Philosophical Magazine Series 5

ISSN: 1941-5982 (Print) 1941-5990 (Online) Journal homepage: <http://www.tandfonline.com/loi/tphm16>

LXVI. On cumulative resolution

Edmund J. Mills D.Sc. F.R.S.

To cite this article: Edmund J. Mills D.Sc. F.R.S. (1877) LXVI. On cumulative resolution , Philosophical Magazine Series 5, 3:21, 492-500, DOI: [10.1080/14786447708639275](https://doi.org/10.1080/14786447708639275)

To link to this article: <http://dx.doi.org/10.1080/14786447708639275>

Published online: 27 Jul 2009.

Submit your article to this journal [↗](#)

Article views: 2

View related articles [↗](#)

nesses of metal as possible, the luminous effect of the different colours, in order to base thereupon some further inferences. It is clear that experiments in this direction will be of the highest interest as regards our knowledge of optical and electrical phenomena.

The results of this investigation are as follows :—

The property of experiencing a diminished electrical resistance under the influence of luminous rays is not confined to the metalloids selenium and tellurium, but belongs also to platinum, gold, and silver, and in all probability to metals in general.

The electrical current diminishes both the conductivity and also the sensitiveness to light, of its conductor; and both of these, after cessation of the current, gradually acquire their former values.

LXVI. On Cumulative Resolution.

By EDMUND J. MILLS, D.Sc., F.R.S.*

1. **I**F a substance, or mixture of substances, combine with itself n times, and each time lose a particular fraction of itself according to a fixed law, it may be said to undergo *cumulative resolution*. The body undergoing cumulative resolution will, in the sequel, be termed the *diapolyte*; and it will be spoken of as cumulatively resolved, or diapolyzed, *with respect to* what it loses (the *apolyte*) in the manner above expressed.

One of the most frequent forms of cumulative resolution is represented by the following general equation :—

$$n A_a B_\beta C_\gamma \dots - (n-m) A_a B_\beta C_\gamma \dots \\ = A_{n(a-a)+ma} B_{n(\beta-\beta)+m\beta} C_{n(\gamma-\gamma)+m\gamma} \dots$$

When n becomes exceedingly large with respect to m (in which case it will be denoted by ν), the right-hand side of the equation becomes

$$\nu [A_{(\alpha-a)} B_{(\beta-\beta)} C_{(\gamma-\gamma)} \dots].$$

I shall apply the term *cumulate* to a product having this general formula, and thus obtained, and designate it by the special symbol $\bigcirc$, which will always include a numerical value, unless when used as an operator.

In the latter case an expression

$$\bigcirc_{n-m}^n X = Y$$

is to be interpreted thus,—“The substance X becomes the substance Y when n units of it lose $(n-m)$ units of apolyte by way of cumulative resolution.”

* Communicated by the Author.

In many cases of chemical action the diapolyte is capable of forming but one cumulate only; but in others a succession of cumulates occurs, each cumulate becoming in turn a diapolyte. Observing that the first cumulate is affected by ν , we have to operate with

$$\nu \{ n [A_{(\alpha-a)} B_{(\beta-b)} C_{(\gamma-c)} \dots] - (n-m) A_a B_b C_c \},$$

which leads to the second cumulate; &c. &c. Proceeding thus we obtain the following series of cumulates:—

$$\begin{aligned} (0) &= [A_{\alpha} B_{\beta} C_{\gamma} \dots]; \\ (1) &= \nu [A_{(\alpha-a)} B_{(\beta-b)} C_{(\gamma-c)} \dots]; \\ (2) &= \nu^2 [A_{(\alpha-2a)} B_{(\beta-2b)} C_{(\gamma-2c)} \dots]; \\ (3) &= \nu^3 [A_{(\alpha-3a)} B_{(\beta-3b)} C_{(\gamma-3c)} \dots]; \\ &\quad \&c. \qquad \qquad \&c. \end{aligned}$$

While these differ in composition by a uniform amount, their operator ν proceeds by powers; and the curve representing the relation of ν to their difference is a logarithmic curve. I have not yet met with an instance in which the series eventually vanishes.

It may appear at first sight unreasonable to suppose that bodies of indefinitely high symbolic value, and consequently of indefinitely low specific heat, can possibly exist. We are, however, as yet ignorant of the exact connexion between the specific heat of such bodies and their chemical formulæ; and a great deal of the evidence we possess points to the conclusion that in their case the ordinary law breaks down. The conception, moreover, of a purely expanding series is familiar to chemists*. It may be that many or all of the cumulates, at the instant after their formation, undergo katamerization†; if so, they can then possess specific heat on the ordinary terms. It is sufficient if some portion of a cumulate is left to undergo the continuous inflections of the resolving power. In any event the "composition," or symbolic coefficients, of the cumulate would remain undisturbed; and the entire process can therefore be followed by practical analytical operations. I will now consider some typical cases of cumulative resolution.

2. AMMONIC CARBONATES.—The obscurity surrounding the formation of these salts has been gradually increasing; and the latest experimental researches, while solving some particular problems in connexion with them, have left the more general ones for the most part untouched.

The formulæ of the different ammonic carbonates (omitting

* The paraffin series, $C_n H_{2n+2}$, is an instance, though here the conception is an erroneous one.

† *Katamer*, the reverse of a polymer.

hydration water), are derivable, with one exception*, from the equations

$$n\text{N}_2\text{H}_8\text{CO}_3 - (n-1)\text{NH}_5\text{O} = \text{N}_{n+1}\text{H}_{3n+5}\text{C}_n\text{O}_{2n+1} \dots, \quad (1)$$

$$\textcircled{1} = \nu[\text{NH}_3\text{CO}_2],$$

and

$$2n\text{NH}_3\text{CO}_2 - (n-1)\text{CO}_2 = \text{N}_{2n}\text{H}_{6n}\text{C}_{n+1}\text{O}_{2n+2} \dots, \quad (2)$$

$$\textcircled{1} = \nu[\text{N}_2\text{H}_6\text{CO}_2]$$

$$\textcircled{2} = \nu^2[\text{N}_4\text{H}_{12}\text{CO}_2]$$

&c. &c.

$$\textcircled{\infty} = \nu^\infty[\text{NH}_3].$$

This will be evident from the following Tables, in which r denotes the ratio of N to C in the known carbonates, as above referred to.

TABLE I. (Equation 1).

n	$r_1 = \text{N} : \text{C}.$
$-1\cdot\dot{6}$	2 : 5
$1\cdot\dot{4}$	2 : 7
0·0	1 : 0
$+1\cdot\dot{0}$	2 : 1
$1\cdot\dot{1}4285\dot{7}$	15 : 8
$1\cdot\dot{3}$	7 : 4
$1\cdot\dot{5}$	5 : 3
$1\cdot\dot{6}\dot{3}$	$3\frac{2}{9} : 2$
2·0	3 : 2
3·0	4 : 3
$\textcircled{1}$ or ∞	1 : 1

TABLE II. (Equation 2).

n	$r_2 = \text{N} : \text{C}.$
0·0	0 : 1
$0\cdot\dot{1}\dot{6}$	2 : 7
0·25	2 : 5
1·0	1 : 1
2·0	4 : 3
3·0	3 : 2
$4\cdot\dot{1}4285\dot{7}$	$3\frac{2}{9} : 2$
5·0	5 : 3
7·0	7 : 4
15·0	15 : 8
∞	2 : 1

* Rose's nine-fourths carbonate, already recognized as quite isolated in its composition.

According to these Tables, the different ammoniac carbonates may be produced either by deammoniating diammoniac carbonate, or by decarbonating hydroammoniac carbonate. We have also to note the relations

$$r_1 = \frac{n+1}{n},$$

$$r_2 = \frac{2n}{n+1},$$

and

$$r_1 r_2 = 2.$$

These relations are graphically expressed by rectangular hyperbolic curves. A drawing of the equation to r_2 is here

given, where the dots represent portions, at present unknown, of the resulting curve. Considered as far as the first cumulate, all the values of r_2 lie between -1 and $+2$.

3. AMMONIAC SULPHIDES.—Aqueous solutions of these bodies are gradually converted by exposure to air into ammonia, water, and sulphur.

The terms corresponding to $n=1$, $n=2$ are known. The equation to the cumulate suggests the possible presence of a sulphur derivative of hydroxylamine.

$$2n \text{ N}_2 \text{ H}_8 \text{ S} - (n-1) \{ (2n \text{ H}_3) \text{ H}_2 \} = \text{N}_{2n+2} \text{ H}_{8n+8} \text{ S}_{2n}. \quad (2)$$

$$\textcircled{1} = \nu [\text{N}_2 \text{ H}_8 \text{ S}_2],$$

$$\textcircled{2} = \nu^2 [\text{N}_2 \text{ H}_8 \text{ S}_4],$$

$$\&c. \quad \&c.$$

$$\textcircled{\infty} = \nu^\infty [\text{S}_\infty].$$

Of this series, the ratios in the first, fourth, fifth, and seventh cumulates are known. The decompositions themselves, however, admit of various modes of representation, according to the starting-point selected.

4. MANGANIC OXIDES.—The derivatives of manganic dioxide can be represented as follows,—

$$2n \text{ MnO}_2 - (n-1) \text{O}_2 = \text{Mn}_{2n} \text{O}_{2n+2}.$$

Known ratios of Mn to O correspond to the following values of n ; viz. .5, 1, 1.2, 2, 3, and ∞ .

FERRIC OXYCHLORIDES.—When ferric chloride is treated with water, it decomposes, eventually producing a body whose composition is very near to that of ferric oxide. Its formula shows that there must be six distinct stages in this continuous process. These are united, for the first time, in the equations

$$n \text{ Fe}_2 \text{ Cl}_6 \cdot 3 \text{ H}_2 \text{ O} - (n-1) \text{HCl} = \text{Fe}_{2n} \text{ Cl}_{5n+1} \text{ H}^{5n+1} \text{ O}_{3n},$$

$$\textcircled{1} = \nu [\text{Fe}_2 \text{ Cl}_5 \text{ H}_5 \text{ O}_3],$$

$$\textcircled{2} = \nu^2 [\text{Fe}_2 \text{ Cl}_4 \text{ H}_4 \text{ O}_3],$$

$$\&c. \quad \&c.$$

$$\textcircled{6} = \nu^6 [\text{Fe}_2 \text{ O}_3].$$

Ferric compounds of the above nature are somewhat repulsive to analysts; and hardly an attempt at their formulæ appears in systematic works.

5. BISMUTHIC NITRATES.—The action of water on normal bismuthic nitrate is necessarily represented as containing three distinct continuous stages:—

$$n \text{ Bi}_2 \text{ O}_3 \cdot 3 \text{ N}_2 \text{ O}_5 - (n-1) \text{N}_2 \text{ O}_5 = \text{Bi}_{2n} \text{ O}_{3n} \cdot \text{N}_{4n+2} \text{ O}_{10n+5}.$$

$$\textcircled{1} = \nu [\text{Bi}_2 \text{ O}_3 \cdot \text{N}_4 \text{ O}_{10}],$$

$$\textcircled{2} = \nu^2 [\text{Bi}_2 \text{ O}_3 \cdot \text{N}_2 \text{ O}_5],$$

$$\textcircled{3} = \nu^3 [\text{Bi}_2 \text{ O}_3].$$

In the first stage, ratios are known for $n = .1$ and 1; for the second, $n = 2$; for the third, $n = \frac{6}{5}, \frac{5}{4}, \frac{4}{3}, 1$, and ∞ .

6. SILICATES.—A large number of silicates are derivable

from two silicic hydrates, of which the second is the cumulate of the first.

After the first cumulate, the second series is $\nu \text{H}_2 \text{Si}_n \text{O}_{2n+1}$.

For the mixed series,

whence

Series 1.—Peridot*, phenakite, zircon, almandine, grossularia, tetrthylic silicate ($n=1$).

Analime? ($n=1\cdot5$).

Okenite ($n=2$).

Magnesite, Labradorite ($n=3$).

Diopside, enstatite, chlorophæite, amphigene, pyrophyllite, talc, emerald, diethylic silicate ($n=\infty$).

Series 2.—Anorthite ($n=5$).

Fremy's hydrate ($n=1\cdot5$).

Diethylic disilicate ($n=2$).

Doveri's hydrate ($n=3$).

Mixed Series.—Orthose ($n=4, m=2$).

Analime ($n=-1, m=5$).

Fuchs's hydrate ($n=\infty, m=\infty$).

Before proceeding to the consideration of carbon compounds, it is necessary to consider the relation of homology to cumulative resolution.

7. HOMOLOGU. — If we take any starting-point X, and proceed to form homologues $X \cdot \text{CH}_2$, $X \cdot 2\text{CH}_2$, $X \cdot 3\text{CH}_2$, &c., we have in general $\bar{X} \cdot \text{C}_n \text{H}_{2n}$. When, therefore, n becomes very large, the composition of a member of any homologous series is undistinguishable from that of an olefine. Such composition is moreover attained by a perfectly continuous approach. Take, for example, the fatty alcohols, $\text{C}_n \text{H}_{2n+2} \text{O}$, which are homologues of water: $\bigcirc_1$ is evidently νCH_2 , as must also be the case with the aromatic alcohols $\text{C}_n \text{H}_{2n-6} \text{O}$

* I have taken Wurtz's authority for the formulæ (*Leçons de Phil. Chim.* p. 181. In this place will be found some of the earlier suggestions of a theory).

and any other homologous series. Eventually, then, all homologous series tend to become the same.

The complexity of any member of such series as the above clearly depends on the value of n and on the ratio r of C to H; and these are its only variables. We have, in the series of fatty alcohols,

$$r = \frac{n}{2n+2},$$

a hyperbolic relation between r and n . A similar relation holds good in all homologous series, excepting that of the olefines, where $r = .5$, and the complexity (determined by n alone) is altogether linear. *But, this series omitted, it obviously follows that the physical properties of homologous bodies cannot be a linear function of their symbolic value.* Kopp's law, therefore, has no chance of demonstration except in the case of the olefines.

The following equation includes the results of Thorpe and Young*,

$$C_n H_{2n+2} - \alpha CH_2 = C_{n-\alpha} H_{2n-2\alpha+2}.$$

On the whole, it appears that the olefines, not the paraffins, constitute the basis of carbon combinations, to which they are in fact asymptotic.

8. PLANT-PRODUCTS. *Celluloids*.—When a living plant takes up carbonic dioxide and water it loses oxygen, and forms cellulose, cannose, glucose, glucosides, and other products. If we take the equation

$$[(n+1) CO_2 + nH_2 O] - (n+1) O_2 = C_{n+1} H_{2n} O_n,$$

and give successive integral values to n , we obtain the ratios of cellulose, starch, dextrin, or glucosan ($n=5$), hydric kinate ($n=6$), cannose ($n=11$), and glucose ($n=\infty$). The ratios in the cumulate ① are $CH_2 O$. These confirm Debus's law†, that $\frac{O}{C} = 1$ is a maximum value in the case of alcohols.

Acid Bodies.—The composition of vegetable-acid bodies cannot be represented by a lower formula than $CH_2 O$, nor, according to Debus's† law, by a higher one than $C_n H_{x+b} O_{n+b}$, if b stand for the "basicity." In systematic works the general type of the formulæ of these bodies is $C_n H_{2n-2p} O_m$, which has the advantage of keeping the coefficient of H necessarily even. The maximum formula is most simply constructed thus,

$$[nC O_2 + (n-p)H_2 O] - O_{p+s} = C_n H_{2n-2p} O_{3n-(2p+s)},$$

* Proc. Roy. Soc. vol. xx. p. 488.

† Chem. Soc. Journ. vol. xix. p. 256.

whence $\textcircled{1} = \nu(\text{CH}_2 \text{O}_3)$. The ratio $\frac{\text{O}_3}{\text{C}}$ in this cumulate is the highest permissible in any formula, according to the law referred to, while H_2 is a minimum. It appears, then, that $(\text{CH}_2 \text{O})$ and $(\text{CH}_2 \text{O}_3)$ are the extremes of composition for acid vegetable bodies; that is, it ranges between that of glucose and hydric carbonate. Obviously also the symbolic ratio $\frac{\text{H}}{\text{C}}$ cannot exceed 2, nor x exceed $3n$. Moreover, since these bodies are, as a series, much less deoxidized than the glucoses and sugars, it is natural to find them the precursors of the latter in plant-life.

Glucosides are intermediate between celluloids and acid bodies.

9. *Fermentation Alcohols*.—During the fermentation of glucose (or its isomers or polymers) by means of yeast, it is found that not only is ethylic alcohol present, but several of its higher homologues; methylic alcohol, however, is not found. Carbonic dioxide is given off in abundance. The following equation appears to me to connect these facts continuously,—

(which is the same as $\text{C}_n \text{H}_{2n+2} \text{O}$, the general formula for a fatty alcohol). For $n=0$, the result is O_2 ; for $n=1$, $-2 \text{H}_2 \text{O}$; for $n=2$, methylic alcohol; for $n=3$, ethylic alcohol, &c. &c. In all values of n up to 3, the process is one of oxidation, as is evident from the consequent values of $\{-(n-3)\text{O}_2\}$; hence the equation is irrational, as far as the formation of alcohols is concerned, until n is equal to or greater than 3. The condition for the production of alcohols is then attained; and the first to be formed is necessarily ethylic.

It appears that a very small percentage of the glucose present is katamerized, in part hydrogenized, and in part oxidized during fermentation. In this manner a little glycerine ($3 \text{CH}_2 \text{O} + \text{H}_2$) and hydric succinate ($4 \text{CH}_2 \text{O} - \text{H}_2$) are formed.

Since $\textcircled{1} = \nu \text{CH}_2$, it appears that the composition of the series of fatty alcohols lies between O_2 and CH_2 . And the same principle that presides over the formation of plant-products conducts us continuously through the genetic relations of fermentation alcohols.

10. *POLYGLUCOSIC and PLYGLYCERIC ALCOHOLS*.—In the case of polyglucosic acohols, we have, according to Watts*,

* Fownes's 'Manual of Chemistry' (1868) p. 683.

Hence $\textcircled{1} = \nu \text{C}_6 \text{H}_{10} \text{O}_5$; $\textcircled{6} = \nu^6 \text{C}_6$. Water and carbon are the extremes of composition for this series.

For polyglyceric alcohols, according to the same authority*,

$$n \text{C}_3 \text{H}_8 \text{O}_3 - (n-1) \text{H}_2 \text{O} = \text{C}_{3n} \text{H}_{6n+2} \text{O}_{2n+1}.$$

Hence $\textcircled{1} = \nu \text{C}_3 \text{H}_6 \text{O}_2$ or glycide; $\textcircled{3} = \nu^3 \text{C}_3 \text{H}_2$. $\text{H}_2 \text{O}$ and $\text{C}_3 \text{H}_2$ represent the two extremes of this series.

Caramels.—By a similar process, applied to cannose, the series of caramels is formed,

$$n \text{C}_{12} \text{H}_{22} \text{O}_{11} - (n-1) \text{H}_2 \text{O} = \text{C}_{12n} \text{H}_{20n+2} \text{O}_{10n+1}.$$

Of its members, $\textcircled{1} = \nu \text{C}_{12} \text{H}_{20} \text{O}_{10}$, $\textcircled{2} = \nu^2 \text{C}_{12} \text{H}_{18} \text{O}_9$ (caramelane), $\textcircled{6} = \nu^6 \text{C}_{12} \text{H}_{10} \text{O}_5$, and $\textcircled{7} = \nu^7 \text{C}_{12} \text{H}_8 \text{O}_4$ (caramelene) are known. Caramelin seems to be exactly intermediate between $\textcircled{5}$ and $\textcircled{6}$.

11. ETHERIFICATION.—In the case of the fatty alcohols, it is usual to form ethers by what, in effect, is a dehydrating process. This is accurately represented by the equation

whence $\textcircled{1} = \nu \text{C}_2 \text{H}_4$. In conformity with this result, we find that the action of oil of vitriol on fatty alcohols, when pushed to an extreme, yields olefines, but not methylene. Here also we find striking evidence of the correctness of the theory of cumulates as enunciated in (1).

12. CONCLUSION.—The process of cumulative resolution, of which a brief sketch has been given in the foregoing sections, is one of very general prevalence in chemical operations. In the particular form of it there illustrated, the transition from one compound to a successor in multiple proportion is effected in hyperbolic paths, whose successive points at infinity lie on a logarithmic curve. Such points at infinity are actually realized as conditions of unstable equilibrium, under which a new ordinal compound commences to take its rise.

Having regard to the fact that the same theory that applies to plants is also found to regulate the deportment of ordinary reagents and mineral substances, we must so far regard the latter as living beings.

Anderson's College, Glasgow.

* Fownes's 'Manual of Chemistry' (1868), p. 666.