Here the precipitate on the filter must consist of barium carbonate, together with a certain quantity of the insoluble sodium barium carbonate, which is attacked and partially decomposed by hot water, yielding an alkaline solution (Na_2CO_3). Now, what actually must occur in this process is the following:—

1. Loss of alkalimetric value through partial conversion of $\text{Ba}(\text{OH})_2$ into BaCO_3 by the CO_2 of the laboratory atmosphere during filtration.

2. Slight compensation for above loss through the final washing out of sodium carbonate by hot water (partial decomposition of the insoluble compound). This is only after protracted washing with hot water, and titration, first adding excess of acid and then determining the excess with soda.

Such a case of error in some of our analytical methods was not far to seek. A method is given in certain of our text-books on quantitative analytical chemistry, for the analysis and estimation of the constituents of "heavy spar," or natural barium sulphate. The sulphate is to be fused with sodium carbonate, the fusion, after cooling, being boiled out with water, and thoroughly washed. Certain of our books then recommend that the barium carbonate, after thus washing thoroughly, shall be treated in the crucible (already weighed), carefully and gradually, with sulphuric acid in excess, and that this treatment be followed by heating, to drive off SO_3H , and final ignition, the residue being taken as pure barium sulphate. Once or twice the method has been tried in our laboratory at The Owens College, but each time too high a result was obtained, and the method was finally abandoned. To put the question to a thoroughly practical test, Messrs. Glendinning and Gow first prepared a quantity of chemically-pure barium sulphate, and the following analytical experiments were then made by Mr. H. Glendinning:—

1. 1.1565grm. pure barium sulphate gave 1.1725grm. of a barium sulphate after fusion and treatment, as above described; but $1.1725 - 1.1565 = 0.016\text{grm.}$ excess, due to sodium sulphate, derived from sodium carbonate, retained by the BaCO_3 in the insoluble form. This 0.016grm. as Na_2SO_4 = 1.36 per cent. of Na_2SO_4 in the 1.1725grm. of barium sulphate yielded. The 1.36 of Na_2SO_4 = 0.985 of Na_2CO_3 . Hence the amount of sodium carbonate which must have been

retained by the barium carbonate in the insoluble state is 1.5 per cent. The 1.1725grm. of barium sulphate, containing sodium salt, was now treated with boiling water, filtered, and thoroughly washed. Filtrate evaporated to dryness gave a residue consisting of pure Na_2SO_4 . This residue weighed 0.0145 grm., nearly agreeing with the differential excess above deduced, viz., 0.016grm.

2. 1.022grm. barium sulphate (pure) gave 1.029grm. of a barium sulphate; excess here—0.07grm., or 0.68grm. Na_2SO_4 is contained in the barium sulphate.

3. 1.2035grm. barium sulphate gave 1.208grm.; excess—4.0045grm., or 0.37 per cent. Na_2SO_4 retained in the barium sulphate.

4. 1.134grm. BaSO_4 gave 1.139grm.; excess=0.005grm., or the barium sulphate contained 0.44 per cent. of Na_2SO_4 .

5. 2.047grms. barium sulphate gave 2.062grms. barium sulphate. Hence, excess=0.015grm., or the barium sulphate contained 0.727 per cent. Na_2SO_4 . Residue, after washing out and evaporating (as in No. 1), weighed 0.013grm., which is nearly equal to the excess found above by mere subtraction.

Mr. Gow's results were as follows:—

1. 1grm. pure barium sulphate gave 1.008grm. of a barium sulphate; excess=0.008grm., which means, 0.79 per cent. Na_2SO_4 was contained in the barium sulphate yielded. The weight of Na_2SO_4 actually extracted was 0.011grm., which is slightly in excess of that deduced, 0.008grm.

2. 1.186grm. barium sulphate gave 1.1945grm.; excess=0.0085grm., or 0.12 per cent. Na_2SO_4 contained in the barium sulphate.

3. 1.5915grm. barium sulphate gave 1.5935grm.; excess=0.002grm., or 0.12 per cent. Na_2SO_4 in the barium sulphate.

4. 1.1235grm. barium sulphate gave 1.129grm.; excess=0.0055grm. This equals 0.49 per cent. Na_2SO_4 contained in the barium sulphate yielded. On treating the barium sulphate (the 1.129grm.) with boiling water, and washing thoroughly, and evaporating filtrate to dryness, a residue was obtained which consisted of pure sodium sulphate, and weighed 0.0015grm., very nearly corresponding with the number obtained by difference, viz., 0.0055grm.

A discussion followed, in which Dr. J. Campbell-Brown, Dr. Hurter, Mr. J. H. Crossley, Mr. Campbell, Mr. E. W. Parnell, Dr. Schaeppi, and Mr. Macellwaine took part.

ON THE SEPARATION AND ESTIMATION OF SODIUM SULPHIDE, SULPHITE, AND THIOSULPHATE.

BY GEORGE E. DAVIS.

To those interested in alkali-making, a ready method, at once easy and accurate, for the separation and estimation of the combinations of sulphur, and sulphur and oxygen, with the alkali metals, would tremendously shorten the work, and make what has hitherto been a laborious and unsatisfactory process an easy and exact branch of analysis. It is to be regretted that our text-books treat so lightly upon the subject, and though there may be manuals treating of the estimation of all those compounds of sulphur with the alkali metals which are formed solely by the oxidation and subsequent decomposition of sodium sulphide, still I have not been able to find such a one. It is true that Fresenius gives a scheme for the analysis of gunpowder residues; but it may be easily seen that in many cases it is hardly applicable to the analysis of concentrated soda lye; and all of those processes where titration is made, after

acidifying with acetic acid, may be proved by experiment to be inaccurate. Soda liquors are of a complicated composition. They contain, besides the chloride, carbonate, hydrate, silicate, and aluminate of sodium, sulphate of sodium, together with sulphide and thiosulphate; but the liquors known to the manufacturer as red liquors, are even still more complicated, for they contain the products of the oxidation of the sulphide, and also the decomposition of the newly-formed products. The sulphur compounds found in these red liquors are: Sodium bisulphide, sulphide, sulphite, thiosulphate, and sulphate, together with sodium sulphocyanide; and when working with substances so liable to change, it may be seen how necessary is a rapid process. It is my intention now to speak only of a rapid method for the separation and estimation of sodium sulphite, sulphide, and thiosulphate.

In setting out a scheme for the analysis of these substances, it seemed necessary (1) to separate the sulphite; and in looking about for a salt which would form with the sodium sulphite an insoluble sulphite, strontium chloride was selected, the sulphite of this latter metal being insoluble, or nearly so, in water, 40,000 parts of water at 65° to 70°C. being required to dissolve one part of strontium sulphite; and the sulphide and thiosulphate of strontium are so very soluble that no error could be introduced by their formation. Now, suppose, for the sake of illustration, we have a mixture of these three sulphur compounds with sodium, a measured quantity should be largely diluted with carbonic acid water, starch solution added, and titrated with decinormal or centinormal iodine. In all cases where alkalies are present it is necessary that they be converted into bicarbonates, and that the water is free from oxygen. It is imperative that this precaution be observed, and that the solution is not neutralised with any acid likely to displace sulphurous anhydride, for in this case the nascent SO_2 would form polythionic acids, and the equilibrium of the solution be thereby disturbed. (2) To another portion of the solution is then added strontium chloride in slight excess, care being taken to keep the solution slightly alkaline throughout the operation, and the whole kept at a temperature of 65° to 70°C. for about half an hour in a flask closed with a caoutchouc stopper, through which passes a tube surmounted with an indiarubber valve opening outwards. After digestion the solution is filtered, the precipitate washed with air-free water, well diluted with carbonic acid water, starch solution added, and titrated with iodine solution. If the Bunsen pump is used care must be taken that air is not drawn between the folds of the filter, as in this case the sodium sulphide will suffer oxidation. A third portion is treated as in (2) with an excess of strontium chloride, and an excess of cadmium carbonate added, and, as in (2), kept at 65° to 70°C. for half an hour. The whole is filtered, and the precipitate is washed, and after treatment, as in (2), the filtrate is titrated with decinormal iodine. Here, then, we have every element for our calculations, which are of the simplest kind. In (1) we have the total iodine-consuming power of the solution; in (2) we have the amount of iodine consumed by the sulphide and thiosulphate, plus the amount of strontium sulphite dissolved by reason of its imperfect solubility; and in (3) we have the measure of the thiosulphate, with also the dissolved sulphite, as in (2). Now, at 65° to 70°C., 100c.c. of a saturated solution of strontium sulphite consume nearly 0.3c.c. of decinormal iodine, but only 0.16c.c. at 12.7°C.; so if one of these deductions be made for every 100c.c. of filtrate, the calculations may approach nearly absolute accuracy, which will be shown hereafter; but first may be cited