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DYNAMICAL THEORY OF ALBUMINOID AMMONIA.[1]

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The following investigation was suggested by committee work of the American Association for the Advancement of Science, on water analysis. It is an attempt to apply well established principles of mass action to certain questions involved in the determination of albuminoid ammonia. The following points have been kept in view:

1. Can some probable correction be made for the error incurred by stopping the distillation while ammonia is still coming off?
2. What modification of the original method seems rational?
3. What insight can be gained into the nature of the chemical process?

The experimental basis of the following paper will be found in Mallet's report on the determination of organic matter in potable water,[2] with the addition of some details kindly communicated by Dr. Charles Smart.

I. *Distillation of Free Ammonia.*

In the distillation of albuminoid ammonia, two stages must be distinguished: first, oxidation of the nitrogenous body by the alkaline solution of permanganate; and, second, the separation of

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[1] Prepared for the Toronto meeting of the American Association for the Advancement of Science.

[2] Report of the National Board of Health for 1882.

ammonia thus formed by distillation. It will be most convenient to begin with the discussion of this second process, which is essentially physical. As in any other case of fractional distillation, water and ammonia both pass from the fluid to the gaseous or vapor condition, in accordance with their respective tensions and mass.

Let $x =$ volume of fluid in retort,
$y =$ weight of ammonia in retort,
$z =$ weight of ammonia in distillate.

Then $\frac{y}{x} =$ concentration of fluid in retort,

$\frac{dy}{dx} = \frac{-dz}{dx} =$ concentration of any small portion of distillate.

The coefficient of volatility may be defined as the ratio of the concentration in any small portion of distillate to that of the fluid in retort. Designating this coëfficient as k,

$$\frac{dy}{dx} = k . \frac{y}{x}. \qquad (1)$$

In the ordinary distillation of ammonia, k is found to be approximately constant, and it will be so regarded here. By integration,

$$\log_e y = k . \log_e x + \text{constant};$$

using zero subscript to denote initial conditions,

$$\log_e y_0 = k . \log_e x_0 + \text{constant},$$

$$\therefore \quad \log_e \frac{y}{y_0} = k . \log_e \frac{x}{x_0},$$

or

$$\log \frac{y}{y_0} = k . \log \frac{x}{x_0}, \qquad (2)$$

a very useful formula for determining the coefficient of volatility and tracing the progress of distillation. Curve *A*, in the figure, represents y as that function of x defined by equation (2).

Wanklyn,[1] who was the first to use and define the term coefficient of volatility, reports four experiments for its determination. One liter of dilute aqueous ammonia was distilled in each case until 50 cc. of distillate had been collected. As nearly one-half the ammonia taken was distilled with the first 5 per cent. of water (the concentration in the retort being gradually reduced at the same

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[1] Phil. Mag. [4], **45**, 132 (Feb. 1873).

time), Wanklyn estimated k equal to "about thirteen or fourteen." The experimental data are given below with more precise values of k, as calculated by equation (2). In each case, $x_0 = 1000$, $x = 950$. The quantities of ammonia taken, and that found in the distillate, are expressed in milligrams under y_0 and z respectively; the difference (remaining in retort) under y:

y_0.	z.	y.	k.
1000	480	520	12.74
1	.50	.50	13.50
.5	.235	.265	12.39
.2	.095	.105	12.55
		Mean	= 12.8

This value may be rather too low, as no account is taken of a possible loss from imperfect condensation, a loss averaging 7.2 per cent. in Smart's experiments.

The same author observes also[1] that in the distillation of one-half liter of water, the ammonia found in the first measure of 50 cc. is three-fourths of the whole quantity of ammonia obtained. By equation (2), assuming that any loss affects each part in the same proportion,

$$\log \tfrac{1}{4} = k \, . \log \tfrac{9}{10},$$
$$\therefore \quad k = 13.14.$$

Thirty experiments by Smart to determine the loss of ammonia by imperfect condensation are also available for the estimation of k, the successive measures of distillate having been nesslerised separately.[2] A single distillation affords several values, as each fraction determined may be compared with the whole quantity found in subsequent fractions. The values thus deduced vary from 10 to 16, with a few instances beyond these extremes. The variations in the values of k do not show any well marked relation to the whole quantity of ammonia present, to the amount of loss, nor to the rate of boiling. The experimental work was done wholly for another purpose, and probably with just such care as the conscientious analyst would ordinarily give. We may then assume 13 as a mean value for k, remembering that considerable allowance must be made for unexplained variations.

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[1] Wanklyn's *Water Analysis*, 6th and 7th editions, p. 41.

[2] Most of these data appear in the Report of the National Board of Health for 1882, pages 312–314.

II. *Application of Formula to Estimation of Free Ammonia.*

In the analytical process it is usual to distill three or four fractions, each nearly equal to one-tenth of the original volume. For 100 parts of free ammonia present, when $k = 13$, theory would lead us to expect, in four successive fractions, the increments named below under Δz, with loss of 0.13; vertical lines in the figure, *a*, *a*, *a*, represent these increments geometrically. The ratio of each increment to the next is stated under r. The mean values of the ratios obtained in the experiments to determine loss of ammonia are given under r':

No.	Δz.	r.	r'.
1	74·6	3·75	4·23
2	19·9	4·4	5·26
3	4·53	5·4	5·65
4	·84		

In the analyses of natural waters reported (*loc. cit.* pp. 321–330), considerable variation appears in the ratios of successive increments, but usually not more than might be expected from the observed variations in k. Analyses No. 18 and No. 54 are exceptional and happen to give identical results, the free ammonia being .015, .01, and .01 mgm. in the three fractions nesslerised, with ratios 1.5 and 1. In such cases there is a strong probability that some more complex body is gradually decomposed by simple boiling with sodium carbonate. Small ratios between the successive fractions of "free ammonia" may lead to suspicion of urea contamination, though of course due caution should be used in drawing such conclusions. The analyst will at least find it instructive to enter the ratios in his note-book, together with the separate results of nesslerising; this will appear more plainly in the following sections. The slowness of the chemical action usually retards the distillation of albuminoid ammonia, giving rise to much smaller ratios between successive fractions than those named above.

III. *Action of Mass in Formation of Albuminoid Ammonia.*

We must now attempt to follow the chemical as well as the physical aspect of the process. In the former the reactions may be much involved, and various formulas may be required to represent the successive formation and destruction of different substances. Let us consider, as an ideal case, a single chemical reaction, involving one molecule each of three reacting bodies; the formation of ammonia taking place at each moment of distillation, in each cubic centimeter of the fluid, in proportion to the product of the quantities of the nitrogenous body, the potash, and the permanganate present therein.

Retaining the use of x, y, and z as explained in section I, let

$u =$ weight of the nitrogenous body in the retort,
$v =$ weight of potash in the retort,
$w =$ weight of potassium permanganate in the retort,
$t =$ time, in minutes, from the beginning of the reaction,
$a =$ coefficient of speed.

Assume also a uniform rate of distillation, in which

$b =$ volume distilled per minute,
$bc =$ volume of fluid in retort at the beginning of the action;

whence

$$x = bc - bt,$$

and

$$dx = -bdt.$$

Then $\frac{u}{x}$, $\frac{v}{x}$, and $\frac{w}{x} =$ weights of the three active substances in each cubic centimeter of fluid in the retort,

$$\frac{-du}{dt} = b\,\frac{du}{dx} = \text{rate of change},$$

and, by the law of mass action,

$$b\,\frac{du}{dx} = a\,.\,\frac{u}{x}\,.\,\frac{v}{x}\,.\,\frac{w}{x}\,.\,x = avw\,.\,\frac{u}{x^2},$$

$$\therefore\quad \frac{du}{u} = \frac{avw}{b}\,.\,\frac{dx}{x^2}. \tag{3}$$

The reagents are present in such large excess that v and w may be regarded as constants (unless the permanganate suffers from an unusual amount of pollution), and by integration,

$$\log_e u = -\frac{avw}{b}\,.\,\frac{1}{x} + \text{constant},$$

$$\log_e u_0 = -\frac{avw}{b}\,.\,\frac{1}{x_0} + \text{constant},$$

$$\therefore\quad \log_e \frac{u}{u_0} = -\frac{avw}{b}\,.\,\frac{x_0 - x}{x_0 x},$$

which may be written

$$-\log \frac{u}{u_0} = \frac{avw}{bx_0 \log_e 10}\,.\,\frac{x_0 - x}{x} = A\,.\,\frac{x_0 - x}{x}. \tag{4}$$

This equation represents any one reaction of the kind specified during the concentration required in an ordinary estimation of albuminoid ammonia, but the mathematical expression must not be pressed too far. Thus, if we make $x = 0$, this not only implies that the contents of the retort are evaporated to dryness, but also that the reagents have gained infinite concentration, and therefore act with resistless force, effecting complete alteration of any remaining traces of the nitrogenous body. The form of the curve varies greatly with the value of A. Two examples are given in the figure. Curve B represents this equation when $A = 1$; curve C when $A = \frac{1}{10}$. Since the quantity of ammonia present at any moment (both in retort and distillate) is proportional to the weight of the nitrogenous body transformed, we may write

$$u_0 - u : u_0 :: (y + z) : (y + z)_\infty,$$

where subscript ∞ is used to denote the ultimate value theoretically possible; or, in another form (since $y_\infty = 0$),

$$\frac{u}{u_0} = \frac{z_\infty - (y + z)}{z_\infty}. \qquad (5)$$

The curves B and C are so drawn that ordinates represent $(y + z)$ as a function of x.

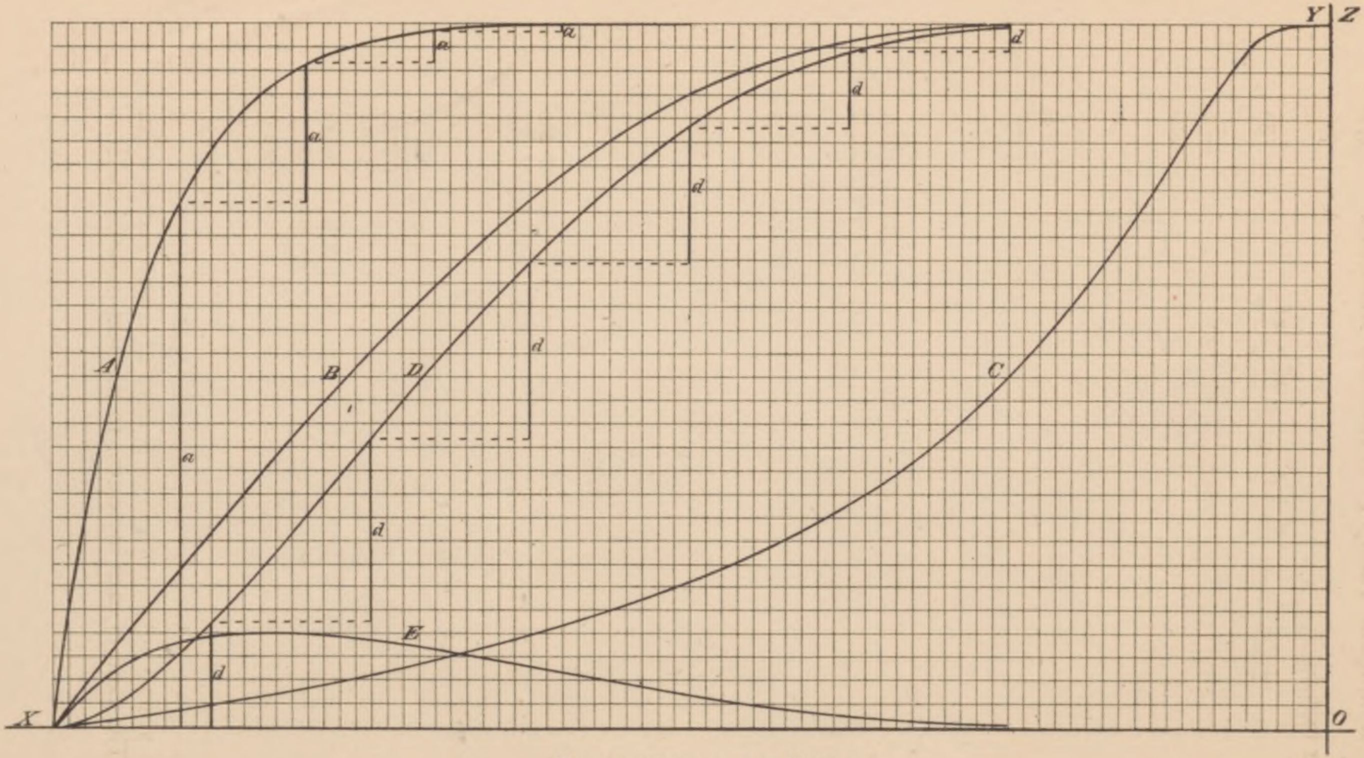
It will be seen at once that when $A = 1$ the quantity of ammonia increases very rapidly during the first part of the distillation, but when $A = 0.1$, $(y + z)$ increases but slowly until the fluid is considerably concentrated. Equation (4) suggests various modifications by which A may be altered at pleasure; for example, by increasing the quantity of permanganate used (represented by w), or by distilling a less quantity (b) each minute. Thus Smart noted several instances of increased action by slower boiling.

Curves of similar properties express the progress of other reactions which take place during concentration in large excess of reagents. Equations of the following forms are obtained by varying the exponent of x in equation (3) and using the appropriate constants. For reactions involving the concurrence of two molecules only,

$$-\log \frac{z_\infty - (y + z)}{z_\infty} = -A \cdot \log \frac{x}{x_0}. \qquad (6)$$

For three molecules,

$$-\log \frac{z_\infty - (y + z)}{z_\infty} = A \frac{x_0 - x}{x}. \qquad (7)$$



EXPLANATION OF THE FIGURE.

A. Curve of distillation of free ammonia. *a*, *a*, *a*. Fractions, each $\frac{1}{10}$ the original volume. *B*. Formation of albuminoid ammonia, eq. (7); $A = 1$. *C*. Formation of albuminoid ammonia, eq. (7); $A = \frac{1}{10}$. *D*. Ammonia in distillate, from curve *B*. *d*, *d*, *d*. Fractions, each $\frac{1}{8}$ the original volume. *E*. Ammonia in retort, from curve *B*. Values of x, although positive, are measured towards the *left*, in order that time may be counted towards the *right*.

For four molecules,

$$-\log\frac{z_\infty-(y+z)}{z_\infty}=A\,\frac{x_0^2-x^2}{x^2}. \tag{8}$$

In all such cases the formation of ammonia may take place most rapidly in the early, middle or latter part of the distillation, according to the value of A.

If the ammonia, instead of appearing directly, is the final product of a succession of different reactions, a complete theory must take account of the gradual formation and disappearance of the intermediate products. Some evidence on this point will appear in section VI.

IV. *Distillation of Albuminoid Ammonia.*

Equation (1) applies to the distillation of ammonia only when the total quantity $(y+z)$ remains constant; otherwise we must write $-dz$ in place of dy. Thus,

$$\frac{-dz}{dx}=k.\frac{y}{x}, \tag{9}$$

or

$$y=-\frac{x}{k}\cdot\frac{dz}{dx}. \tag{10}$$

Substituting in equation (7),

$$-\log\left(1+\frac{xdz}{kz_\infty dx}-\frac{z}{z_\infty}\right)=A\,\frac{x_0-x}{x}. \tag{11}$$

This equation (as soon as a fixed value is given to A) expresses a perfectly definite relation between the ammonia distilled and the volume remaining in the retort. It is not easy, however, to obtain an integral in form suitable for computation, and an indirect method was used. The ordinates of curve B represent the sum of y and z when $A=1$; these ordinates were divided into two parts, in accordance with the condition implied in equation (9). Curve D thus represents the gradual increase of z, and curve E shows the increase and subsequent decrease of y. A few corresponding points of these three curves are also indicated in the following table, increments of z being placed under the symbol Δz. These increments are shown on the figure as *d*, *d*, *d*. For convenience, z_∞ is taken as unit of weight for ammonia, and x_0 is made equal to 8; as when a volume of 400 cc. is distilled in fractions of 50 cc. each. The ratio of each increment to the next is stated under r.

x.	$y+z$.	y.	z.	Δz.	r.
8	.000	.000	.000	...	...
7	.280	.129	.151	.151	.58
6	.535	.122	.413	.262	1.05
5	.749	.087	.662	.249	1.31
4	.900	.047	.853	.191	1.74
3	.978	.015	.963	.110	3.23
2	.999	.002	.997	.034	...
0	1.000	.000	1.000	...	...

When $A = 1$ (as in this table), y reaches a maximum when $x = 6.7$, during the collection of the second fraction of distillate; and this fraction contains the largest quantity of ammonia. The third fraction contains nearly the same amount, but later increments show a rapid decrease. The large increase of ammonia indicated for the second measure is due in very small part to the increased concentration of the permanganate, but chiefly to the fact that sufficient time has elapsed for the accumulation of ammonia in the retort. An increase in the second measure has been rarely observed in practice, except in a few experiments on pure chemicals, such as urea, theine, glychocholic acid, and notably in cyanuric acid. In the 59 samples of natural waters already referred to, the first measure always contained as much as 1½ times that found in the second; in 11 instances the ratio is 2, and in 33 instances it is more than 2. On the other hand, instead of an increase in this ratio for succeeding portions (as indicated by theory for a single reaction), it usually decreases, the ratio of the last two determinations being from 1 to 2. This want of agreement between the theory for a single reaction and observations on a natural water are exactly what we should expect; for the water may contain a great number of different substances, each undergoing change according to equation (6), (7) or (8), so that the actual rate of distillation depends upon the sum of the ammonia derived from all these sources. As curve E shows a rapid rise from zero to a maximum, followed by a gradual decrease to zero, so we may conceive a multitude of similar curves, with their several maxima at various points, but with a large share of them near the origin; implying $A > 1$, for the most part. The resultant of all such curves might have a single maximum, like the type given, or it might have a succession of maxima and minima. On the theory of averages, the former seems more probable. This resultant curve might have a great variety of form in details, answering to the various behavior of different waters.

V. *Exterpolation Formula for Residue in Retort.*

Many chemists, feeling that the task is not completed by nesslerising three measures, have pushed the distillation much farther. Mallet[1] suggests a certain limit as criterion when the distillation has been carried far enough. If the ammonia found in the successive portions is reported, we can rudely plat the curves for ammonia distilled, ammonia in retort, or total ammonia formed. Each of these curves may be the resultant of many similar curves having different parameters. Can we find an empirical equation for the resultant that will conform to the analytical results, and thus enable us to apply a probable correction for the ammonia that would be obtained if the distillation were completed?

We may assume a curve of the form

$$y = Ax + Bx^2 \tag{12}$$

to indicate the varying quantity of ammonia in the retort under the condition that this is all distilled away when the fluid is gone. Substituting in equation (9),

$$\frac{-dz}{dx} = kA + kBx.$$

Integrating between the limits z_1 and z_2,

$$z_2 - z_1 = kA(x_1 - x_2) + \tfrac{1}{2}kB(x_1^2 - x_2^2);$$

or, for brevity,

$$\varDelta_1 z = kA\varDelta_1 x + \tfrac{1}{2}kB\varDelta_1 x^2. \tag{13}$$

In like manner, for a second increment of z and for the undetermined portion,

$$\varDelta_2 z = kA\varDelta_2 x + \tfrac{1}{2}kB\varDelta_2 x^2,$$

$$\varDelta_\infty z = kA\varDelta_\infty x + \tfrac{1}{2}kB\varDelta_\infty x^2. \tag{14}$$

Those who follow Wanklyn's directions for 500 cc. of water begin the distillation of albuminoid ammonia with 350 cc. of fluid, and distill three measures of 50 cc. each, rejecting the last 200 cc. Taking 50 cc. as unit of volume, $x_1 = 6$, $x_2 = 5$, and $x_3 = 4$, while $\varDelta_1 z$ and $\varDelta_2 z$ represent the ammonia found in the second and third measures. Assume $\varDelta_1 z = r\varDelta_2 z$, then

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[1] *Loc. cit.* p. 208.

$$r\Delta_2 z = kA\,(6-5) + \tfrac{1}{2}kB\,(36-25) = kA + 5.5kB\,,$$
$$\Delta_2 z = kA\,(5-4) + \tfrac{1}{2}kB\,(25-16) = kA + 4.5kB\,.$$

By elimination,

$$kB = (r-1)\,\Delta_2 z \text{ and } kA = (5.5 - 4.5r)\,\Delta_2 z\,.$$

But
$$\Delta_\infty z = 4kA + 8kB\,,$$
$$\therefore\quad \Delta_\infty z = (14 - 10r)\,\Delta_2 z\,. \qquad (15)$$

If
$$r = 1\,,\ \Delta_\infty z = 4\Delta_2 z\,;$$

that is, if the second and third measures yield like quantities of ammonia, the best correction we can make is to assume that the distillation of four times 50 cc. still remaining in the retort would yield four times that quantity.

If $r > 1\tfrac{2}{9}$, the value of A becomes negative, and therefore y becomes negative for small values of x. This involves a physical impossibility, but we may meet the difficulty by treating the equation

$$y = Ax^2 + Bx^3 \qquad (16)$$

in the same manner as equation (13), whence

$$\Delta_\infty z = \frac{188 - 100r}{37}\,\Delta_2 z\,, \qquad (17)$$

a correction which again fails if $r > \tfrac{81}{61}$.[1]

We may test these formulas by means of Smart's experiments with pure chemicals; but, as he began the action with 400 cc. of fluid instead of 350, $\Delta_1 z$ and $\Delta_2 z$ represent his third and fourth fractions, with the advantage of greater distance from the beginning of the operation, where equation (12) is wholly inapplicable. The available data (for values of r between 1 and 1.5) are given in the following table, which states under

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[1] To obtain a more general formula for the correction proposed, we may assume

$$y = Ax^n + Bx^{n+1}\,, \qquad (18)$$

whence, by the same treatment illustrated above,

$$\Delta_\infty z = \frac{(\Delta_1 x^{n+1} - r\Delta_2 x^{n+1})\,\Delta_\infty x^n - (\Delta_1 x^n - r\Delta_2 x^n)\,\Delta_\infty x^{n+1}}{\Delta_2 x^n \Delta_1 x^{n+1} - \Delta_1 x^n \Delta_2 x^{n+1}}\,\Delta_2 z\,, \qquad (19)$$

where A is positive or zero when

$$r \leq \frac{\Delta_1 x^{n+1}}{\Delta_2 x^{n+1}}\,. \qquad (20)$$

We may either make n the smallest integer consistent with the condition (20), or we may determine n by making the fraction equal to r. The function $\Delta_\infty z = \phi(r)$ will be a smooth curve in either case, consistent with the theory as developed above and with the analytical results.

A, per cent. ammonia found in the first four fractions;
B, per cent. ammonia found in "exhaustive experiments";
C, per cent. ammonia obtainable after the first four fractions; and
D, per cent. ammonia indicated by the exterpolation formulas.

	A.	B.	C.	D.
Silver and potassium cyanide,	2.25	[17.1]	14.85	2.4
Prussian blue,	.3	25.8	25.5	.2
Urea, from urine,	8.7	43.10	34.4	8.8
	8.65	...	34.45	6.6
Urea, from ammonium cyanate,	7.7	43.4	35.7	8.0
	7.5	...	35.9	8.0
Alloxan,	6.55	21.3	14.75	2.5
	6.6	...	14.7	2.4
Thiocarbanilide,	4.15	11.85	7.7	1.6
Thiocarbamide,	15.25	22.50	7.25	1.7
	15.0	...	7.5	1.6
Strychnine sulphate,	4.0	5.4	1.4	.4
	3.75	...	1.65	1.0
Codeine,	5.0	5.32	.32	.5

A glance at the last two columns shows that the ammonia actually obtainable after one-half the fluid had been distilled was many times the proposed correction. An explanation of this discrepancy will next be considered.

VI. *Evidence of Intermediate Compounds of Nitrogen.*

Making some allowance for the difference between equation (7) (which was selected for study) and equations (6) and (8), it is safe to conclude from the table in section IV, that if the action of alkaline permanganate upon a pure compound of nitrogen could be represented by any single chemical equation (no matter how complex), we should have reason to expect this change to take place with such speed that fully 70 per cent. of the theoretical yield of ammonia would be obtained by distilling one-half the fluid, or else with such slowness that the first measure would contain far less ammonia than the second. Published experiments with at least eight bodies[1] contradict both these conditions, and we are forced to believe that in the earlier stages some molecules of the original body yield ammonia with promptness, while others

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[1] These are the first six named in the last table, besides parabanic acid and theine.

are converted into more stable forms and resist the action with great stubbornness. The nature of these intermediate products is not yet clear, except only that *a* (as defined in section III) is small, in their reaction with alkaline permanganate. Perhaps they may be chiefly condensation products. Alloxan, which yielded 4 per cent. ammonia in the first fraction (eighth) of distillate, and only 2.57 per cent. in the next three, but 21.3 per cent. by prolonged action, is a marked example of such behavior; this, no doubt, is partly converted into parabanic acid. So, likewise, in a water analysis, many substances may yield a small part of their nitrogen as ammonia, while the greater part is converted into more stable forms which elude detection. It has been supposed that the organic matter of potable water is more like asparagine, yielding its nitrogen readily under the action of permanganate. Of this, however, I have found no proof. In about 40 per cent. of the natural potable waters referred to, the ratio of the third and fourth fractions is 1.5 or less, giving grave suspicion of incompleted action when the distillation was stopped. Even if the yield of ammonia in some fraction has fallen below the limit of delicacy in nesslerising, what evidence have we that prolonged treatment would not develop a much larger amount of ammonia than that already obtained?

VII. *Applications to the Analytical Process.*

A debt of gratitude is due to Professor J. Alfred Wanklyn, as the author of a valuable method of analysis which has done much in the interest of public health. "The ammonia process," which originated in 1867, is still described in the 7th edition of "Water Analysis" (1889) essentially as in the author's first paper upon the subject. In a process of such delicacy, where the results may be influenced by a multitude of variable conditions, it is desirable that these should be accurately defined and conscientiously followed. According to the author's latest directions, 500 cc. of water are reduced to 300 cc. (to remove free ammonia) and 50 cc. of the reagent added; three measures of distillate are then collected, when "the distillation may be stopped. . . . It is necessary to nesslerise each separate 50 cc. of distillate, and to add the amounts together, in order to arrive at the total albuminoid ammonia." Besides this process, a second is described upon a scale of one-fifth, with this important modification, that the operation is "continued so long as 10 cc. of distillate shows a sign of ammonia"; if, then, with a delicate Nessler reagent, ammonia is found in the sixth measure of distillate, the fluid must be evaporated to dryness!

But why should 350 cc. be distilled until only $\frac{3}{7}$ have gone over, while 70 cc. are distilled up to a very different limit? Probably because the *time* required to evaporate 30 cc. from the smaller retort proved insufficient for both the chemical action required and for the separation of the ammonia. Professor Wanklyn's method, as conducted in his own laboratory and by his own hands, has doubtless done valuable service, yielding good comparable results; but more definite conditions must be adopted if we would avoid discrepancies among different places and persons. Its value depends upon giving constant and comparable results under fixed conditions. For the absolute estimation of organic nitrogen, it is worthless.

It will be instructive to divide the free or albuminoid ammonia found in each measure of distillate by that found in the next, and to record the ratio so found; especially if care is taken to boil at a constant rate. According to Smart,[1] with pure animal or vegetable albuminoids, $r = 2$; but if these have passed into the putrefactive condition, $r = 3$; while in the case of urea (after the preliminary stage is passed) $r = 1$, both for free and for albuminoid ammonia. The successful detection of recent sewage is reported, when the chemical evidence consisted in the persistent evolution of free ammonia, followed by persistent evolution of twice as much albuminoid ammonia.

The term "albuminoid ammonia," like "reverted phosphoric acid," has a technical significance determined by the method adopted in the analysis. The actual market value of reverted phosphoric acid cannot be so high under the rule for extraction at 65° as under the rule for extraction at 40°; so also 0.1 mgm. of ammonia obtained by prolonged and intense action is of less real importance than the same quantity obtained by less vigorous measures. Many modifications of the original process have been proposed; among these Breneman's[2] are worthy of special consideration. If the fluid is brought nearly to dryness, as he suggests, it may be possible to apply an exterpolation formula, such as equation (19), to the measured residue. The detailed record of

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[1] Public Health (Minn.), Vol. II, No. 3, May, 1886.

[2] Jour. Amer. Chem. Soc. 8, No. 9.

ammonia found in seven successive fractions (with greatly increased temperature and concentration at the last) may help to distinguish between different kinds of nitrogenous matter, yielding ammonia more readily and less readily; but care should be used in regard to the volume of the residue; if this is 4 cc. in one case and 7 cc. in another, there may be considerable difference in the oxidation of that comparatively inert matter which we have been led to suspect.

If the ammonia process should be applied to investigations of the relative stability of organic compounds,[1] the formulas given above may be adapted to numerous possible modifications. The use of return-flow condenser (to prolong the chemical action apart from distillation), and variations in the proportions of potash and permanganate, do not seem to have yet been tried. It is difficult to see why the alkali should always be used in so much greater excess than the oxidiser (in spite of inconvenient bumping), but it is especially strange that the distinguished author, ignoring Mallet's report of 1882, and republishing his directions without any revision, should leave the important question of *time* entirely out of account. "Suffering persecution for the sake of the truth" should make the scientist keenly alive to any truthful criticism, and ready to study the contributions of his colleagues. The "ammonia process" has now passed from one laboratory into a hundred. If "discovered about a generation before chemists were prepared for it," the time is now fully ripe to collect the testimony of those who have used it; to agree upon the general conditions of quantity, rate of boiling, and limit of distillation, and even upon such details as the matter of paper or rubber connections. When a satisfactory compromise is effected we may hope to have a uniform method of procedure and a real definition of albuminoid ammonia.

WASHINGTON, D. C., *August*, 1889.

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[1] It may be of interest to compare such results with those of Dreyfus, who studied the rate of oxidation with acid solution of permanganate. Compt. rend. **105**, 523.