

CCLV.—*The Isomerism of Metallic Oxides. Part I.*
Lead Monoxide.

By MALCOLM PERCIVAL APPLEBEY and ROBERT DOUGLAS REID.

LEAD MONOXIDE occurs naturally in two crystalline forms, litharge and massicot, which are yellow and red, respectively. These can also be obtained in the laboratory by artificial means. It has been long known that the red form can be converted into the yellow by heating and the yellow into the red by long-continued action of light at the ordinary temperature. The difference between the two forms has been attributed by many investigators to polymorphism, the red being regarded as the more stable form at the ordinary temperature and at all temperatures up to a transition point which has not been precisely determined. This explanation is supported by the difference of density of the two forms observed by Geuther (*Annalen*, 1883, **219**, 56) and by Ruer (*Z. anorg. chem.*, 1906, **50**, 265), whose observations agree in ascribing the lower density to the red form, although their actual values are somewhat widely divergent (Geuther, red 9.13, yellow 9.29; Ruer, red 9.37, yellow 9.52). Ruer also determined by a conductivity method the solubility of the two forms in water, which he found to be 1.00×10^{-4} gram-equiv. per litre for the yellow form and 0.56×10^{-4} for the more stable red form. Solubilities determined by the conductivity method for substances like litharge are not very trustworthy, but the values for the two forms probably give a fairly correct idea of the relative solubility.

The crystallographic evidence also points to polymorphism. Nordenskiöld (*Pogg. Ann.*, 1861, **114**, 619) determined the form of the yellow modification to be rhombic bipyramidal and that of the red to be tetragonal. Larsen (*U.S.A. Geol. Survey Bull.*, 1921, **679**, 105), working both with mineral forms and with laboratory products, confirmed Nordenskiöld's conclusions, and found, moreover, that the yellow form is always biaxial and positive in its action on polarised light, whilst the red is uniaxial and negative.

The explanation of these differences as due to polymorphism has recently been attacked by Glasstone (T., 1921, **119**, 1689, 1914). Using preparations of lead monoxide obtained by the action of alkali of various strengths on solutions of lead salts, he has found, both by gravimetric and electrometric measurements, approximately identical solubility for lead oxide preparations irrespective of their colour, and has drawn the conclusion that the differences of colour are due, not to polymorphic change, but to variations of the state of division of the substance. The change of red to yellow on heating is attributed to formation of larger agglomerates, which on rubbing will

break down again into a reddish-brown powder, consisting of particles rather smaller than the original red form. The crystallographic evidence is regarded as indecisive and that from density and from solubility, determined by conductivity, is rejected for the reasons stated above.

Methods for the preparation of both the red and the yellow varieties in the form of definite crystals of fair size had already been worked out in this laboratory, and experiments on their solubility relations were being developed at the time when Glasstone's papers appeared. It was therefore at once apparent to us that Glasstone's theory could not be correct. Any differences of property which could be measured could not be due to differences in the state of division when both forms could be obtained in plainly visible crystals. There seemed also an inherent improbability in the view that the change from yellow to red could be effected by light if the change simply consisted in alteration of the size of particle. This argument has also been brought forward by Baly (*Ann. Reports*, 1921). We have, however, thought it advisable to carry out solubility measurements both by gravimetric and electrometric methods with the crystalline oxides, following Glasstone's procedure in every detail, before expressing ourselves as satisfied with the polymorphism theory. These determinations have now definitely shown that the two forms have widely differing solubilities and are perfectly distinct and different. We have drawn the conclusion that the results obtained by Glasstone are possibly due to the fact that none of his methods of preparation gave a pure red oxide, with the result that all his solubility determinations gave values approximating to the solubility of the yellow form which was present.

Methods of Preparation.

The methods used in the preparation of crystalline lead monoxide are based upon experiments made by Lambert in the course of his researches on the corrosion of lead (T., 1915, **107**, 210). We are greatly indebted to him for much information and advice in carrying out the preparations, and also for providing us with a specimen of his purest redistilled lead, which we have used as an electrode in the electrometric measurements to be referred to later. The method consists in the dehydration of Kahlbaum's purest lead hydroxide by digestion with strong potassium hydroxide solution at temperatures approaching the boiling point. The operation is performed in a small flask fitted with an air-condenser, at the upper end of which is a soda-lime tube to prevent the formation of carbonate. The hydroxide goes into solution in considerable quantity when the temperature is raised, and, on slowly cooling, the oxide is deposited

in a well-crystallised form. Which form is obtained depends on the concentration of the alkali, high concentrations giving the red form, moderate concentrations the yellow, and low concentrations apparently a black or steel-grey variety which is similar in form to the yellow oxide and has not yet been subjected to detailed investigation. The rate of cooling is also not without effect on the product, rapid cooling favouring the yellow form. The following table summarises these observations.

TABLE I.
Preparation of lead monoxide.

Normality of KOH.	Colour.	Crystalline form.
15	Red	Square plates. Tetragonal, uniaxial, —ve.
10	Mixtures of red and yellow Yellow	Needle-like, rhombic, bipyramidal, biaxial, +ve.
	Varying shades of green	„
3	Steel-black	„

The red crystals produced by this method show a beautiful iridescence when in contact with their mother-liquor. If the conditions are carefully adjusted, microscopic examination shows no trace of the lemon-yellow needles. When shaken up with water, the solution is quite clear and gives no indication of the existence of ultramicroscopic particles. There can therefore be little doubt that we are here dealing with a pure substance. Both the red and the yellow forms were analysed for peroxide content and showed only a negligible quantity (0.67 per cent. in the yellow and 0.63 per cent. in the red).

With regard to the black form, the appearance of which certainly suggests either lead suboxide or metallic lead, we are not in a position to make any definite statement. It may be a third variety of the oxide, or it may possibly be a yellow form which has in some way suffered superficial reduction. We record, however, an interesting observation we have made as to the action of sunlight on the yellow needle form. Two samples were exposed to light for a period of nine months, the one in a vacuum and the other in a tube exposed to the air. Both were largely transformed into the steel-grey and not into the red form, whilst identity of behaviour showed that atmospheric oxygen could have played no part in the change. A similar blackening has been observed by Renz (*Z. anorg. Chem.*, 1921, **116**, 62), and is attributed by him to the photochemical dissociation of the oxide and the formation of metallic lead.

Mr. T. V. Barker has kindly made a microscopic examination of the red and yellow modifications and reports:—"The colour of the

first is extremely variable, passing from red through brown to light yellow. It crystallises in square plates which exhibit a negative uniaxial figure in convergent light, and the system is therefore presumably tetragonal. The second modification, which is uniformly yellow when freshly prepared, crystallises in elongated, strongly doubly refracting plates with straight extinction. The ray vibrating parallel to the direction of elongation has the greater refractive index, so that even if the system be tetragonal (which is in doubt) the sign of the double refraction is positive. The two forms, then, exhibit distinctly different optical properties and must be held to present a true case of dimorphism."

We have determined the densities of the red and yellow oxides, taking care to remove all traces of occluded air in a vacuum desiccator. The values, 9.27 for the red and 8.70 for the yellow, are quite distinct, although, strange to say, the difference is in the opposite direction to that observed by Geuther and Ruer (*loc. cit.*).

If the yellow crystalline form is ground in a mortar, a brownish-red powder is obtained. The change of colour, attributed by Glasstone to fineness of division, is, in our view, to be explained as a change to the red, stable form, analogous to the change of the unstable yellow form of mercuric iodide to the stable red form under similar treatment.

If the black form of oxide is ground, it first becomes yellow and then reddish-brown. On further violent grinding, streaks of bright red are plainly visible under the pestle, but it seems impossible, probably owing to mechanical difficulties, to reduce the whole mass to this condition. If, however, the finely ground material is shaken in a tube with water and allowed to settle, the deposit shows an interesting gradation of colour from black at the bottom to scarlet at the top. The red form is here, then, undoubtedly the ultimate product of grinding and has the smallest particle. Every investigator so far has shown it to be the least soluble, a fact which does not support any theory connecting the solubility with size of particle.

Solubility Determinations.

Gravimetric Method.—The solubility of the two forms was measured in solutions of sodium hydroxide prepared according to the method of Ming Chow (*J. Amer. Chem. Soc.*, 1920, **42**, 458) and was standardised with hydrochloric acid of constant boiling point. It was found that during the electrolysis of sodium hydroxide solution, in the former preparation, the temperature had to be kept below about 60°, otherwise black "mercurous oxide" was formed. The solutions were placed in contact with pure well-crystallised specimens of the oxide and stirred by a slow current of purified air as recommended

by Glasstone in order to avoid the abnormalities due to fracture of crystals which easily occur with more violent agitation. The results in Table II show that, in the case of the red form, no supersaturation effect is observed and the solubility rises towards a constant maximum. With the yellow form, there is initial supersaturation due to fineness of particle. It is clear, however, from the results that final equilibrium is only obtained by such methods after a very considerable time. Further experiments of much longer duration are shown in Table III. In these experiments there was no continuous stirring, but the containing tubes were inverted each day. The solutions were analysed by precipitation of the lead with sulphuric acid, the solubility of the lead sulphate being reduced by the addition of as much alcohol as could safely be used without throwing out sodium sulphate, which is very sparingly soluble in strongly alcoholic solutions.

It was found that alcohol to the extent of 25 per cent. of the final mother-liquor could be safely employed; the amount of lead unprecipitated being then very slight.

TABLE II.

Solubility of lead monoxide in *N*-sodium hydroxide with stirring by slow air-stream at 20.0°.

Form.	Time (days).	Conc. (Gram-mol./litre).	Form.	Time (days).	Conc. (Gram-mol./litre).
Red	3	0.0104	Yellow	3	0.0344
	5	0.0116		7	0.0289
	8	0.0126			
	11	0.0132		3	0.0359
	2	0.0088		8	0.0263
	2	0.0085			
	4	0.0099			
	6	0.0105			

TABLE III.

Solubility of lead monoxide in *N*-sodium hydroxide, without stirring, at 20.0°.

Form.	Time (days).	Conc. (Gram-mol./litre).	Form.	Time (days).	Conc. (Gram-mol./litre).
Red	4	0.0185	Yellow	5	0.0376
	7	0.0149		7	0.0334
	10	0.0165		9	0.0342
	5 months	0.0138		5 months	0.0240
	"	0.0136		"	0.0233
	"	0.0145		"	0.0239
Mean final value for the yellow oxide in <i>N</i> -NaOH				0.0237	gram-mol./litre.
"	"	"	"	0.0140	"

These experiments show definitely that the yellow form is nearly twice as soluble in *N*-sodium hydroxide as the red form, the actual

ratio (1.7 : 1) agreeing well with the ratio of the solubilities in water (1.8 : 1) determined by Ruer (*loc. cit.*).

Electrometric Method.—These were made by means of a Gambrell potentiometer reading to 0.0001 volt. It was calibrated against resistance boxes correct to 1 in 20,000. A cadmium cell was made in the usual manner and compared with a standard cell made by Gambrell. For the lead electrode the pure metal was melted under hydrogen, and a previously prepared platinum electrode dipped in it while in the molten state. The subsequent procedure was identical with that recommended by Glasstone. The standard alkali electrode described by Donnan and Allmand (T., 1911, 99, 845) was used to complete the cell. Throughout the experiments the electrodes were tested against three freshly prepared calomel electrodes, and any deviation from the value given by the authors was introduced as a correction. We have therefore some record of the working of this standard cell over a considerable period and the results are not without interest. The type of vessel used was exactly as described, with a three-way tap.

The mercuric oxide was prepared by heating Kahlbaum's pure mercuric nitrate. The cells in all *E.M.F.* experiments were placed in a thermostat kept at 20° within 0.05°.

TABLE IV.

E.M.F. of cell Hg/HgCl in KCl solution/HgO in NaOH solution/Hg.

Age (days).	<i>E.M.F.</i> (volt).	Donnan and Allmand's value.	Normality of electro- lytes.	Age (days).	<i>E.M.F.</i> (volt).	Donnan and Allmand's value.	Normality of electro- lytes.
1.2	0.1504	0.1504	1.00	9.5	0.1505	0.1504	1.00
9.1	0.1507			13.8	0.1505		
				47.0	0.1503		
* 0.4	0.1391			* 0.7	0.1397	0.1479	0.10
3.5	0.1393			1.6	0.1398		
17.0	0.1398						
0.6	0.1500			0.1	0.1472		
4.0	0.1501			4.9	0.1474		
6.6	0.1502			8.7	0.1474		

It will be seen from Table IV that the electrode behaved very well and can evidently be kept for very long periods without suffering appreciable change. In the two cells shown by an asterisk, however, the value is very much lower than normal; this was found to be due to the fact that a little undecomposed nitrate was present in the mercuric oxide. It is evident that this source of error must be carefully guarded against in setting up the standard alkali electrode. Table V shows the readings obtained with a cell where the liquid was stirred by an air-current. The process of solution, although

irregular, shows no tendency to exhibit supersaturation, the *E.M.F.* slowly decreasing and the solubility therefore increasing. Bubbling was in all cases stopped some time before making the reading in order to avoid any oxygen electrode effect.

TABLE V.

E.M.F. of cell Hg/HgO in *N*-NaOH/Red PbO in *N*-NaOH/Pb, with stirring.

Age (days).	<i>E.M.F.</i>	Age (days).	<i>E.M.F.</i>
0	0.6920	8	0.6859
1	0.6885	10	0.6868
2	0.6876	13	0.6847
3	0.6873	14	0.6827
4	0.6864	15	0.6828
6	0.6851		

Without stirring, approximately constant minimum values of *E.M.F.* for the red oxide, 0.6758, 0.6755, 0.6768 volt, were obtained at from four to seven days. These correspond with a state of supersaturation, after which the *E.M.F.* steadily increases over a long period to its constant value. As with the gravimetric experiments, the solutions were left for five months at 20° in contact with the solid, after which, on being placed in the cells, they gave definite values for the *E.M.F.* in the course of several days.

TABLE VI.

E.M.F.'s of cells Pb/PbO in *N*-NaOH/HgO in *N*-NaOH/Hg with five months' old solution of PbO in *N*-NaOH, without stirring.

Yellow form.	Red form.
0.6735	0.6807
0.6735	0.6806
0.6734	0.6810
0.6735	0.6806
0.6733	0.6808
	0.6811
Mean 0.6734	Mean 0.6808

The difference between the ultimate solubilities of red and yellow forms is represented by an *E.M.F.* of 0.0074 volt. The difference which would be predicted from the gravimetric solubilities, namely, 0.0140 and 0.0237 gram-mol. per litre, by the expression $RT/nF \cdot \log c/c'$ is 0.0066 volt.

The ratio of solubilities of the yellow and red forms by the electrometric method is thus in good agreement with the gravimetric determinations.

Table VII shows some of the more important constants which can be derived from the measurements made. A column of Glasstone's results for what he regards as the single oxide is added for com-

parison. He worked at 25°, and corrections have been introduced according to the temperature coefficient which he gives. It will be seen that his values for the first three quantities (dependent on each other) fall between those we have obtained for the two forms. They approximate to the values for the more soluble or yellow form, as might be expected were he dealing with a mixture. The evaluation of the dissociation constant for the amphoteric plumbous hydroxide, as an acid, involves a knowledge of the solubility of lead monoxide in water. Ruer, from his conductivity measurements, gives the two values, 0.50×10^{-4} and 0.28×10^{-4} gram-mol. per litre, which have been used in our calculations. Pleissner (*Arb. Kaiser. Gesundh.*, 1907, **26**, 384) gives a whole series of values, by the same method, varying from 0.077×10^{-3} to 0.403×10^{-3} . He does not differentiate at all clearly between the two forms, and it seems fairly certain that he was dealing with mixtures. Glasstone uses one of the values, 0.26×10^{-3} , for his calculation.

TABLE VII.

Various constants at 20°.

	Red form.	Yellow form.	Glasstone's form.
<i>E.M.F.</i> of electrode Pb/PbO in <i>N</i> -NaOH, volts.	0.5668	0.5594	0.562
Pb ⁺⁺ conc. in <i>N</i> -NaOH, gram-ion per litre.	0.90×10^{-15}	1.80×10^{-15}	1.6×10^{-15}
Solubility product [Pb ⁺⁺][OH'] ²	0.47×10^{-15}	0.91×10^{-15}	0.82×10^{-15}
Dissociation constant of Pb(OH) ₂ as an acid.	0.33×10^{-11}	0.39×10^{-11}	1.3×10^{-12}

Summary.

1. The necessary conditions for preparing the yellow and red varieties of lead monoxide in well-crystallised forms have been explored.

2. The solubilities of the two forms in *N*-sodium hydroxide have been measured both gravimetrically and electrometrically. The solubility of the yellow form at 20° is about 1.8 that of the red form.

3. The evidence from solubility and from examination of crystalline form shows clearly that the yellow and red forms are polymorphic modifications.

4. The standard alkali electrode, Hg/HgO in *N*-NaOH, has shown itself to be easily reproduced and constant over long periods.

INORGANIC CHEMISTRY LABORATORY,
OXFORD.

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