CLXXIII.—*Physical Chemistry of the Oxides of Lead. Part V. The Electromotive Behaviour of Lead Dioxide.*

By Samuel Glasstone.

During the course of the work described below, the electromotive behaviour of ordinary chemical lead dioxide was compared with that of the dioxide deposited electrolytically from neutral or acid lead nitrate solution, and of the so-called hydrated lead dioxide deposited from slightly alkaline lead tartrate solution. The system lead–lead dioxide having been found to be unstable, measurements were made on the plumbic–plumbous electrode, $\mathrm{Pt}\left|\begin{array}{c}\mathrm{PbO}\\\mathrm{PbO_2}\end{array}\right.N\text{-NaOH}$, where the lead dioxide was either introduced as a powder or deposited on a smooth or platinised platinum electrode. The electromotive behaviour of all the electrolytic products was the same, there being no distinction between the deposits from alkaline, neutral, or acid solution. In each case, however, there was evidence for the existence of an unstable higher oxide of lead, traces of which were present in solid solution in the dioxide. These results rendered desirable a redetermination of the normal plumbic–plumbous potential first measured by Cumming (*Trans. Faraday Soc.*, 1907, **2**, 199), who used electrolytic lead dioxide.

Experimental.

The chemical lead dioxide used in this work was prepared (unless otherwise stated) by the action of bleaching powder solution on a boiling solution of lead acetate; the product was washed with hot dilute nitric acid and with water, and dried.

The System Lead–Lead Dioxide.

For the purpose of electromotive measurements it was desirable to know whether the system lead–lead dioxide was stable in the

presence of alkali. To test this, lead dioxide was mixed with pure spongy lead (made by the action of zinc dust on lead acetate solution and freed from excess of zinc) and kept in contact with 15 per cent. sodium hydroxide solution for some months. The colour of the oxide became more and more red, and after six months analysis indicated the formula Pb_3O_4. The system lead–lead dioxide–alkali must therefore be regarded as unstable. This fact was further confirmed by potential measurements on a $Pb|PbO_2$ N-NaOH electrode. Immediately after setting up, the potential was -0.559 volt, which is that of $Pb|PbO$ N-NaOH, showing that the first reaction was $Pb^{····} + Pb \longrightarrow 2Pb^{··}$, or $PbO_2 + Pb \longrightarrow 2PbO$. On the next day the $P.D.$ was 0.296 volt, all the lead which had been deposited on the platinum electrode having been dissolved. The potential remained constant at this value, which corresponds with that of the $Pt\Big|^{Pb_2O_3}_{PbO_2}$ N-NaOH electrode; evidently the second reaction had been $PbO + PbO_2 \longrightarrow Pb_2O_3$. By renewing the lead deposit on the platinum electrode from time to time, the potential eventually rose to 0.320 volt, which is that of the $Pt\Big|^{Pb_3O_4}_{PbO_2}$ N-NaOH electrode, showing that the final reaction was $PbO + Pb_2O_3 \longrightarrow Pb_3O_4$.

$$The \ Pt\Big|^{PbO_2}_{PbO} \ N\text{-NaOH} \ Electrode.$$

Owing to the instability of the $Pb|PbO_2$ electrode, the electromotive properties of lead dioxide were investigated in the plumbic–plumbous electrode, $Pt\Big|^{PbO_2}_{PbO}$ N-NaOH, since the dioxide in solution almost certainly gives a definite concentration of $Pb^{····}$ ions, whilst the monoxide gives a definite $Pb^{··}$ ion concentration. In the preliminary experiments lead dioxide was mixed in separate electrode vessels with various forms of lead monoxide and with hydrated monoxide, in fortuitous amounts. The vessels were then filled with N-sodium hydroxide, smooth platinum electrodes were inserted, and the potentials measured from day to day, the vessels being gently shaken in the intervals. In every case the potential at room temperature was initially about 0.27 volt, remained almost constant for two or three days, and then decreased slightly. After two or three weeks, a distinct reddening of the solid was observed in all the half-elements, whilst in some cases a layer of red solid had formed on the sides of the vessel. At the same time the potentials of some of the electrodes became very erratic, whilst others had increased to 0.31—0.32 volt. In view of previous work (this vol., p. 1456) the explanation of these phenomena is as follows. Lead monoxide

and dioxide combine to form red lead; if the original mixture contained excess of monoxide, the final potential would be erratic, since $\text{Pt}\left|\begin{matrix} \text{PbO} \\ \text{Pb}_3\text{O}_4 \end{matrix}\right.$ does not give a definite potential value; if the dioxide had been present in excess, the final potential would be that of the $\text{Pt}\left|\begin{matrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_3 \end{matrix}\right.$ N-NaOH half-element, that is, of the order of 0·32 volt. These conclusions were confirmed by making up mixtures containing known proportions of monoxide and dioxide, and measuring the potential of the $\text{Pt}\left|\begin{matrix} \text{PbO} \\ \text{PbO}_2 \end{matrix}\right.$ N-NaOH half-element from day to day.

Measurements at room temperature (about 17°). Scale $H_2|N$-$H^{\cdot} = 0$.

I. 3PbO:PbO₂.		II. 2PbO:PbO₂.						III. PbO:2PbO₂.	
		(a)		(b)		(c)			
Days.	P.D.	Days.	P.D.	Days.	P.D.	Days.	P.D.	Days.	P.D.
0	0·271	0	0·273	0	0·274	0	0·278	0	0·273
1	0·270	4	0·266	4	0·260	4	0·268	4	0·266
3	0·268	5	0·265	7	0·260	25	0·266	5	0·266
7	0·261	7	0·265	11	0·260	39	0·322	7	0·265
10	0·258	14	0·258	20	0·272	53	0·321	14	0·258
33	0·237	28	0·271	26	0·308	Final	0·321	19	0·297
Erratic after		30	0·308	40	0·316			75	0·314
this period.		45	0·312	56	0·315			Final	0·314
		60	0·316	Final	0·315				
		Final	0·316						

The forms of lead monoxide used were, red in Series I, II a, and III; reddish-brown in II c; yellow in II b. In Series I, where the potential had become erratic after thirty-three days, a red solid had formed on the sides of the electrode vessel. The remainder of the solid was emptied out, and fresh dioxide and N-sodium hydroxide put in; the potential was now found to be 0·312 volt, a value which suggests that the red solid was a mixture of red lead and lead sesquioxide.

Similar series of experiments using lead dioxide prepared by the action of nitric acid on red lead gave exactly similar results.

Allowing for the initial high values due to the presence of very small particles, the value of the $\text{Pt}\left|\begin{matrix} \text{PbO} \\ \text{PbO}_2 \end{matrix}\right.$ N-NaOH electrode potential is probably of the order of 0·27 volt; this result was confirmed by the measurements on electrolytic lead dioxide described below.

Electrolytic Lead Dioxide.

Hollard (*Compt. rend.*, 1903, **136**, 229; 1904, **138**, 142) found that lead dioxide deposited electrolytically on a platinised platinum

anode from a slightly acid solution of lead nitrate does not agree in composition with the formula PbO_2. He weighed the deposits obtained from various known amounts of lead nitrate, and suggested that the substance formed is an oxide, PbO_x, where x is greater than 2 and increases as the lead nitrate solution becomes more dilute. In the most dilute solution examined (0·0106 gram of lead in 300 c.c. of solution) the ratio, $Pb|PbO_x$, was found to be 0·74; this would correspond with a value of about 4·5 for x. No suggestion was, however, made that all or part of this extra mass may be due to the presence of adsorbed or combined water (compare Wernicke, *Pogg. Annalen*, 1870, **141**, 109). Using smooth platinum electrodes, Hollard found that in every case almost pure lead dioxide was deposited independent of the concentration of the lead nitrate solution. In order to investigate the possible electromotive differences in the various electrolytic products, a number of smooth and platinised platinum electrodes were coated with lead dioxide by electrolysis of various solutions of lead nitrate. After half an hour's deposition with a current of 0·01 ampere, the electrodes were rapidly washed with water, then with N-sodium hydroxide, and placed in electrode vessels containing lead monoxide and N-alkali. The potentials were measured immediately, and variations carefully followed. Every form of electrolytically deposited lead dioxide showed the same peculiar behaviour independent of the electrode material, current density, time of deposition, and concentration of the lead nitrate solution. The potential was in every case initially very high, 0·69 to 0·49 volt (compare the value 0·27 volt for the ordinary dioxide); this decreased very rapidly at first, then more slowly with a distinct break in the rate of fall at 0·40 volt. After this, the slow decline of potential continued sometimes for days or weeks, depending on the amount of the electrolytic deposit, until in every case the final value was 0·268 volt, corresponding with the normal $Pt\left|\begin{array}{c}PbO\\PbO_2\end{array}\right.$ N-NaOH potential. At this value, the potential remained constant apparently indefinitely, probably due to the very slow rate of combination of electrolytic dioxide with the monoxide in the formation of red lead. No visible change could be observed in the dioxide during the fall of potential from 0·69 to 0·268 volt. A typical example of the rate of fall of the electrode potential is given below; it should be stated that the initial value can have no definite meaning, because it must depend on the very small period of time that elapses between setting up the electrode and finding the balance point on the potentiometer. The initial rate of fall is so great that even a very small interval would cause an appreciable fall in the potential.

Time.	P.D.	Time.	P.D.	Time.	P.D.	Time.	P.D.
0	0·593	7½ mins.	0·477	71 mins.	0·420	5 days	0·326
1 min.	0·558	15 ,,	0·455	104 ,,	0·416	7 ,,	0·310
2½ mins.	0·534	19 ,,	0·445	177 ,,	0·412	10 ,,	0·294
3 ,,	0·520	28 ,,	0·434	8 hours	0·407	13 ,,	0·284
3½ ,,	0·512	37 ,,	0·430	25 ,,	0·362	20 ,,	0·272
6 ,,	0·492	54 ,,	0·426	2 days	0·346	28 ,,	0·268

Initial Values.—The initial value measured appeared to depend to some extent on the current density used in depositing the dioxide; for example, with a current density of 0·004 amp./cm.², the initial potential was 0·59 volt, but with 0·1 amp./cm.² it was 0·70 volt. As explained above, these values can only be regarded as comparative.

Breaks.—In some cases there was an indication of a break at 0·49 volt, but this was not very definite, and may have been due to the normal diminution of the initial very high rate of fall.   In every case, however, a break was noted in the vicinity of 0·40 volt, after which there was a steady fall to the normal value of 0·268 volt.

Rate of Fall.—This depended to a great extent on the amount of dioxide that had been deposited.   In one case, after deposition for five minutes with a current of 0·02 ampere on a platinum surface of about 1 sq. cm., the final steady state was reached in eighteen hours.   Where a platinised electrode had been used and dioxide deposited for two hours with the same current, the steady state was reached only after fifty-six days.

Hydrated Lead Dioxide.

Before describing further experiments on the electrolytic dioxide, reference must be made to the hydrated dioxide, H_2PbO_3, claimed to have been prepared by Wernicke (*Pogg. Annalen*, 1870, **139**, 132) by the electrolysis of an alkaline solution of lead tartrate.   Schreber (*Wied. Annalen*, 1889, **36**, 662) suggested that the product obtained had the formula $Pb(OH)_4$ or $PbO_2 2H_2O$.   Streintz and Neumann (*ibid.*, 1890, **41**, 97) confirmed Wernicke's results, and measured the potentials of the elements $Pb|PbO_2$ (chemical) and $Pb|H_2PbO_3$ in sulphuric acid, against zinc.   The *E.M.F.*'s of these cells were 2·41 volts and 0·96 volt respectively; it appears from this that the anhydrous oxide is metastable with respect to the hydrated form. Owing to the great instability of the system lead–lead dioxide, it is probable that the potential measured is not that of $Pb|PbO_2$ or H_2PbO_3 in sulphuric acid, but rather a plumbic–plumbous potential.   In the case of chemical lead dioxide, the solution surrounding the electrode would soon become saturated with lead sulphate, and so a stable potential would rapidly result.   The electrolytic product (H_2PbO_3) is less reactive, probably owing to state

of division (compare the formation of red lead on p. 1472), and therefore the solution would become saturated with plumbous salt very slowly. The potential measured would thus depend on the time elapsing between setting up and measurement.

Attempts were made to prepare this hydrated oxide by Wernicke's method (*loc. cit.*). Unless the current density was very low and the liquid stirred from time to time, the difficulty was experienced that a basic salt separated round the anode owing to local diminution of the hydroxyl-ion concentration. Even when there was no visible formation of basic salt, some may have possibly been deposited with the dioxide on the anode. After drying in a desiccator, the composition of the product varied in different specimens ; three samples gave the percentage loss on heating as 11·7, 10·8, and 10·0, respectively (H_2PbO_3 requires loss on heating $= 13·22$ per cent.). The substance was therefore not a pure hydrate, and may have belonged to the same category as the electrolytic deposits of Hollard (*loc. cit.*). The electromotive activity of the Wernicke product was investigated in the same way, and the results obtained were identical with those given by electrolytic lead dioxide deposited from acid or neutral lead nitrate solution. In every case where the so-called hydrate was examined, the initial potential was about 0·6 volt, falling rapidly to 0·40 volt, and then more slowly to the stable value, 0·268 volt. The existence of a pure hydrated dioxide, H_2PbO_3, is doubtful, and it is very probable that the substance is merely electrolytic lead dioxide containing about 3 per cent. of adsorbed water, which it is known to retain very tenaciously, Although the existence of H_2PbO_3 has by no means been disproved, yet considering its electromotive behaviour, its variable composition, and the fact that no salts of the type $M_2^IPbO_3$ * are definitely known, but only those of the type $M_2^IPb(OH)_6$ which are derived from the very unstable $H_2Pb(OH)_6$ (Bellucci and Parravano, *Z. anorg. Chem.*, 1906, **50**, 107), its existence seems improbable.

Stability of the Initial Electrolytic Product.

The following experiments refer to lead dioxide deposited from lead nitrate solutions ; similar experiments with the Wernicke product gave similar results.

Evidently during electrolytic deposition a highly metastable substance is formed which decomposes rapidly in the presence of lead monoxide and alkali. A series of experiments was carried out with the object of determining the stability of the product in other reagents and under differing conditions. Lead dioxide was

* See, however, Grube's work (*Z. Elektrochem.*, 1922, **28**, 273), which appeared after this paper was written.

deposited electrolytically from a 5 per cent. lead nitrate solution containing a little nitric acid; the electrode was washed and subjected to some physical or chemical treatment. It was then placed in an electrode vessel containing lead monoxide and N-sodium hydroxide, and the potential measured. The treatment and results are tabulated below.

Treatment.	Initial $P.D.$ (volt).	Remarks.
a. In $4N$-HNO_3 for 18 hours	0·44	No break at 0·40 volt.
b. In $4N$-H_2SO_4 ,, ,,	0·43	Normal fall.
c. In $4N$-H_2SO_4 and $PbSO_4$ for 2 hours	0·45	,, ,,
d. In electrolytic bath for $1\frac{1}{2}$ hours with current off	0·37	
e. In 5% lead nitrate for 1 hour	0·39	
f. In N-sodium hydroxide for 2 hours	0·48	Normal fall.
g. In slightly acid hydrogen peroxide for 1 hour	0·35	Rose to 0·44 volt in 13 mins. and then fell steadily.
h. In boiling water for 5 minutes	0·30	Fell to 0·276 volt in 3 hours.

The following experiments were also made. (i) The freshly deposited lead dioxide was made up into a plumbic–plumbous half-element by placing it in a vessel containing about $4N$-nitric acid and $0.01M$-lead nitrate; after three days, when the potential was only 0·01 volt higher than that given by stable lead dioxide, the electrode was removed and its potential measured in lead monoxide and N-sodium hydroxide; the initial value was 0·45 volt.

(j) The lead dioxide was deposited from a nitrate bath surrounded by boiling water; the initial potential was 0·432 volt.

(k) An electrode prepared in the normal way was washed with water, alcohol, and ether, and placed in a desiccator for eighteen hours; the initial potential was 0·483 volt, and the fall normal.

We thus see that the substance giving the high electrode potentials decomposes comparatively slowly in acids and alkalis, but rapidly by the action of heat or sodium plumbite solution. The explanation suggested is that all the forms of electrolytic dioxide contain a higher metastable oxide in solid solution. The amount of this higher oxide present must be very small, as it could not be detected by analysis; there might, even so, be sufficient to show pronounced electromotive activity.* Owing to its dilution by a

* Since this paper was written MacInnes and Townsend (*J. Ind. Eng. Chem.*, 1922, **14**, 420) have reported the estimation of lead by electrolytic deposition as dioxide, the latter being immediately estimated by the direct iodometric or oxalic acid method. Since the results are in excellent agreement with theory, the authors claim to have definitely established that no higher oxides can be present in the electrolytic deposit. It should, of course, be added that a higher oxide may be present in an amount insufficient to be detected by ordinary methods of analysis.

large excess of dioxide, the rate of decomposition of the higher oxide would be greatly decreased, and would become smaller as the concentration became less. Theoretically, therefore, the rate of fall of potential should gradually decrease, and the potential for pure lead dioxide should be approached asymptotically; qualitatively this is the actual behaviour. Apparently acids and alkalis do not affect the rate of decomposition, but as is to be expected, rise of temperature accelerates it. A curious result is that of experiment (i), where practically normal potential values were obtained in the nitric acid half-element, yet the same electrode gave very high metastable values in the alkaline half-element. Evidently the higher oxide of lead, for which the formula PbO_3 is tentatively suggested, like most other higher oxides, is acidic (compare PtO_3, Wöhler and Martin, *Ber.*, 1909, **42**, 3326), and therefore gives negative ions electromotively active with other negative ions, for example, plumbite and plumbate, but not with plumbous and plumbic ions, which would be present in the nitric acid electrode. The presence of a very small concentration of Pb^{VI} ions might account for the slightly higher results obtained in the nitric acid half-element before stability was attained.

Another possible explanation is that the initial high values are due to adsorbed oxygen (compare Elbs and Forssel, *Z. Elektrochem.*, 1902, **8**, 760). A potential of 0·69 volt would require an oxygen pressure of about 10^{19} atms., and although adsorption pressures are known to be great, yet they would scarcely be of this order of magnitude. Whilst standing in nitric acid, gas bubbles were observed to be coming from the electrolytic deposit, but this may have been due either to displacement of adsorbed oxygen, or to the decomposition of the higher oxide, PbO_3.

The Break at 0·40 *Volt.*—A potential of 0·40 volt corresponds with that of a reversible oxygen electrode at a pressure of about 1 atmosphere, in *N*-sodium hydroxide. A break at this point would be expected, for the rate of escape of oxygen from the electrode would become slower when it was being evolved at a pressure equal to that of the oxygen in the atmosphere. It has been found that electrolytic lead dioxide deposited on lead electrodes does not show this break, which may have been due, therefore, to an oxide of platinum. Decomposition of this oxide by nitric acid would explain why lead dioxide electrodes kept in nitric acid (see expt. [a], p. 1475) do not show a break at 0·40 volt.

The Normal Plumbic–Plumbous Potential.

In measuring the normal $Pb^{····} \longrightarrow Pb^{··}$ potential, Cumming (*loc. cit.*), who used electrolytically deposited lead dioxide, and noted

that in nitric acid half-elements the potential first fell, then became steady for many hours, and finally diminished slowly and apparently indefinitely, used the first steady value and attributed the subsequent fall to the presence of impurities. In view of the results obtained in the present investigation with electrolytic dioxide in alkaline electrodes, the determination of the normal plumbic–plumbous potential was repeated, using chemical lead dioxide only. Half-elements were made up from nitric acid solutions of known concentration containing known amounts of lead nitrate, and excess of solid dioxide. The potential of a smooth platinum electrode inserted well into the solid was measured, after a week, against that of a normal calomel electrode, using a saturated solution of ammonium nitrate as intermediate liquid. The results were compared with those obtained with electrolytic dioxide in the same solutions, and it was found that, in general, when the first (apparent) steady state was reached, the potentials of the latter were about $0 \cdot 02$ volt higher than those given by the chemical dioxide. After several days, both types of electrode gave identical potential values. The normal $Pb^{\cdots\cdots} \longrightarrow Pb^{\cdots}$ potential is calculated below from the results obtained with the chemical dioxide, use being made of Cumming's empirical formula for the plumbic-ion concentration in nitric acid solutions saturated with lead dioxide, namely, $[Pb^{\cdots\cdots}] = [HNO_3]^4 [H_2O]^2 \times 2 \cdot 4 \times 10^{-7}$ gram-ion per litre at $25°$.

Measurements at $25°$. Scale $H_2 | N\text{-}H^{\cdot} = 0$.

HNO_3.	$Pb^{\cdot\cdot}$.	E (volts).	E_0 (volts).	HNO_3.	$Pb^{\cdot\cdot}$.	E (volts).	E_0 (volts).
$0 \cdot 483\,N$	$0 \cdot 005\,M$	$1 \cdot 519$	$1 \cdot 686$	$1 \cdot 90\,N$	$0 \cdot 05\,M$	$1 \cdot 587$	$1 \cdot 713$
,,	$0 \cdot 05$	$1 \cdot 494$	$1 \cdot 689$	,,		$1 \cdot 624$	$1 \cdot 730$
$0 \cdot 965$	$0 \cdot 01$	$1 \cdot 547$	$1 \cdot 686$	$3 \cdot 81$	$0 \cdot 01$	$1 \cdot 653$	$1 \cdot 723$
,,	$0 \cdot 05$	$1 \cdot 522$	$1 \cdot 684$	,,	$0 \cdot 05$	$1 \cdot 642$	$1 \cdot 734$
$0 \cdot 980$	,,	$1 \cdot 531$	$1 \cdot 690$	$6 \cdot 00$	$0 \cdot 01$	$1 \cdot 694$	$1 \cdot 743$
$1 \cdot 729$	$0 \cdot 005$	$1 \cdot 598$	$1 \cdot 699$	,,	$0 \cdot 05$	$1 \cdot 682$	$1 \cdot 754$
,,	$0 \cdot 05$	$1 \cdot 570$	$1 \cdot 700$				

The steady increase in the value of E_0, the normal plumbic–plumbous potential, may be due to three causes, (a) the failure of ammonium nitrate solution to eliminate diffusion potential at high nitric acid concentrations, (b) the solubility of lead dioxide in the more dilute solutions is smaller than that calculated by the Cumming formula, and (c) in concentrated acid solution the thermodynamic activity of the plumbous ions is very much smaller than unity. The first point was tested by using saturated potassium chloride solution as intermediate liquid, when identical results were obtained; no further method for testing this possibility could be found. With regard to the second possibility, it would appear from the results obtained that the solubility of lead dioxide in N-nitric acid is about

one-hundredth part of that calculated by the Cumming formula; in dilute solutions, however, owing to the greater degree of ionisation of the nitric acid, one would expect a relatively greater solubility instead of a very much smaller one. As regards the third point, Cumming (*loc. cit.*) has shown that in fairly dilute acid solution, for example, $0.897N$-nitric acid, the ratio of the lead nitrate concentrations in 0.1 and 0.01 molar solutions is a good measure of the ratio of the plumbous-ion concentrations. In 4.22 N-acid, however, even at such low lead nitrate concentrations as 0.01 and 0.0001, the ratio of the plumbous-ion concentrations, instead of being $100 : 1$, was $18 : 1$ (this value has been calculated from Cumming's *P.D.* measurements). This discrepancy is also seen in the results of the present series of measurements; with $3.81N$- and $6.00N$-acids, where the ratio of lead nitrate concentrations is $5 : 1$ in each case, requiring a difference of potential of 0.021 volt, the actual differences are 0.011 and 0.012 volt, respectively. Further, if the Cumming formula is generalised in the form $[Pb^{····}] = [H^·]^4[H_2O]^2 \times 2.4 \times 10^{-7}$, the normal plumbic–plumbous potential may be calculated from the known value of the $Pt\begin{vmatrix}PbO\\PbO_2\end{vmatrix}$ N-NaOH electrode (0.268 volt). In this case, the $Pb^{··}$-ion concentration is known to be 2.2×10^{-15} (T., 1921, **119**, 1914) and the $Pb^{····}$ concentration may be calculated from the above formula as 2.2×10^{-63}; the normal $Pb^{····} \rightarrow Pb^{··}$ potential is thus 1.684 volts at $25°$. This result is in striking agreement with those obtained in the more dilute nitric acid solutions.

Taking these facts into consideration, as well as the fact that electrolytic dioxide gives results that are probably slightly too high, the author is of opinion that the normal $Pb^{····} \rightarrow Pb^{··}$ potential, 1.82 volts, adopted by Cumming, is in excess of the true value. It is suggested that a potential of 1.75 volts at $25°$ would be more correct, although probably still too high. This value will be adopted in subsequent calculations.

The Solubility Product of Lead Dioxide.

From the known value of the potential of the $Pt\begin{vmatrix}PbO\\PbO_2\end{vmatrix}$ N-NaOH electrode (0.268 volt), and of the plumbous-ion concentration produced by dissolving lead monoxide in N-sodium hydroxide (2.2×10^{-15} gram-ion per litre), the plumbic-ion concentration in the electrode is 1.30×10^{-65} gram-ion per litre, assuming that the normal $Pb^{····} \rightarrow Pb^{··}$ potential is 1.75 volts. Since N-sodium hydroxide is dissociated to the extent of 72 per cent., the solubility product of the dioxide is given by

$$L_i = [Pb^{····}][OH']^4 = 1.30 \times 10^{-65} \times (0.72)^4 = 3.25 \times 10^{-66}.$$

The Instability of the System Lead–Lead Dioxide.

If metallic lead is in contact with a solution containing $Pb^{····}$ and $Pb^{··}$ ions, an equilibrium is set up as follows :

$Pb^{····} + Pb \rightleftharpoons 2Pb^{··}$.   Hence, at equilibrium, $[Pb^{··}]^2/[Pb^{····}] = K$.

This constant may be calculated from a consideration of the electrode potentials of the reactions $Pb^{··} \rightarrow Pb$ and $Pb^{····} \rightarrow Pb^{··}$; when these potentials are equal, the system is in equilibrium. The normal electrode potentials are -0.130 and 1.75 volts, respectively; hence, at equilibrium, we have :

$1.75 + 0.0295 \log [Pb^{····}]/[Pb^{··}] = -0.130 + 0.0295 \log [Pb^{··}]$

whence $\qquad\qquad [Pb^{··}]^2/[Pb^{····}] = K = 10^{63\cdot7}$.

Suppose in this mixture of lead, plumbic, and plumbous ions solid lead dioxide is also present, then $[Pb^{····}][OH']^4 = L_i = 10^{-66}$ (omitting the integers). When the system is in equilibrium, $[Pb^{··}]^2[OH']^4 = KL_i$, that is, $[Pb^{··}][OH']^2 = \sqrt{KL_i}$, which is equal to $\sqrt{10^{-2\cdot3}}$ (approx.).

In a solution saturated with lead monoxide (or hydroxide) the solubility product, $[Pb^{··}][OH']^2 = 1.1 \times 10^{-15}$ (T., 1921, **119**, 1914); hence at equilibrium in the system lead–solid lead dioxide, the solubility product of the monoxide is very greatly exceeded ($[Pb^{··}][OH']^2 = \sqrt{10^{-2}}$) and therefore this oxide will be precipitated. This will disturb the equilibrium, more $Pb^{····}$ ions will react with metallic lead to form $Pb^{··}$ ions, which will again be removed from the system as solid monoxide, and these processes will continue until either all the solid lead is dissolved or only a minute amount of lead dioxide remains.   These results demonstrate the essential instability of the system lead–lead dioxide.

Dissociation Pressures.

By considering the cell $Pt\begin{vmatrix} PbO \\ PbO_2 \end{vmatrix} N\text{-NaOH}$ $H_2(1\ \text{atm.})|Pt$, the E.M.F. of which is $0.268 - (-0.810) = 1.078$ volts at $17°$, as an oxygen–hydrogen cell, the pressure of oxygen in the reaction $PbO_2 \rightarrow PbO + \tfrac{1}{2}O_2$ may be calculated as 2.4×10^{-11} atm. Using the value $12,100$ calories (Tscheltzow, *Compt. rend.*, 1885, **100**, 1458) as the heat of this reaction, the dissociation pressure calculated by Nernst's theorem is 7.1×10^{-12} atm. at $17°$.

In view of the fact that lead dioxide on heating forms a series of solid solutions with the resulting lead monoxide (Reinders and Hamburger, *Z. anorg. Chem.*, 1914, **89**, 71), it did not appear desirable to make any detailed calculations as to the temperature of complete dissociation in air.   One determination by the use of the integrated

form of the van't Hoff isochore gave a temperature of 394° for an oxygen dissociation pressure of 0·21 atm. By extrapolation from the results of Reinders and Hamburger, it appears that lead dioxide containing only a small amount of monoxide in solid solution would have a dissociation pressure about a hundred times as great, at that temperature.

E.M.F.'s Calculated by Nernst's Theorem.

The $E.M.F.$ of the cell $\mathrm{Pt}\begin{vmatrix} \mathrm{PbO} \\ \mathrm{PbO_2} \end{vmatrix}$ N-NaOH H_2(1 atm.)|Pt involving the reaction $PbO_2 + H_2 = H_2O + PbO$, the water being in the form of ice, may be calculated for 0°. For the reaction at 17°, we have :

$$Q_T = 68,400 \ (H,O) + 1580 \ (\text{ice, water at } 17°) -12,100 \ (PbO,O)$$
$$= 57,880 \text{ cals.}$$

The molecular heats of the reactants are 15·5 for the dioxide and 6·8 for hydrogen; those of the resultants are 11·8 for the monoxide and 9·5 for ice. These lead to a value of 57,228 cals. for Q_0, and $-0·0043$ for β, from which the $E.M.F.$ of the cell is calculated as 1·092 volts at 0°. By the more approximate method in which water is involved instead of ice, Q_0 is found to be 56,880 cals., and β is $-0·019$, leading to an $E.M.F.$ of 1·109 volts at 17°. The actual $E.M.F.$ of the cell at 17° is 1·078 volts.

Summary.

(1) The stability of the system lead–lead dioxide in alkali has been investigated practically and theoretically.

(2) Electromotive measurements have shown that lead monoxide and dioxide combine in the presence of N-alkali to form red lead.

(3) The electromotive behaviour of electrolytically deposited lead dioxide suggests that a trace of a higher, acidic oxide (possibly PbO_3) is present in the deposit.

(4) The evidence for the existence of a definite hydrated lead dioxide, H_2PbO_3, is criticised.

(5) The normal plumbic–plumbous potential has been redetermined, and a maximum value of 1·75 volts at 25° is indicated.