ON THE ELECTROCHEMISTRY OF LEAD.

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In all the well-known salts lead is a diad metal, but it has been proved that other salts exist in which it is tetrad. For example, Kikoljukin (*Berichte* 1885, p. 370, Ref.) by suspending lead chloride in strong hydrochloric acid and passing chlorine through the solution, obtained PbCl_4 , which could be precipitated as the double salt $\text{PbCl}_4 \cdot 2\text{KCl}$ by addition of potassium chloride. Elbs and Nübling (*Zeit. für Electroch.* 1903, p. 777) have prepared plumbic sulphate, $\text{Pb}(\text{SO}_4)_2$, and various double salts by electrolytic methods. Various other experimenters have prepared plumbic salts, usually as a double salt with an alkali salt. The simplest of these methods seems to be that of Seyewitz and Tawitz (*Comptes Rendus*, 136, p. 686), who, by the action of ammonium persulphate on lead chloride and hydrochloric acid at a low temperature, obtained plumbic ammonium chloride.

Although the double salts have been obtained in an approximately pure state, it has not yet been found possible to prepare any pure, simple plumbic salt. Elbs and Fischer (*Zeit. für Electroch.* 7, p. 343 (1901)) have shown that plumbic sulphate is formed when a current is passed between two lead plates in strong sulphuric acid, and the electromotive force of an accumulator may therefore be regarded as caused by the tendency of plumbic ions, formed from the lead peroxide and sulphuric acid, to transform into plumbous ions with liberation of the extra electric charges (Abel, *Zeit. für Electroch.* 7, p. 731).

The tendency of any ion (*i*) to be transformed into an ion (*o*) with a lower valence may be measured by means of an oxidation electrode. If the difference in valence between the *i* and *o* form be *n*, the electromotive force in volts—

$$= P + \frac{RT}{nF} \log_n \frac{C_i}{C_o}$$

$$= P + \frac{0.591}{n} \log_{10} \frac{C_i}{C_o} \text{ (at } 25^\circ \text{)}$$

where *P* is the tendency of the *i* form to change into the *o* form when the concentrations are equal, while C_i and C_o are the actual concentrations of the *i* and *o* ions respectively, which are used in the experiment.

The value *P* is always given in comparison with some standard such as the normal hydrogen electrode (Wilsmore, *Zeit. für physik. Ch.* 35, p. 291 (1900)) on account of the uncertainty of the absolute values, and is characteristic of the particular element under investigation.

Further—

$$P = \frac{RT}{nF} \log_n k$$

where k is that particular ratio $\left(\frac{C_i}{C_o}\right)_x$ of the i and o ions with which the tendency becomes equal to that of the standard taken, so that we have

$$\frac{RT}{nF} \log_n k = -\frac{RT}{nF} \log_n \left(\frac{C_i}{C_o}\right)_x = \frac{RT}{nF} \log_n \left(\frac{C_o}{C_i}\right)_x.$$

Up to the present no estimate of the magnitude of k or P for $\text{Pb} \cdots \rightarrow \text{Pb}^{\cdot\cdot}$ has been made, though for a knowledge of the chemistry of lead this determination is as important as the value $\text{Pb}^{\cdot\cdot} \rightarrow \text{metallic Pb}$.

In order to obtain k or P , the values of C_i and C_o must be known; or for the special case of lead, the concentrations of plumbous and plumbic ions must be known.

The easiest method would naturally be to obtain the two types of salt separately and mix them in known proportions. Attempts were made to prepare plumbic chloride and plumbic sulphate by the methods given above, but very poor yields were obtained, and these proved to be very crude. No method for the purification of a plumbic salt is at present known. This line of attack was soon given up, as it was found that plumbic chloride and sulphate were too unstable in aqueous solution to be of service, since the former evolved chlorine and the latter oxygen.

Lead superoxide contains the lead in the tetrad condition, and if it could be brought into solution, should yield a plumbic salt. It dissolves readily in strong hydrochloric acid, but with evolution of chlorine, though doubtless some plumbic salt is also formed. The high solubility alone does not, however, prove that all the lead is not in the plumbous form, since much more plumbous chloride dissolves in strong hydrochloric acid than in water (von Ende, *Zeit. anorg. Ch.* 26, p. 129).

It is generally stated that lead peroxide is insoluble in nitric acid, but as 'insolubility' is only a relative term, experiments were made to determine the extent of the solubility. It was found that at ordinary dilutions, the solubility was not analytically measurable, but that it became appreciable in strong solutions.

It then became necessary to determine whether any estimate of the transformation tendency could be made in strong solutions, and what value could be placed on such an estimate; and the following experiments were carried out with this aim.

The temperature at which all experiments were performed was 25°.

It was first found under what conditions the same potential could be obtained. The same nitric acid solution, approximately 5 N, was used in each experiment. Some of this acid was shaken for several days with lead superoxide, bought as pure from Kahlbaum, and to 20 c.cs. of this solution, 5 c.cs. of a plumbous nitrate solution were added. Two platinised platinum points, which had been polarised in dilute sulphuric acid against one another, served as electrodes. The potential varied irregularly at first, but after some hours both points were at the same potential. This came about much quicker if the points were placed in the lead superoxide at the bottom of the vessel. This potential was obtained still more quickly, if a platinum point which had been electrolytically coated with lead superoxide was used. Further, if a platinum point, coated with lead peroxide, were placed in a solution of the same strength for nitric acid and plumbous nitrate, but which

had not previously been shaken with lead superoxide, an electromotive force was obtained which rose to the same value as had been obtained in the former experiments, and remained constant at that value.

Evidently, then, this was a definite oxidation potential. The best form of electrode was found to be a small platinum plate, which was first platinised and then coated with lead peroxide, usually from a solution containing N nitric acid and some lead nitrate, as this was found to give a durable coat.

Some incidental observations on lead superoxide may be mentioned here. The ordinary commercial lead superoxide is dark purple, and remains of this colour on long shaking with water. If shaken with nitric acid of any strength it becomes quite black, while with sodium hydroxide it becomes a bright red. When electrolytically deposited it is usually quite black, but on two occasions it was obtained with a reddish colour. On both occasions, a high voltage was used (10 volts), and there was nitric acid, about N, in the solution. The ordinary superoxide, which had been turned black by nitric acid, became purple and then red in caustic soda, but a sample of electrolytically prepared lead superoxide showed no trace of red after a week in 5 N soda.*

The figures for one typical potential measurement may be given in some detail as an example of the results obtained. Throughout the research, two electrodes, freshly coated with PbO_2 , were used, and if these did not agree the experiment was repeated. This, however, rarely happened. Unless specially mentioned, the measurement was made against a N calomel electrode with saturated ammonium nitrate as the connecting solution.

- I. The solution was 4.64 N for nitric acid, and contained 0.0100 grm.-mols. of plumbous nitrate per litre.
- II. The solution was 4.64 N for nitric acid, and contained 0.0100 grm.-mols. of plumbous nitrate per litre. Before the measurement it had been shaken for two hours at 25° with lead superoxide.

I.				II.			
Time in Hours.		Potentials in Volts. Electrode.		Time in Hours.		Potentials in Volts. Electrode.	
		1	2			1	2
0	...	1.391	...	0	...	1.420	...
2	...	1.401	...	0.1	...	1.409	...
17	...	1.406	...	0.3	...	1.406	...
18	...	1.407	...	0.5	...	1.409	...
20	...	1.408	...	16	...	1.408	...
23	...	1.406	...	18	...	1.408	...
24	...	1.408	...	20	...	1.407	...
25	...	1.408	...	23	...	1.407	...
			1.395				1.409

In both cases the potential became steady about 1.408 volt.

It will be noticed that in the last reading with electrode 2 in Experiment I. there is a sudden drop of 0.011 volt. This was due to some lead superoxide dropping off, and the potential would later rise to the same value as before. It was found that such variations occurred too often when the nitric acid had to saturate itself with plumbic salt at the expense of the electrode, since that

* The following explanation of these phenomena has occurred to me since writing the above. The purple and black varieties of PbO_2 are allotropic modifications. The bright red substance is almost certainly PbO . It is a well-known fact that substances of high oxidation potential, such as PbO_2 , are much more stable in acid than in alkaline solution, and in the latter more readily evolve oxygen. Therefore PbO_2 in alkaline solution becomes red since it is transformed into PbO with evolution of oxygen. This was not observed with the black variety. It may be that the change is very slow, in which case the PbO would be dissolved by the alkali as quickly as it was formed.

is what must occur here. Consequently the nitric acid was always shaken with lead peroxide for several hours before use, and the lead peroxide was then found to stick to the electrode. It was found to be immaterial how long this preliminary shaking lasted, as the same results were obtained with acid shaken for 30 minutes and for 14 days. If, however, the plumbous concentration was to be very small, it was thought advisable not to prolong the time lest some decomposition of the plumbic nitrate should occur, with consequent formation of plumbous nitrate. Once the potential had become steady it remained so for many hours, and then started to fall slowly. Usually this fall in potential first became appreciable after about 24 hours, and appeared to proceed indefinitely. This may be due to the presence of a trace of chloride, or to a minute trace of platinum dissolved from the electrode.

Solubility of Lead Superoxide in Nitric Acid at 25°.

The nitric acid used contained no weighable amount of solid impurity in 200 c.cs. of concentrated acid. No chloride could be detected. The lead superoxide was washed several times with nitric acid before use. The solution was first evaporated to dryness, then some sulphuric acid added, dried, and weighed as sulphate.

HNO ₃ normality. <i>a</i>	Time in thermostat. days.	C.cs. of solution taken for estimation.	Weight of PbSO ₄ grms.	Milligram. mols. of Lead per litre. <i>b</i>	$\frac{b}{a^4}$	$\frac{b}{a^4(\text{H}_2\text{O})^2}$
5.30	7	500	0.0157	0.104	0.000131	0.00020
7.50	5	200	0.0254	0.419	0.000132	0.00024
7.50	20	200	0.0250	0.412	0.000130	0.00024
9.20	6	150	0.0381	0.836	0.000117	0.00024
9.20	7	150	0.0350	0.767	0.000107	0.00023
11.5	6	100	0.0458	1.51	0.000086	0.00025
11.5	8	150	0.0723	1.57	0.000091	0.00026
Mean = 0.00024						

If the lead in PbO₂ be tetrad, then by the law of mass action—

and since—

$$\text{OH}' = \frac{K_w}{\text{H}^+},$$

$$\frac{(\text{Pb} \cdots)}{(\text{H}^+)^4(\text{H}_2\text{O})^2} = \text{constant}.$$

In the above table $\frac{(\text{concentration Pb})}{(\text{concentration HNO}_3)^4} = \frac{b}{a^4}$ has been taken as an approximation for $\frac{(\text{Pb} \cdots)}{(\text{H}^+)^4}$. The active mass of pure water has been taken as 1, and the calculation made on the assumption that the active mass of water decreases 3.6 per cent for each gram.-molecule of acid in the solution. A more exact estimate would have been obtained from the vapour pressures, but with the inexact values for Pb $\cdots$ and H $^+$, this is quite close enough. Since *a* and *b* are only approximations for H $^+$ and Pb $\cdots$, the

constant is as close as could be expected, considering the very small value of b , the results agree with the hypothesis that PbO_2 , when dissolved in HNO_3 , yields tetrad lead ions.

With this knowledge of the solubility, an approximate value for P may be obtained. To obtain the true value of P , the concentrations of plumbous (C_o) and plumbic (C_i) ions in a solution, together with its oxidation potential, must be known. The electromotive force e was always measured at 25° against a N calomel electrode, and as it is usual to take the N hydrogen electrode as standard, we have—

$$P = e + 0.283 + 0.0295 \log \frac{C_o}{C_i} \text{ volt.}$$

It was not possible to measure C_i and C_o , but as an approximation the values of S_i and S_o , the total concentrations of the plumbic and plumbous salts, were taken. According to the Abegg-Bodländer theory (*Zeit. anorg. Ch.* 20, p. 453, 1899), the tendency to form complex ions is in inverse order to the strength of the ions. Of the common ions NO_3' is one of the strongest, and in accord with this theory, Labendzinski (*Inaug. Dissert.*, Breslau, 1904) found from E.M.F. measurements that there was far less formation of complex ions with metallic nitrates than with chlorides or sulphates. Spencer (*Zeit. anorg. Ch.* 44, p. 379, 1905) in a more exhaustive investigation of the particular case of thallium, found the same thing.

Nominally any salt might be used for the determination of P , but the ionic equilibrium with a salt that forms both simple and complex ions is too involved to allow of calculation. Accordingly, P for lead was determined with the nitrate, on the assumption that it yields almost entirely simple ions.

Elimination of Diffusion Potential.

If nitric acid solutions of the same concentrations as were used in the solubility experiments were to be employed, only a very rough approximation could be obtained, unless some method of removing the diffusion potential was found. The application of Planck's formula (*Pogg. Ann.* 40, p. 561, 1890) to calculate this potential was obviously out of the question, so other methods were tried. The use of potassium chloride (O. F. Tower, *Z. physik. Ch.* 20, p. 198, Bjerrum, *Z. physik. Ch.* 53, p. 428) and of saturated potassium and ammonium nitrates (Cumming, *see further*, pp. 213-220) as connecting solution between the cells was first tried at a comparatively low dilution so that the results might be checked by calculation.

The electromotive force of a cell containing 0.897 N nitric acid and 0.100 mol. lead nitrate with lead superoxide as electrode, against a N calomel electrode, was as follows:—

CONNECTING SOLUTION.			OBSERVED E.M.F. VOLT.		DIFFERENCE FROM E.M.F. WITH DIRECT CONNECTION.	
Direct connection	...	...	...	1.221	...	—
Saturated potassium chloride	...	...	...	1.242	...	0.021
Saturated potassium nitrate	...	...	...	1.233	...	0.012
$\frac{1}{2}$ saturated ammonium nitrate	...	...	...	1.242	...	0.021
$\frac{3}{4}$ " " "	...	...	...	1.255	...	0.034
1 " " "	...	...	...	1.256	...	0.035

The diffusion potential between two binary electrolytes of the same ionic concentration (Planck, *loc. cit.*)—

$$e = \frac{RT}{F} \log \frac{u_1 + v_2}{u_2 + v_1}$$

where u_1 and u_2 are the velocities of the cations and v_1 and v_2 the velocities of the anions.

If we neglect the lead nitrate, and take the nitric acid and potassium chloride as of approximately equal concentration, we obtain—

$$e = 0.059 \times \log_{10} \frac{350 + 75}{74 + 71} \\ = 0.029 \text{ volt.}$$

The saturated potassium chloride removed 0.021 volt, and the saturated ammonium nitrate 0.035 volt. The latter value is probably nearer correct.*

Nitric acid = 7.97 N, and 0.01 grm. mols. of lead nitrate with lead superoxide electrode, against a N calomel cell.

CONNECTING SOLUTION.				E.M.F.	DIFFERENCE FROM <i>a</i> .	
Direct connection (<i>a</i>)	...	...	...	1.440	...	—
Saturated potassium chloride	...	...	...	1.490	...	0.050
" " nitrate	...	...	...	1.457	...	0.017
$\frac{1}{2}$ " ammonium "	...	...	...	1.451	...	0.011
$\frac{1}{2}$ " " "	...	...	...	1.483	...	0.043
1 " " "	...	...	...	1.515	...	0.065

As the observed E.M.F., with saturated ammonium nitrate as the connecting solution, is probably nearest to the true value, it was used in the following experiments :—

Determination of P.

In the next table will be found the results of a series of experiments to determine P within the same limits of nitric acid concentration as in the solubility experiments. The nitric acid was determined by titration ; the plumbic

Strength of HNO ₃ .	Concentration of Pb ^{iv} S _t	Concentration of Pb ⁱⁱ . S _o .	E.M.F. against N calomel.	E.M.F. against hydrogen standard.	P
8.8	0.00060	0.000238	1.549	1.832	1.825
8.8		0.000455	1.533	1.816	1.815
8.8		0.00238	1.534	1.817	1.829
8.8		0.00238	1.539	1.822	1.834
8.8		0.0100	1.530	1.813	1.850
7.97	0.00050	0.001	1.529	1.812	1.821
7.97		0.010	1.515	1.798	1.826
7.15	0.00026	0.025	1.477	1.760	1.827
7.15		0.025	1.476	1.759	1.826
7.15		0.025	1.479	1.762	1.829
7.15		0.025	1.476	1.759	1.826
7.15		0.025	1.476	1.759	1.826
6.88	0.00022	0.050	1.465	1.748	1.817
6.88		0.100	1.459	1.742	1.820
					Mean = 1.83

* In a paper to be read before the Faraday Society in December, 1906, an account of a systematic investigation into the use of strong ammonium nitrate to remove the diffusion potential will be found. It was shown that a saturated ammonium nitrate solution was the best method at present available for the elimination of diffusion potential in strong solutions.

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concentration was taken from the table of solubility of lead superoxide in nitric acid; and the total plumbous concentration was known, since a definite amount of a standard plumbous nitrate solution had been added.

S_i has been used in the calculation of P, instead of $\frac{C_i}{C_o}$. The constancy of S_o has been used in the calculation of P, instead of $\frac{C_i}{C_o}$. The constancy of the results makes it certain that $\frac{C_i}{C_o}$ must be proportional to $\frac{S_i}{S_o}$, and the simplest assumption would be to take them as equal.

There is a possible error in that all the lead dissolved by nitric acid has been taken as lead superoxide dissolving to form plumbic lead. If for any reason some really formed plumbous lead, the true value of S_o would be higher, and that of S_i lower, so that 1.82 volt against the hydrogen standard is probably a minimum value.

Experiments in more Dilute Solutions.

It has been shown that the equilibrium constant for PbO_2 dissolving in HNO_3 to form tetrad lead ions is of the form—

$$\frac{(Pb^{IV})}{(H^+)^4(H_2O)^2} = \text{constant.}$$

If it were possible to determine (H^+) and (H_2O) , it would then be possible to calculate the value of Pb^{IV} in any strength of nitric acid solution. Our knowledge of strong solutions is at present too imperfect to enable this to be done, but as a first approximation we may, as before, take the total nitric acid concentration as a measure of H^+ , and calculate (H_2O) as before. In this way values for Pb^{IV} in dilute solutions may be obtained, from which P can be calculated, and some such results are included in the following table. The formula used for the calculation of the amount of tetrad lead was :—

$$Pb^{IV} = (HNO_3)^4(H_2O)^2(0.00024) \text{ grm.-equivalents per litre.}$$

HNO_3 normality.	Active Mass of (H_2O) .	Concentration of Pb^{IV} . S_i .	Concentration of Pb^{II} . S_o .	$\frac{S_o}{S_i}$	E.M.F. against N calomel.	P.
4.82	0.827	0.000098	0.1	1,130	1.425	1.79
4.82	0.827		0.1	1,130	1.424	1.79
4.82	0.827		0.01	113	1.443	1.78
4.82	0.827		0.01	113	1.439	1.78
4.40	0.842	0.000064	0.1	1,570	1.417	1.79
4.22	0.848	0.000055	0.01	183	1.407	1.76
4.22	0.848		0.01	183	1.409	1.76
4.22	0.848		0.0001	18	1.444	1.74
3.44	0.876	0.000026	0.1	3,900	1.379	1.77
3.44			0.1	3,900	1.380	1.77
3.44			0.01	390	1.394	1.75
3.44			0.01	390	1.393	1.75
3.44			0.001	39	1.413	1.74
3.44			0.0001	4	1.422	1.72
3.44			0.0001	4	1.423	1.73
0.897	0.976	0.0000002	0.1	645,000	1.256	1.71
0.897	0.976		0.01	64,500	1.283	1.71
0.897	0.976		0.001	6,450	1.308	1.70

The divergence in P from the value found in stronger solutions is not greater than one might expect. Any errors introduced by taking Pb^{IV} as

equal to the total amount of tetrad lead dissolved, and in the value for the active mass of water will be minor ones, but the substitution of $(\text{HNO}_3)^4$ for $(\text{H}^+)^4$ must produce a large error. Unfortunately, however, these errors cannot yet be eliminated, but it may be said that the experimental results agree with the theory within the limits of these known errors. The value of P determined within the limits within which the amount of Pb^{IV} was analytically estimated should be the most exact, but all the experiments agree in showing that the tendency $\text{Pb}^{\cdots\cdots} \rightarrow \text{Pb}^{\cdots}$ is one of the largest known.

Plumbous Ion Concentration in Various Solutions.

Further experiments were carried out in the hope that some estimate of C_1 and C_2 might be obtained.

It may be assumed that in a nitric acid solution in which excess of lead superoxide is present, the plumbic concentration will remain constant, though the plumbous concentration may be altered by alteration of the amount of salt added. Dilution of the plumbous ion concentration to one-tenth will raise the potential by 0.0295 volt, or, generally, if C_1 and C_2 be the two concentrations of plumbous ions, the difference will be—

$$0.0295 \log_{10} \frac{C_1}{C_2}.$$

That the ionic concentrations C_1 and C_2 do not vary proportionately with the alteration of the total plumbous concentration, is clearly shown by the following results. The last column gives the calculated difference if $\frac{C_1}{C_2}$ were equal to $\frac{S_1}{S_2}$, i.e., if the ratio of the ionic concentrations were equal to the ratio of the total amounts of plumbous salt.

HNO_3 normality.	Total Pb. ^{II} grm.-moles.	E.M.F. against N calomel.	Difference.	Calculated difference.
0.897	0.1	1.256	}	0.029
0.897	0.01	1.283		
0.897	0.001	1.308		
3.44	0.1	1.380	}	0.029
3.44	0.01	1.394		
3.44	0.0001	1.422		
4.22	0.01	1.407	}	0.059
4.22	0.0001	1.444		
7.97	0.01	1.515	}	0.029
7.97	0.001	1.529		

Solubility of Lead Nitrate in Nitric Acid.

Incidental observations during the research had proved that lead nitrate was only slightly soluble in nitric acid, so some measurements were made to

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determine if the solubility varied in a regular manner, and in the hope of information as to how the plumbous ion concentration varied on alteration of the nitrate ion concentration. In some cases the solutions were super-saturated by shaking with excess of lead nitrate at about 28°, before placing in the bath at 25°.

Solubility of Lead Nitrate in Nitric Acid at 25°.

HNO ₃ normality.	Hours above 25°.	Hours at 25°.	C.c.s. of solution taken for analysis.	Wt. of PbSO ₄ .	Pb(NO ₃) ₂ grms. per litre.	Pb(NO ₃) ₂ grm.-mols. per litre.
water	—	170	20	9'912	541	1'64
water	—	210	5	2'43	531	1'61
2'02	95	240	5	0'813	178	0'536
4'64	67	70	20	1'120	61'2	0'185
4'64	—	112	25	1'416	61'4	0'186
4'64	—	130	20	1'125	60'5	0'183
8'77	—	114	25	0'303	13'2	0'040
8'77	67	220	20	0'270	14'7	0'044
14'35	—	170	20	1'0102	0'536	0'0017

Plumbous Ion Concentrations from Potential Measurements.

It is, of course, not possible to measure the plumbous ion concentration in nitric acid solutions with a lead electrode, but measurements were made in potassium nitrate solution, as it was thought that the equilibrium would be very similar. S. Labendzinski (*loc. cit.*) has made a few comparable measurements, which are included in the table for comparison.

The electrodes used were platinum points plated with lead from a solution of lead acetate and a little acetic acid. When sufficiently coated they were washed with water, and then with a little of solution to be measured, and as quickly as possible placed in the cell and the measurement made. The E.M.F. was found to be at once constant, to remain so for some hours, and then slowly fall.

In the following tables *a* is the observed potential when the lead cell was connected with the N calomel cell by a saturated ammonium nitrate solution, *b* is the potential when the two cells were directly connected with one another, and *c* are measurements of Labendzinski, comparable with *b*.

E.M.F. of Lead Nitrate Solutions.

Lead nitrate grm.-mols. per litre.	E.M.F.			<i>e</i> ₂ against N calomel.	<i>e</i> ₁ against hydrogen.
	<i>a</i> (Ammon. nitrate).	<i>b</i> (direct)	<i>c</i> (Labendzinski).		
1'00	—	—	0'434	(0'434)	(0'151)
0'100	0'449	0'455	0'455	0'420	0'137
0'010	—	—	0'485	(0'426)	(0'143)
0'001	0'500	0'500	—	0'412	0'129

ϵ_1 is the normal potential of plumbous lead, the measure of the tendency $\text{Pb}^{++} \rightarrow$ metallic lead. The best value is that from the measurement in 0.100 N solution, as it is the result of several concordant experiments, and in more dilute solutions the potential is less steady. The normal potential of plumbous lead at 25° is therefore — 0.137 volt against the hydrogen standard.

In the next table are the results obtained when an alkali nitrate was also added to the solution. C_0 is the concentration of plumbous ions, if the normal potential $\text{Pb}^{++} \rightarrow$ metallic lead be 0.137 volt.

$\text{Pb}(\text{NO}_3)_2$ grm.-mols. per litre.	Alkali salt grm.-mols. per litre.	E.M.F.			C_0 from a .
		a (amm. nitrate).	b (direct).	c (Labendz.).	
0.10	0	0.449	0.455	0.455	0.10
0.10	0.10 KNO_3	0.454	0.460	0.462	0.078
0.10	0.50 KNO_3	0.465	0.469	—	0.030
0.10	1.00 KNO_3	0.478	0.480	0.483	0.0105
0.10	1.00 $(\text{NH}_4)\text{NO}_3$	0.474	0.479	—	0.015
0.10	1.00 NaNO_3	0.465	0.469	—	0.030
0.10	2.00 KNO_3	0.490	0.490	—	0.0042
0.10	3.00 KNO_3	0.499	0.498	—	0.0021
0.10	5.00 $(\text{NH}_4)\text{NO}_3$	0.512	0.510	—	0.00076
0.10	10.0 $(\text{NH}_4)\text{NO}_3$	0.529	0.529	—	0.00020

Solubility of Lead Nitrate at 25°.

Solvent.					Normality.	Pb(NO ₃) ₂ grms. per litre.	Pb(NO ₃) ₃ grm.-mols. per litre.
Water	...	...	...	...	—	536	1.62
Nitric acid	...	...	...	...	2.02	178	0.536
KNO ₃	...	...	...	...	2.00	660	2.00

It was at first thought that the plumbous ion concentration in nitric acid might be taken as the same as that found in a corresponding strength of an alkali nitrate. It will be seen, however, that the addition of N sodium, potassium, and ammonium nitrates diminish the Pb^{++} concentration in widely different degrees.

That this difference in the behaviour of sodium and potassium nitrate really exists had already been proved by experiments of Le Blanc and A. A. Noyes (*Zeit. physik. Ch.* 6, 386), who found that lead nitrate is more soluble in potassium nitrate solution than in water, but in sodium nitrate solution it was less soluble than in water.

They also determined the freezing points of some solutions. Their figures, when considered with the above results, clearly prove that between KNO_3 and $\text{Pb}(\text{NO}_3)_2$ there is extensive complex formation, but not so between NaNO_3 and $\text{Pb}(\text{NO}_3)_2$.

From the solubility experiments it appears very unlikely that there is any appreciable complex formation between HNO_3 and $\text{Pb}(\text{NO}_3)_2$,

but in view of these abnormalities, it seems unsafe to draw any deductions as to the actual plumbous ion concentrations in nitric acid solutions, from experiments with alkaline nitrates.

Since both the plumbous and plumbic ionic concentrations remain uncertain, all that can be done is to accept the total concentrations as the nearest estimates at present possible. The two errors will to some extent balance one another, but to what extent cannot be said.

If + 1.82 volt against the hydrogen standard be taken as the value for the tendency $\text{Pb}^{\cdots} \longrightarrow \text{Pb}^{\cdot\cdot}$, there are several interesting deductions.

Luther (*Zeit. physik. Ch.* **34**, p. 488; **36**, p. 385) has shown that if a metal exhibits two valences a and b (higher), and the normal potential for ion $a \longrightarrow \text{metal} = e_1$, that of ion $b \longrightarrow \text{ion } a = e_2$, and that of ion $b \longrightarrow \text{metal} = e_3$

$$e_3 = a \times e_1 + \frac{(b-a)}{b} e_2$$

For lead, $e_1 = -0.137$ volt, $e_2 = +1.82$ volt, while a and b are 2 and 4, respectively, so that

Sulphate.—The normal potential P may theoretically be determined with any salt, but, for reasons which have been given, the nitrate is probably the best. A few experiments were made with the sulphate for comparison with the results already quoted. The potential of PbO_2 in sulphuric acid, *i.e.*, of plumbic sulphate, was measured with a platinum electrode, which had been coated with platinum black and lead peroxide, placed in a paste of plumbous sulphate and lead superoxide in acid of known concentration. The E.M.F. was measured against a N calomel electrode with saturated ammonium nitrate as the connecting solution. This was really the measurement of the potential on the peroxide plate of an accumulator.

$\frac{1}{2} \text{H}_2\text{SO}_4$ normality.				E.M.F. against N calomel.
7.45	...	...	...	1.479
4.82	...	...	...	1.434

From the method of experiment, the sulphuric acid must have been saturated with plumbous and plumbic lead. No estimation of the solubility of PbO_2 in H_2SO_4 was made, but an approximation can be arrived at from the results with nitric acid. The equilibrium between lead superoxide and tetrad lead ions must be

and $K_w = (\text{OH}')(\text{H}^\circ)$, where k and K_w are constants, so that in any solution the amount of $\text{Pb}^{\cdots}$ varies with H° . In any sulphuric acid solution, then, the amount of $\text{Pb}^{\cdots}$ ions dissolved will be the same as in that of a nitric acid solution of equal hydrogen ion concentration. In this way 3×10^{-4} grm.-mols. per litre is found as the approximate solubility of plumbic sulphate in 7.45 N sulphuric acid. The amount of lead sulphate dissolved by 29 per cent. sulphuric acid was estimated by Gladstone and Hibbert (Ref. in Dolezalek, *Theorie des Bleiaccumulators*) as 0.012 grms. $= 0.4 \times 10^{-5}$ grm.-mols. per litre at 18° . The solubility of plumbous sulphate in 7.45 N acid may be taken as approximately 6×10^{-6} grm.-mols. per litre. From these data, $P = 1.74$ volt against the hydrogen standard, as compared with 1.82 volt, found with the nitrate.

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Proper estimation of the solubilities of lead sulphate and lead superoxide in sulphuric acid might bring about better agreement, but it is not surprising to find a lower value with the sulphate than with the nitrate, as this is a general phenomenon (*e.g.*, compare Spencer, *loc. cit.*).

Plumbous Ion Concentration in Alkaline Solution.

While working at plumbous ion concentrations, a few experiments were carried out in alkaline solution. Lead monoxide, PbO, is a typical inorganic amphoteric electrolyte. It dissolves in acids to form the ordinary lead salts, and can also behave as an acid anhydride, as with alkaline hydroxides it forms quite a different type of salt.

The tendency to act as a basic radicle is much greater than the acid tendency, since it dissolves in water to a slight extent to form an alkaline solution.

The concentration of plumbous ions in alkaline solution may be determined by the electromotive force of the solution with a lead electrode. Pure caustic soda was shaken for some hours with PbO, and lead electrodes were prepared as in previous experiments. Care was taken to prevent the admission of atmospheric carbon dioxide, and no unnecessary time was lost in transferring the electrodes to the solution; but there does not seem to be any special difficulty about the measurement of plumbous potentials, as the same result was obtained in an experiment where nothing more than the usual analytical precautions were taken to exclude atmospheric carbon dioxide, and in a similar experiment in which all vessels were filled with nitrogen, and a stream of nitrogen played on the solution while pouring from the bottle to the measuring vessel. If PbO dissolves in caustic soda according to the formula—

the equation for the ionic equilibrium will be—

$$\text{Pb(OH)}_3' = k(\text{PbO})(\text{OH}')$$

Since the total amount (*a*) of PbO dissolved must be practically the same as $\text{Pb(OH)}_3'$, this may be written—

$$a = k(\text{PbO})(\text{OH}')$$

It is also known that—

$$(\text{Pb}^{++})(\text{OH}')^2 = L \text{ (solubility product)}$$

and PbO remains constant, so that—

$$a \sqrt{\text{Pb}^{++}} = \text{constant } (k')$$

The following are the results of four independent experiments. The potential was measured against a N calomel electrode with direct connection.

NaOH normality.	PbO dissolved. Grm.-mols. per litre.	E.M.F. against N calomel.	E.M.F. against N hydrogen.	Pb ⁺⁺	k'.
1'00	0'0576	0'822	0'539	$1'8 \times 10^{-13}$	24×10^{-9}
1'00	—	0'821	0'538	$1'7 \times 10^{-13}$	—
0'100	0'0089	0'767	0'484	390×10^{-13}	55×10^{-9}
0'100	—	0'767	0'484	390×10^{-13}	—

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The difference found in k' may be due to the non-elimination of the diffusion potential. Up to the present no work has been done on the elimination of the diffusion potential at the surface of two liquids, one of which contains hydroxyl ions. The two values for k' are therefore sufficiently close to support the formula $\text{NaPb}(\text{OH})_3$ for the compound formed when PbO dissolves in NaOH .

Solubility of Lead Monoxide in Water.

Some yellow PbO , which had been thoroughly washed, was shaken for several hours with water at 25° , and the Pb^{++} concentration measured from the potential with a lead electrode. Two concordant experiments gave the E.M.F. against N calomel as 0.614 volt within 0.005 volt. If 0.137 volt against hydrogen be taken as the N plumbous potential, the concentration of Pb^{++} in the above solution was 3.8×10^{-6} gm.-mols. per litre.

In conclusion, I have much pleasure in expressing my best thanks to Professor Abegg for his advice and assistance during this research.

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