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ON THE USE

OF

CENTIGRADE TESTING

IN

PHARMACY.

BY JOHN JOSEPH GRIFFIN, F.C.S.

[From the PHARMACEUTICAL JOURNAL for JANUARY, 1851.]

THE objects of this paper are, to show the use of Centigrade Testing in the examination of the solutions of the acids and alcalies that are employed in Pharmacy; to point out easy and accurate methods of preparing such solutions of any required strength; to urge reasons for a greater simplicity and uniformity in the standards for acids and

alcalies prescribed in the three British Pharmacopæias.

The Chemical Strength of Acids and Alcalies a more important character than their Specific Gravity.—The chemical strength, quoted in the last column of the following Table, expresses the saturating power of equal measures of the respective solutions. Thus, diluted nitric acid of sp. gr. 1.092, the chemical strength of which is 150, will saturate twice its bulk of caustic potash of sp. gr. 1.072, the chemical strength of which is 75. I propose to indicate the comparative chemical strength of solutions by the term Degree, or by the symbol °. Thus, Nitric acid of 150° will indicate the acid of sp. gr. 1.092, and Potash of 75° will indicate that solution, the sp. gr. of which is 1.072. Acids and alcalies of the same degree, are of equal chemical strength, measure for measure.

The fact, that the Specific Gravity of a chemical solution is a character of inferior importance to its Chemical Degree, will be best

demonstrated by a few examples:-

a. The specific gravity of the diluted ammonia of the London and Edinburgh Pharmacopæias is .96, while that of the Dublin Pharmacopæia is .95. There does not appear to be much difference

	,	
	Specific gravity.	Approximate Chemical Strength.
DILUTE MINERAL ACIDS.		
Diluted sulphuric acidL	1.1132 ?	212
DittoE	1.09	166
Ditto	1.084	155
Diluted muriatic acidL		
		134
DittoE	1.05	168
Diluted mitric soid	1.045	150
Diluted nitric acidL	1.08 ?	130
DittoE	1.077	125
Ditto	1.092	150
CONCENTRATED MINERAL ACIDS.		
Sulphuric acidL	1.8457	
Ditto commercial E	1.84	
Ditto purumE	1.845	2100
DittoD	1.846	and the state of
Muriatic acidL	1.16	598
DittoE	1.18	658
Ditto, purumE	1.17	617
Ditto, paralli	1.176	642
	The second secon	The Control of the Co
Nitric acidL	1.5	1250
DittoE	1.5	1250
DittoE	1.39	790
DittoE	1.38	757
DittoE	1.28	500
DittoD	1.5	1250
ACETIC ACID.	2 9 9 9	and the filter
Acetic acidL	1.048	320
Distilled vinegarL	1.0085 ?	55
Acetic acid commonly E	1.063	925
Dittoto E	1.065	915
Dittonot above E	1.0685	900
Pyroligneous acidE	1.034	240
British vinegarfrom E	1.006	35
Dittoto E	1.019	120
Distilled vinegarE	1.005	30
French vinegarfrom E	1.014	83
		140
Dittoto E	1.022	Contract to the second
Acetic acid, glacialD	1.065	915
Ditto strongD	1.066	540
Ditto diluteD	1.006	35
Ditto commercialD	1.044	300
ALCALIES.	AL COLUMN TO S	No. Bearing St.
Diluted ammoniaL	.96	320
DittoE	.96	320
DittoD	.95	400
Strong ammoniaL	.882	944
DittoE	.88	960
Ditto	.9	800
Caustic potashL	1.063	66
DittoE	1.072	75
Ditto	1.068	71
Caustic soda	1.056	75
	1.473	530
Carbonate of potashL		320
Ditto	1.31	28
Carbonate of soda	1.026	20

between these numbers. The expressions differ only about one per cent. But sp. gr. .96 indicates a solution of ammonia, the chemical strength (or degree) of which is 320, whereas sp. gr. .95 indicates a solution the strength of which is 400. While, therefore, the densities differ as 96 to 95, the degrees differ as 4 to 5.

b. I received recently an estimate from a manufacturing Chemist in

London, of which the following is a copy:—

"Our Price for Nitric Acid, 1360 is 5d. per fb. 1425 is 10d. per fb.

Intermediate strengths in proportion."

Now the degree of nitric acid of sp. gr. 1.360 is 700, and that of acid of sp. gr. 1.425 is 900, and since 5:10=7:14, the price de-

manded for the stronger acid was one-third too high.

c. The glacial acetic acid of the Dublin Pharmacopæia has a sp. gr. of 1.065, and the acid of the next strength is directed to be made by mixing six measures of the glacial acid with four measures of water. The sp. gr. of the resulting solution is 1.066. This difference of sp. gr. is less than one in a thousand, a difference absolutely inappreciable by the hydrometer—and, indeed, by all the means of determining densities usually at the command of the Pharmaceutist. The specific gravity is consequently useless as a discriminating character. At the same time, the chemical degree of this acid changes during the dilution from 915 to 540, a difference so remarkable, in comparison with the slight change of density, that I will add a few words to show the progress of the change that occurs.

The strongest acetic acid that can be prepared at the temperature of 62° F. has a specific gravity of 1.058286. Its degree is 955. When this acid is diluted with a *little* water its density *increases*, while its strength decreases. When more water is added, the density as well

as the strength decreases.

At specific	gravity	1.058286	its degree	is 955
"	"	1.065	"	915
"	66	1.074428	"	800
44	66	1.066	44	540
44	"	1.044043	46	300
"	66	1.016343	"	100

It is consequently impossible to determine the strength of a sample of this acid by taking its sp. gr., whereas the Chemical Degree is always to be depended upon, provided it be accurately determined.*

Proposed Simplification of the Degree of the Acids and Alcalies prescribed in the three Pharmacopæias.—If we look down the column of Degrees that characterise the solutions enumerated in the above Table, we perceive, that, with many divergencies, there are symptoms exhibited of an occasional tendency to uniformity in the prescribed

For an account of the causes of the remarkable effects that attend the dilution of

acetic acid, consult Memoirs of the Chemical Society, vol. iii., p. 175.

^{*} The strength of Acetic acid cannot be accurately determined by any alcaline Carbonate, because the disengaged carbonic acid saturates the solution and makes it act on litmus. The carbonic acid can only be expelled by heat at nearly the boiling point of water, at which temperature acetic acid is liable to be driven off with the carbonic acid. The proper test for acetic acid is ammonia.

strength of the solutions. Thus the nine diluted mineral acids flutter about, and in two cases touch, the point of 150°. It may be said of these acids that all are about 150 degrees of strength. But why are they only about it? Why are they not precisely 150°? The reply to that question I apprehend may be, that hitherto Pharmacy has afforded no sufficiently ready process for preparing and testing diluted acids, so as to ensure the uniformity that is desirable. If this is really the case—if the necessity of uniformity is felt—and if the Genii who preside over the Pharmacopæias and regulate the movements of the Pharmaceutical world, are disposed to adopt uniformity of strength when methods of ensuring that uniformity are produced, I trust that the processes to be described in this paper will receive their concurrence.

But, returning to our examination of the Table, and passing, in the meantime, over the concentrated acids, let us examine the degree of acetic acid. A comparison of the acids cited in the Pharmacopæias with the processes in which acetic acid is used, leads me to fix upon 300° as the strength that appears to be most useful. This is twice the strength of the diluted mineral acids.

The alcalies show a similar tendency towards such a uniformity in chemical degrees as can be expressed by round numbers. Thus, diluted ammonia may evidently be made of 300°, caustic potash of 75°, caustic soda of 75°, the carbonate of potash of 300°, and the car-

bonate of soda of 25° (perhaps of 75°).

Returning to the consideration of the concentrated acids, I may preface my observations by a table which shows the chemical strength of the strongest solutions, not only of the acids, but of the alcalies, which it is possible to prepare, at the temperature of 62° Fah.

Sulphuric acid	21089
Muriatic acid	97909
Nitrie acid	1348°
Acetic acid	955
rotash	810
Potash, carbonate	665°
Soda sub mescribed in the book	
Soda, carbonate	185°
Ammonia 1 701 67 of 001 bas	1000°

When I ap

strengths of

The question, at what degrees of strength concentrated acids and alcalies should be kept by the Pharmaceutist is, I think, a much less important question than that regarding the strength of the officinal preparations to be employed in medicine. The question indeed is more commercial than medical, and might be safely left to the decision of individual judgment. The thing to be demanded, on the score of medical certainty, is, that the diluted solutions should be of fixed and invariable strengths, so that Physicians and Pharmaceutists may equally count upon their efficacy. The strength of the stock liquors, from which the diluted solutions are to be prepared, is of no importance. The preparation of the strongest possible solutions of any of the liquors is, in general, difficult and wasteful, and presents no corresponding advantages, since they have all to be again greatly diluted for medical purposes. At present, the Pharmacopæias make the strong acids their standards. They were adopted for standards when no better were known. They are retained, not because they are good,

but because they are established. It will be an improvement to adopt the dilute acids as standards, leaving the Pharmaceutist to keep his strong acids of any degree he finds convenient. He will be guided in that particular by the chemical manufacturer, whose prices will be regulated by the facility of manufacture and the cost of transport of acids of particular strengths. Thus, muriatic acid can be made pure by a single distillation at the strength of 500° (Gregory), while acid of a little above 300° can be repeatedly distilled without alteration of strength. These pure acids can be made cheaper than impure acids, prepared first of greater density, and then diluted. The nitric acid manufacturers produce liquors of the following strengths (Pereira):—

Single aquafortis sp. gr. 1.22 = 382° Double aquafortis sp. gr. 1.36 = 700°

It would be easy to have these prepared of 300° and 600°, numbers that bear a simple relation to the Officinal acid of 150°. Acetic acid is made for commercial purposes of the strength of 300°, and also at about 800°. Ammonia is very inconvenient and wasteful if made stronger than 800°, or sp. gr. .9, the degree now recommended in the Dublin Pharmacopæia.

TABLE OF THE PROPOSED STRENGTH OF OFFICINAL ACIDS AND ALCALIES.

	Approximate	
Solutions.	Sp. Grav.	Degree.
Sulphuric acid	1.082	150
Muriatic acid	1.045	150
Nitric acid		
Acetic acid		
Ammonia	0.962	300
Caustic potash	1.072	75
Caustic soda	1.056	75
Carbonate of potash	1.287	300
Carbonate of soda	1.067	75

When I apply the term "proposed" to the above strengths, it is not to specify strengths that I prefer above others; but simply to point out the round numbers which seem best to suit the average strengths of the solutions now prescribed in the Pharmacopæias. If the degrees were open to revision, I should prefer 100° to 150° for the mineral acids, and 100° to 75° for the alcalies. Among the advantages that would result from such an alteration, would be the simplification of the processes of testing and adjusting the strength of the various liquors.

On Centigrade Testing by means of Equivalent Test Liquors.—All who have mastered the elements of theoretical chemistry know, that the power of a chemical solution depends upon the number of atoms or equivalents it contains, and not upon the absolute weight of those atoms. Diluted nitric acid of 300° is twice as strong as diluted sulphuric acid of 150°, because there are twice as many chemical atoms present in it, not because the atoms of the nitric acid weigh twice as much as those of the sulphuric acid. Chemical solutions of Equivalent strength, or, what is the same thing, of the same Degree, must contain the same number of chemical atoms. The art of Centigrade Testing depends upon the preparation and use of chemical solutions of given degrees of strength, which subject I now proceed to explain.

System of Decimal Measures.—As the operations of Centigrade Testing are much facilitated when the calculations they require are made decimally, I begin with an explanation of a system, by which the imperial English gallon is divided into decimal measures.

Temperature, 62° F.; Barometer, 30 inches; Weight, avoirdupois.

Imperial grains.	Decimal
Water at 62° Fah.	Measures.*
70000 7000 700 70 70	Gallon Decigallon Centigallon Milligallon Septem Grain

Test Atoms.—The atomic weights of chemical substances, taken according to the scale where oxygen is 100, and weighed in English grains, constitute what I called test atoms. The following Table contains the test atoms of the substances referred to in this paper:—

Sulphuric acid	501.165 grains
Muriatic acid	455.13 "
Nitric acid	677.036 "
Acetic acid	643.19 "
Ammonia	212.5 "
Potash	589.916 "
Potash, carbonate	866.354 "
Soda	390.897 "
Soda, carbonate	667.335
Nitrate of silver	2128.643
Oxygen	100.000

* It forms no part of my present proposal to introduce Decimal Weights as well as Measures; but I may point out that this plan of dividing our Measures is capable of affording also a system of Decimal Weights. I shall sketch the plan in a Table, but without attaching any importance to the names given to the weights.

-	Grains of Water, at 62° Fah.	Decimal Measures.	Decimal Weights.
0	7000000	a decigration whe	Ton
9	700000	dissolvis neare	Hundred weight
ij	70000	Gallon	Stone
Y,	7000	Decigallon	Pound (Avoirdupois)
	700	Centigallon	Ounce, or Decipound
	70	Milligallon	Dram, or Centipound
	7	Septem	Septem
	7 6 7 1	Grain	Grain

If the grain were abolished, and the weight of seven grains made unity, the system would be strictly decimal.

STANDARD TEST SOLUTIONS.—When ONE TEST ATOM of any substance is dissolved in water, and the solution is diluted at the temperature of 62° Fahr., till it occupies the bulk of a decigallon, it constitutes a solution of one hundred degrees (100°). The absolute weight of the anhydrous substance is of no consequence, but there must be as much of it as is represented by the atomic weight weighed in English grains, the series of atomic weights being on the scale where oxygen is fixed at 100.

We have here the means of procuring a full explanation of the precise strengths of the officinal acids and alcalies recommended for

the adoption of the Colleges :-

Sulphuric acid of 150° will contain $1\frac{1}{2} \times 501.165 = 751.747$ grains of anhydrous sulphuric acid in a decigallon of solution.

Ammonia of 300° will contain 3×212.5=637.5 grains of anhydrous

ammonia in a decigallon.

The degree of every liquor, divided by 100, and multiplied by the test atom, will give the number of grains of the anhydrous substance present in a decigallon of the solution. That number, multiplied by 10, will give the number of grains contained in a gallon, and this, divided by 7000, will give the weight of the anhydrous substance in avoirdupois pounds.

Thus, the degree of the strongest ammonia is 1000.

Now $\frac{1000}{100} \times 212.5 = 2125$ grains in a decigallon. $2125 \times 10 = 21250$ grains in a gallon. $\frac{21250}{---} = 3$ lbs. 250 grains of anhydrous ammonia in a gallon.

Processes of Testing.—I shall now briefly describe the Processes by which the formation of liquors of the strengths above described, and the testing of such liquors, are to be regulated. In doing this, I shall confine myself as closely as possible to what relates to the principles of the method, leaving the details of manipulation for treatment elsewhere.

The number of liquors that are required to test all the acids, is only one—Ammonia of 50°. The number of liquors required to test the alcalies, is also one—a Mineral Acid of 100°. But as we cannot weigh out a test atom of an anhydrous acid, or half a test atom of anhydrous ammonia, to be dissolved in water to form these test-liquors, we are forced to prepare them by indirect methods, which require several

additional test liquors.

Preparation of Silver Test of 10°.—Dissolve 212.864 grains of pure crystallized nitrate of silver in six or eight ounces of distilled water, in a bottle graduated to hold a decigallon when filled up to a mark in the neck. When the salt is dissolved, nearly fill the measure with water, bring the solution to the temperature of 62 Fah., and then add water to complete the decigallon. The strength of this solution is 10°. 150 measures of it precipitate all the chlorine in 10 measures of muriatic acid of 150. It is therefore a test for the accuracy of the Degree of that acid.

Preparation of Soda Test of 100°.—Prepare a decigallon of solution containing 667.335 grains of pure anhydrous carbonate of soda. This

liquor will have the strength of 100°.

As a solution of 100 has two-thirds of the chemical strength of a solution of 150°, it follows that 150 measures of this soda test will be exactly neutralised by 100 measures of any of the acids of 150°.

Preparation of Acids of given strength.—Ten measures of the silver test and one measure of the soda test, have exactly the same action

on an equivalent quantity of pure muriatic acid.

a. Consequently, if you dilute muriatic acid till it is equal, measure for measure, to the soda test, and until one measure of it precipitates all the silver contained in ten measures of the silver test, it will be muriatic acid of 100°.

- b. But if you dilute it only till 100 measures of it are equal in chemical strength to 150 measures of the soda test, and if you then find that one measure of it will precipitate all the silver contained in fifteen measures of the silver test, the strength of that muriatic acid will be 150°.
- c. If on the contrary, you dilute the muriatic acid to a still greater degree, and stop at the point where 100 measures of it will saturate only 50 measures of the soda test, and one measure of it will precipitate all the silver from only five measures of the silver test, the strength of that acid will be 50°.

These examples prove that with these tests, we can bring the acids to any degree of strength we desire. I have instanced muriatic acid because we have a double test for it; but with the soda test alone all the mineral acids can be tested and adjusted to any required Degree.

I have said, that if you dilute muriatic acid to such and such an extent, certain results are produced. I proceed now to answer a question that will very naturally be asked,—In what manner can these respective stages of dilution be readily and certainly reached?

a. The first step in the process is to ascertain approximately the degree of your concentrated acid. What I have to say on this head applies equally to the three mineral acids. Mix one septem of the acid with 100 septems of water and a few drops of litmus. Heat the mixture nearly to the boiling point. Fill your alcalimeter, which must be graduated into septems, with soda test of 100°, and ascertain how many septems are required to neutralise the one septem of the concentrated acid. That number of septems expresses the number of Test Atoms of anhydrous acid contained in a decigallon of the concentrated acid. Multiplied by 100, it expresses the Degree of the acid. The following Table represents what must occur in an experiment of this kind:—

Quantity of Acid submitted to trial, one septem of each of the following.	Septems of Soda Test used.	Degree of the Strong Acid.
Sulphuric acid of about sp. gr. 1.845	20 to 21	2000 to 2100
Muriatic acid of sp. gr. 1.16 to 1.18	6 to 7	600 to 700
Nitric acid of about 1.5		1200 to 1300

An important source of error in this experiment is the extreme difficulty of measuring and transversing one septem of strong acid with correctness. A septem delivers from five to ten drops, according to the fluidity of the liquor under operation, and the difference of half a drop may influence the analysis from 10 to 20 per cent.

b. That difficulty is in part overcome by using five septems of the strong acid instead of one septem. The number of septems of soda test required to neutralise the acid will then be five times as much as before, and the result must be divided by five to give the Degree of the acid.

c. Third method. Mix 100 septems of the strong acid with some distilled water in a decigallon bottle, and dilute the mixture, at the temperature of 62° Fah., to the bulk of a decigallon. Fill your alcalimeter (which must be graduated into septems) with soda test of 100°. Put into a mixing-jar 100 septems of the diluted acid, add a little litmus, and neutralise the acid with the soda. (I pass over the description of the precautions necessary to be taken to ensure perfect accuracy in this experiment.) The number of septems of soda test of 100° required to saturate 100 septems of the diluted acid, multiplied

by 10, gives the degree of the concentrated acid.

When the precise degree of the strong acid is ascertained, the next step is to reduce that acid by dilution to the exact strength at which it is required. This is to be done by means of a Test-Mixer, a tall glass jar or bottle, graduated into 100 equal parts. Thus, a gallon jar may be divided into 100 centigallons; or a decigallon jar into 100 milligallons. A certain quantity of the strong acid, ascertained in the manner to be presently described, is accurately measured and mixed in a separate vessel with about three-fourths of the quantity of water known to be requisite for its ultimate dilution. When the heat produced by the mixture has abated, the acid is to be transferred into the test mixer, being carefully washed out of the separate vessel. It is to be diluted in the test mixer nearly to the required measure, allowed to cool to 62° Fah., and is then to be adjusted to the exact measure, with water at the same temperature. By this method a given measure of a strong acid is diluted by a single operation precisely to a given measure of another acid.

It only remains to show in what manner the respective quantities of the strong acid and the required diluted acid are to be ascertained.

Equivalent Volumes of Solutions.—The Equivalent Volume of a solution is the number of septems of it that contain 100 Degrees or one Test atom of its chemical constituent, considered in an anhydrous state. Thus, the Equivalent Volume of muriatic acid of 100° is 1000; that of acid of 200° is 500; and that of acid of 50° is 2000. Consequently, to convert acid of 200° into acid of 100°, 50 measures must be diluted to 100 measures, and to convert acid of 200° into acid of 50°, 25 measures of it must be diluted to 100. When the equivalent volume of a strong acid has been determined, and that also of a required weak acid, we have the exact measures from which the one is to be diluted to the other.

A good many years ago, I calculated an extensive series of Tables of acids and alcalies, in which the equivalent volumes of many thousand solutions are given; but those Tables have not been published. I give, therefore, the following methods for finding the Equivalent Volume from the Degree of a solution.

a. To those accustomed to the use of Logarithmic Tables, I may

state the method as follows:-

The Reciprocal of the Degree, multiplied by 100000, is the Equivalent Volume of the solution.

b. For those not accustomed to such Tables, I may state the following method:

The Equivalent Volume is the product of 1000 divided by the Degree.

The following examples selected from a table of muriatic acid, will render the use of the Equivalent Volumes evident.

Specific gravity.	Degree.	Equivalent Volume
1.2	752.59	132.87
1.1891	700.	142.86
1.1662	600.	166.67
1.1408	500.	200.00
1.1148	400.	250.00
1.0878	300.	333.33
1.0599	200.	500.00
1.0450	150.	666.67
1.0310	100.	1000.0

For the same Degree the Equivalent Volume is the same for all substances.

Preparation of Muriatic Acid Test of 100°.—I have now shown in what manner the Degree of any given sample of muriatic acid can be determined; how, from the degree, is it possible to determine the Equivalent Volume; and with the equivalent volume and a Test-mixer, to prepare any required weak acid from a strong acid.

Thus, to prepare a decigallon of muriatic acid of 100°, you require 166²/₃ septems of acid of 600°, 333¹/₃ septems of acid of 300°, or 666²/₃ septems of acid of 150°. These quantities diluted to 1000 septems give the acid required.

Preparation of Acids of 150°. The equivalent volume of any acid stronger than 150° produces acid of this strength when diluted to the volume of 666\(\frac{2}{3}\); or the equivalent volume of the strong acid, multiplied by 1\(\frac{1}{3}\), diluted to 1000, produces acid of 150°.

Preparation of Ammonia Test of 50°.—a. Ascertain approximately the strength of a pure solution of ammonia, by testing five septems of it in the manner described for the approximate testing of acids, using muriatic acid of 100° in the graduated alcalimeter, to neutralise the ammonia. The mixture of acids and ammonia is best made in a glass bottle of four ounces capacity, provided with a flat headed glass stopper. A few drops of litmus are used, no test paper is required, nor is the liquor to be heated.

b. Dilute the ammonia till it is of about 55° or 60°. Fill the centigrade alcalimeter with it. Put into the mixing bottle 50 septems of muriatic acid of 100°, and neutralise it with the diluted ammonia, of which 80 to 90 septems will be required.

c. Repeat experiment b with all possible care, and ascertain precisely the number of septems of ammonia required to saturate 50 septems of muriatic acid of 100°. That number of volumes diluted in the test-mixer to 100 volumes, constitutes the ammonia test of 50°. Ammonia test of this strength, if kept in a dark cool situation, in a well stoppered bottle, remains constant for a long time.

This completes the series of Test Liquors. Those required for

ordinary use are the ammonia test of 50° and muriatic acid test of 100°. From time to time, the accuracy of the ammonia test is to be examined by means of the muriatic acid test, and the accuracy of the latter by means of the silver test and soda test.

Ordinary Processes of Testing. Problem 1. To test the strength of a mineral acid presumed to be 150°. Put 25 septems into a mixing-bottle, and test with ammonia of 50°. 75 septems should be required

to neutralise the acid.

Problem 2. To test the strength of ammonia presumed to be 300°. Act on 25 septems of the ammonia with the muriatic acid test of 100°, of which 75 septems should be required.

Problem 3. To test the strength of acetic acid presumed to be 300°, Put 10 septems into a mixing bottle, and test with ammonia of 50°, of

which 60 septems should be required to neutralise the acid.

Preparation of Acids and Alcalies of officinal strength.—The degrees of the stock acids having been tested by ammonia, and those of the alcaline liquors by muriatic acid, the officinal solutions are prepared by dilution in the test-mixer. After the solutions are diluted, they should be again tested, to ensure their accuracy.

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