



LXVIII. The precipitation of colloids

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E. *Tetranitroaniline*.

XIII. At 140°.		XIV. At 120·0°.		XV. Derived curve from XIV.	
Time in hours.	Per cent. decomposed.	Time in hours.	Per cent. decomposed.		
<i>t.</i>	<i>x.</i>	<i>t.</i>	<i>x.</i>	<i>x.</i>	$\frac{dx}{dt}$
3	1·0	21	0·93		
5	1·5	45	2·29	·5	·044
21	10·5	70	4·56	1·6	·057
24	16·0	94	7·89	3·4	·091
28·5	29·5	118	12·12	6·2	·139
43	87·0	142	17·27	10·0	·176
49	95·5	167	24·40	13·9	·214
67	99·0	189	32·08	20·8	·286
72·5	100	214	43·47	28·2	·349
75	100	239	57·76	37·8	·456
		262	73·29	50·6	·572
		287·5	94·3	65·5	·672
		310·5	98·4	83·6	·824
		330·5	99·1	96·4	·179
		337	100	99·6	·04
		354·5	100	100	0
Fig. 5, Curve		Fig. 5, Curve II.		Fig. 5, Curve III.	

LXVIII. *The Precipitation of Colloids.* By HUMPHREY D. MURRAY, *Exhibitioner of Christ Church, Oxford* *.

THE author has recently attempted to obtain a general expression for the precipitating effect of ions on colloids. Whilst the attempt has not at present been successful in discovering a general relationship, a special case has been found for which the expression reduces to a simple equation. This, as derived, is applicable only to the effect of univalent cations with the same anion upon the same colloid under equal conditions of temperature and concentration, the colloid carrying a negative charge. It relates the concentration of the cation in gm. atoms required to precipitate the whole of the colloid in a given time, with the atomic number of the cation, and is of the form

$$C = K \cdot N^n,$$

where C represents the concentration of the cation,

N represents the atomic number of the cation,

n is constant for the colloid at that particular concentration,

K is a constant depending upon the nature of the colloid and the anion.

* Communicated by the Author.

In order to test the validity of the equation it was necessary to plot values of $\log N$ against values of $\log C$.

It was difficult to find a series of concentration values of sufficient length to make an experimental verification possible. Failing an independent determination of a series of values for which the author had not sufficient time, an attempt was made with some results of Oden's, given below, on the precipitation of colloidal sulphur, the latter being negatively charged. The left-hand column shows the minimal concentration of cation in gm. atoms per litre required to effect precipitation in a given time. The anion in every case is Cl' :—

TABLE I.
Colloid :—Sulphur 18° – 20° C.

Cation.	Minimal concentration with Cl' anion.	Log_{10} Minimal concentration.	Minimal concentration with NO_3' anion.	Atomic number.	Log_{10} Atomic number.
H^{\cdot}	6.0	0.778	—	1	0
Li^{\cdot}913	1.960	—	3	.477
Na^{\cdot}153	1.185	.163	11	1.041
Al'''0044	3.643	—	13	1.114
K^{\cdot}021	2.322	.022	19	1.279
Ca''0041	3.613	—	20	1.301
Cu''008	3.903	—	29	1.462
Rb^{\cdot}016	2.204	.0175	37	1.568
Cs^{\cdot}009	3.954	.0096	55	1.740
Ba''0021	3.322	—	56	1.748

On plotting the values of \log minimal concentration of the cations associated with Cl' anions (C) against \log atomic number (N), it will be seen that the values of the univalent ions, with the exception of that of potassium, lie approximately upon a straight line to which the equation is

$$C_1 = 5.9 N^{-1.64}.$$

In the case of the divalent ions the values are too few to be of any use in deducing a relation. If, however, we assume that the equations will be of the same form, *i. e.* that the expression $N^{-1.64}$ is constant for sulphur, and that barium

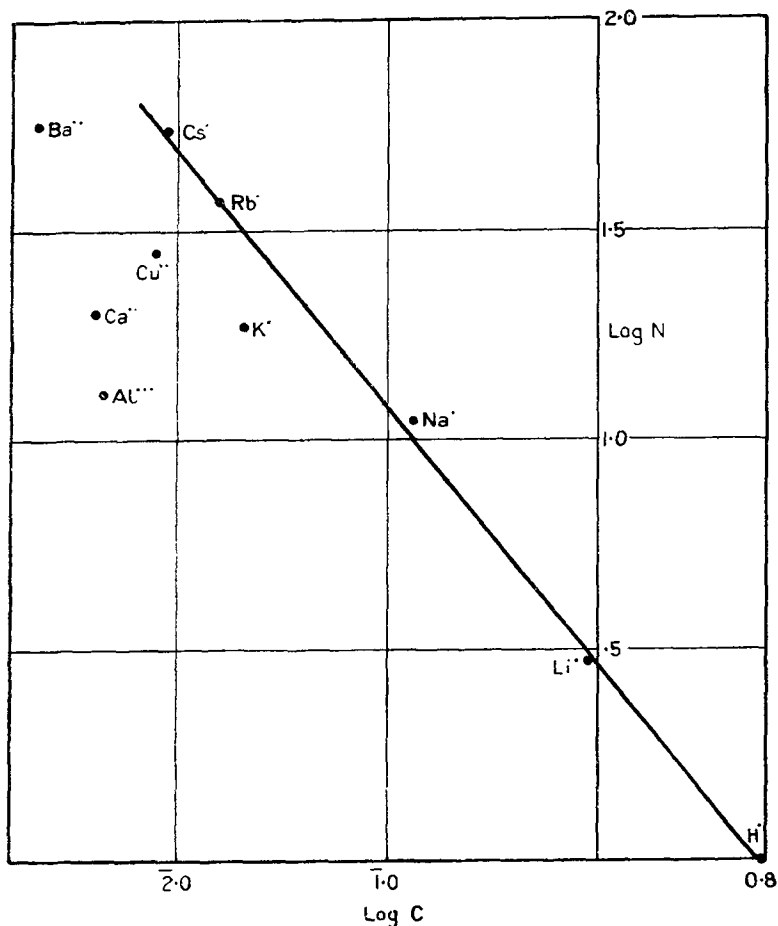
and aluminium are typical divalent and trivalent ions, we obtain the equations

$$C_2 = 1.46 N^{-1.64},$$

$$C_3 = .33 N^{-1.64},$$

where C_2 and C_3 are the minimal concentrations of divalent and trivalent ions respectively. We shall return to these

Fig. 1.



results later. The concentrations of cations with NO_3^- anions are given in some cases to show that they follow approximately the same rule.

The next series of concentration values were taken from some data by Freundlich, corrected for dissociation, so that, as before, the minimal concentration of cations per litre is shown required to precipitate colloidal As_2S_3 , at a concentration of $\cdot 007539$ mols. per litre. The anion in every case is Cl^- . The colloid is negatively charged.

TABLE II.

Cation.	Minimal concentration.	Log_{10} Minimal concentration.	Atomic number.	Log_{10} Atomic number.
H^+	$\cdot 029$	$\bar{2}\cdot 462$	1	0
Li^+	$\cdot 0513$	$\bar{2}\cdot 710$	3	$\cdot 477$
Na^+	$\cdot 045$	$\bar{2}\cdot 653$	11	$1\cdot 041$
Mg^{++}	$\cdot 000717$	$\bar{4}\cdot 855$	12	$1\cdot 079$
Al^{+++}	$\cdot 000093$	$\bar{5}\cdot 968$	13	$1\cdot 114$
K^+	$\cdot 044$	$\bar{2}\cdot 643$	19	$1\cdot 279$
Ca^{++}	$\cdot 00065$	$\bar{4}\cdot 813$	20	$1\cdot 301$
Zn^{++}	$\cdot 000635$	$\bar{4}\cdot 836$	30	$1\cdot 477$
Sr^{++}	$\cdot 000635$	$\bar{4}\cdot 803$	38	$1\cdot 580$
Ba^{++}	$\cdot 00069$	$\bar{4}\cdot 839$	56	$1\cdot 748$

Here again we find the univalent ions lie approximately upon a straight line, to which the equation is

$$C_1 = 0\cdot 55 N^{-0\cdot 09}.$$

The number of values for divalent ions is larger in this case but they do not give a very concordant result. We can, however, draw a line parallel to the first passing through the plotted results, to which the equation is

$$C_2 = \cdot 0008184 N^{-0\cdot 09}.$$

It is to be expected that secondary effects in dissociation will be more evident the higher the valence of the cation.

The question now arises as to the way in which we are to reconcile these results, if real, with Whetham's law. This states that the minimal concentrations of any univalent, divalent, and trivalent ion for the same colloid are in the ratio

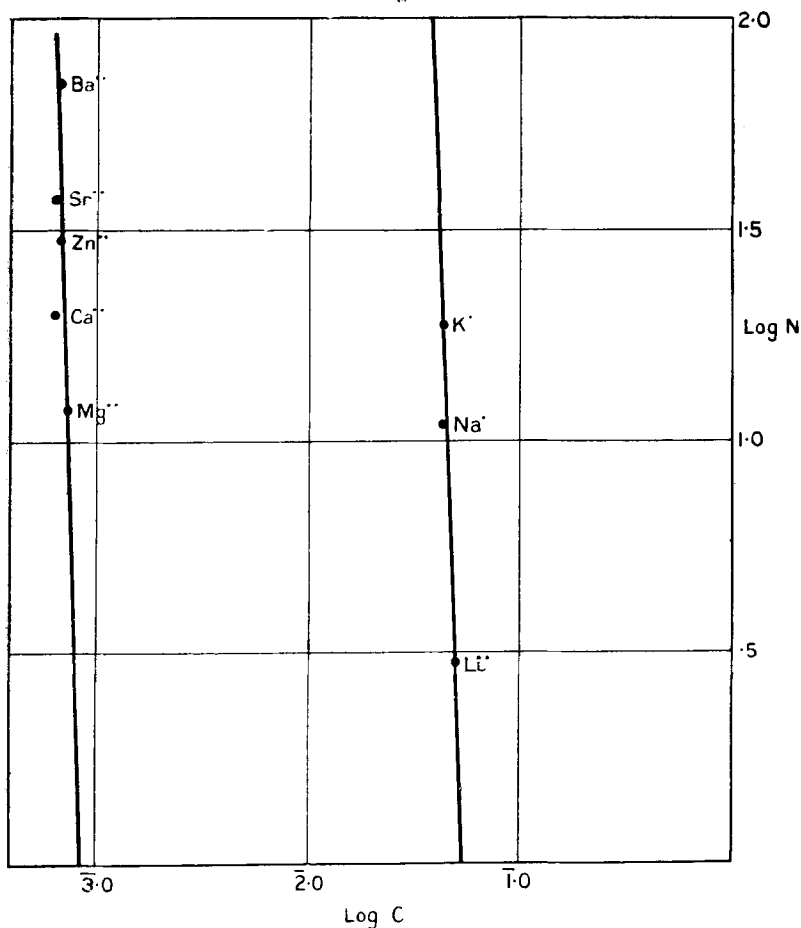
$$K^3 : K^2 : K,$$

or

$$K^2 : K : 1,$$

where K is a constant. Suppose that in the precipitation of sulphur, we have univalent, divalent, and trivalent cations

Fig. 2.



whose atomic numbers, or rather, the values of N^z , are approximately equal, then we may write,

$$\begin{aligned}
 C_1 : C_2 : C_3 &= 5.9 N^{-1.64} : 1.46 N^{-1.64} : 0.33 N^{-1.64}, \\
 &= 5.9 : 1.46 : 0.33 \\
 &= 17.7 : 4.4 : 1 \\
 &= (4.2)^2 : 4.4 : 1,
 \end{aligned}$$

a result in accordance with Whetham's law. It seems probable, therefore, that the latter is only applicable to ions

for which the values of N^n are nearly equal. This result, however, requires confirmation. Freundlich gives one value for a trivalent ion in the precipitation of As_2S_3 , namely, aluminium, which if we take N^n constant, gives the result

$$C_3 = 0.001096 N^{-0.09}.$$

This, combined with the two equations above, gives for the minimal concentration of cations with approximately equal values of $N^{-0.09}$,

$$\begin{aligned} C_1 : C_2 : C_3 &= 0.55 N^{-0.09} : 0.0008184 N^{-0.09} : 0.001096 N^{-0.09} \\ &= 5018 : 7.47 : 1 \\ &= (70.8)^2 : 7.47 : 1, \end{aligned}$$

a bad result from the point of view of the above hypothesis, but which, it may be pointed out, rests only on one result, and that the measurement of a small quantity, the concentration of the aluminium ion being 0.00093 gm. atoms per litre.

It is of interest now to see whether precipitation by anions follows a similar rule. In investigating this matter, we are met with the difficulty of not knowing what value to assign to N in the case of a complex ion, which is the most usual type of anion. We can, however, take three values from some data by Freundlich on the precipitation of colloidal $Fe(OH)_3$. The left-hand column shows the minimal concentration of the anion of potassium salts. The $Fe(OH)_3$ was positively charged and at a concentration of 0.0163 mols. per litre.

TABLE III.

Colloid :— $Fe(OH)_3$ 0.0163 mols. per litre.

Anion.	Minimal concentration.	Log_{10} Minimal concentration.	Atomic number.	Log_{10} Atomic number.
Cl'	0.0848	3.928	17	1.230
Br'	0.120	2.079	35	1.544
I'	0.145	2.161	53	1.724

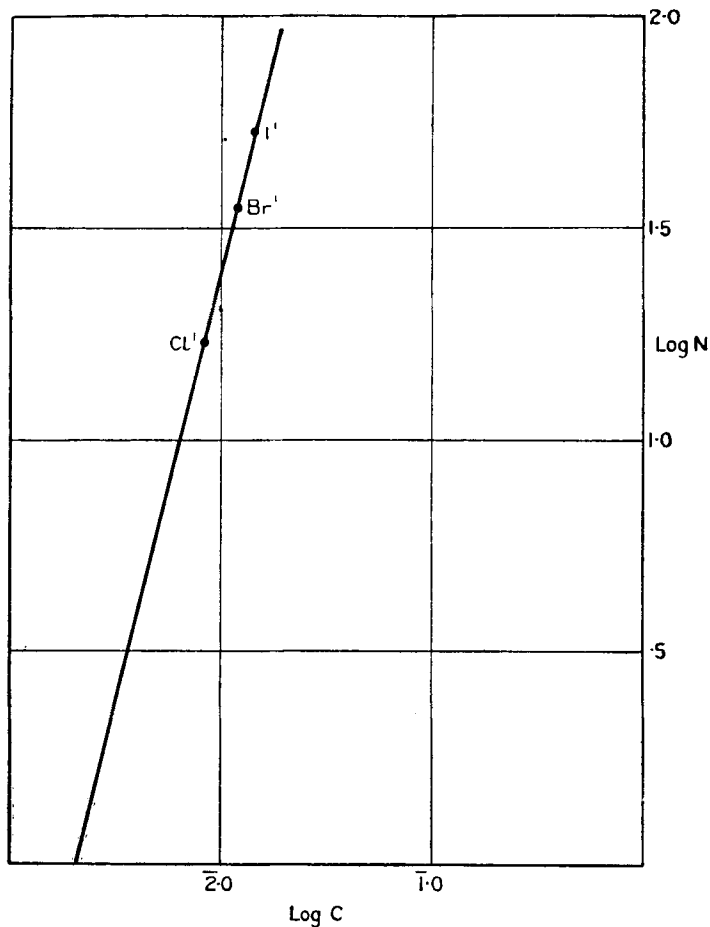
The result, it will be seen, is satisfactory as far as it goes. We obtain the equation

$$C = 0.00215 N^{0.45},$$

in which it will be noticed that the value of n is positive.

It thus seems probable that the minimal concentration of anions is given by an equation of similar form to that for cations.

Fig. 3.



To summarize the results obtained:—

(1) The minimal concentration of univalent cations required to precipitate a negatively charged colloid under similar conditions of concentration and temperature in a given time varies with the atomic number of the cation and, in general, is given by an equation of the form

$$C = K \cdot N^n.$$

(2) The relation can probably be extended to the precipitation of positively and negatively charged colloids by anions and cations respectively of any valence.

(3) If the above is true, it follows that Whetham's law requires modification, probably by comparing the precipitating power of only those ions for which the values of N^n , as given above, are approximately equal.

Christ Church, Oxford.

April, 1920.

LXIX. *The Disappearance of Gas in the Electric Discharge.*

By The Research Staff of the General Electric Company, Ltd., London *. (*Work conducted by* N. R. CAMPBELL and J. W. H. RYDE.)

Introduction.

1. **W**HEN an electric discharge is passed through a gas at low pressure, the pressure often decreases and the gas seems to disappear. In spite of the considerable investigation to which the matter has been subjected, a complete understanding of it has not been reached. It is not known precisely what is the relation between the disappearance and the electrical conditions of the discharge, and it is not known precisely what becomes of the gas that has disappeared. The following pages describe some experiments designed to elucidate further the fundamental principles concerned in the process. It is not certain, of course, that there are any fundamental principles; there may be many totally distinct actions possible, each of which happens to have as one of its consequences the disappearance of gas; any attempt to explain them all by the same theory would then be misleading. Accordingly it may be well to state at the outset that no attempt will be made to cover the whole field, either in experiment or in theory. We shall merely point out certain features of the process which can be traced in certain cases, and must not be left out of consideration in the elaboration of any theory that is proposed to account for it.

2. First some of the main results established by earlier work may be recalled. It seems that by the passage of a current at a sufficiently low pressure, as in an X-ray tube of the old type, any gas whatever, including the inactive

* Communicated by the Director.