CCCXCIII.—*The Polymorphism of Lead Monoxide.*

By Malcolm Percival Applebey and Herbert Marcus Powell.

Lead monoxide occurs naturally in two forms, yellow (orthorhombic) and red (tetragonal). Methods of obtaining these in crystalline form from solutions in various concentrations of potassium hydroxide were described by Applebey and Reid (J., 1922, **121**, 2129). The polymorphism has been demonstrated by the solubility measurements of the same authors (*loc. cit.*) and of Randall and Spencer (*J. Amer. Chem. Soc.*, 1928, **50**, 1572). Crystals of the yellow form were measured by Nordenskiold (*Pogg. Ann.*, 1861, **114**, 619), but no goniometric work has been carried out on the red form. *X*-Radiograms of the two forms made by Kohlschütter and Scherrer (*Helv. Chim. Acta*, 1924, **7**, 337) show that they are distinct. The density determinations of various workers are conflicting (see p. 2823).

Applebey and Reid found that, from solutions of lead hydroxide in 3—4*N*-potassium hydroxide, a black substance of composition PbO was obtained. They also observed that their yellow crystalline lead oxide on exposure to light turned black either in air or in a vacuum. Renz (*Z. anorg. Chem.*, 1921, **116**, 62) records a similar blackening of the yellow oxide when illuminated under dilute hydrochloric acid. He found lead peroxide in the product, and attributed the darkening to the changes $PbO \longrightarrow Pb + \frac{1}{2}O_2$; $\frac{1}{2}O_2 + PbO \longrightarrow PbO_2$, the dark colour produced being due to the lead formed. Applebey and Reid, however, found no peroxide. The question whether their product was another polymorphic form was left open. In preliminary experiments (unpublished) the black form was found to have a higher solubility than the yellow. The present work was carried out with the object of clearing up a number of unsettled points connected with this polymorphism.

Experimental.

Preparation of Specimens.—Kahlbaum's lead hydroxide and Merck's potassium hydroxide were used in carrying out preparations following the method of Applebey and Reid. The yellow form was obtained from solutions in 8—10*N*-hydroxide. Numerous attempts to obtain measurable crystals by slow cooling were unsuccessful. The colour of the substance so obtained was variable, greenish-yellow varieties frequently appearing.

The red form was prepared by using alkali solutions of concentration exceeding 15*N*. Under the microscope, the small square plates obtained were seen to vary in colour from bright orange or

red glittering plates to very deep red, almost purple, crystals with dull surfaces. In this case crystals large enough for goniometric measurement were obtained by slow cooling in a nickel crucible of a solution of 5·5 g. of lead hydroxide in 50 g. of potassium hydroxide and 5 c.c. of water; slow cooling is necessary, but results in the formation of the dull purplish crystals which reflect badly.

The black form was difficult to prepare. Some 40 crystallisations from 3—6*N*-potash solutions were carried out before any black product was obtained. Black solids were produced, however, in a number of experiments carried out to determine solubilities in caustic soda (see p. 2827). Examined under the microscope, these consisted of opaque agglomerates of indefinite shape. On being crushed, they were seen to consist chiefly of yellow oxide with the black substance coating the fragments. Sometimes yellow crystals with black cores were obtained. The amount of black material was very small.

FIG. 1.

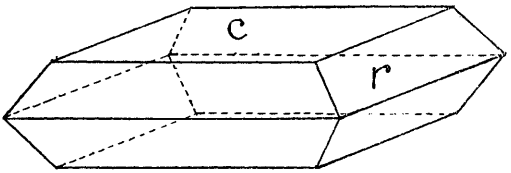


TABLE I.

	Angle.	Limits.	Mean, obs.	Calc.	Diff.
cr	001 : 101	51° 8′—51° 45′	51° 31′	—	—
rr′	101 : 10$\bar{1}$	76 50 —77 25	77 0	76° 58′	0° 2′
rr	101 : 011	65 59 —67 13	66 35	67 12	0 37

Measurement of Crystals of Red Oxide.—Four measurable crystals were obtained, about 1 mm. square and very thin. Reflexions were poor, and those from one or two faces were too faint for measurement. The results are in Table I.

The crystals (see Fig. 1) are of the tetragonal system : forms *c*{001} and *r*{101}. Through *c* a uniaxial interference figure is seen. Axial ratio, $a : c = 1 : 1{\cdot}258$. *X*-Ray workers give values for $a : c$ deduced from the unit cell dimensions from 1 : 1·25 to 1 : 1·297 (van Arkel, *Rec. trav. chim.*, 1925, **44**, 652; Dickinson and Friauf, *J. Amer. Chem. Soc.*, 1924, **46**, 2457).

Our crystallographic axes are chosen in accordance with the recommendations of Barker (" Systematic Crystallography," 1930) : classification angle $cr = 51° 31'$.

Densities.—Densities were determined as follows at 20° by using a 10-c.c. density bottle.

Red (mean) 9·14. Yellow (mean) 9·56.
Black (solid phase from Solubility Expt. S. 8) ..... 9·399.
Black (solid phase from Solubility Expt. S. 5) ..... 9·330.

From the widely differing values recorded in the literature it is clear that the forms of lead oxide used for density determinations by many workers were not homogeneous. Table II gives some of the more significant of the determinations, *viz.*, those of Geuther (*Annalen*, 1883, **219**, 56; specimens prepared by boiling excess of lead hydroxide with caustic soda) (A), Ruer (*Z. anorg. Chem.*, 1906, **50**, 265; specimens crystallised from caustic soda solutions) (B), Applebey and Reid (*loc. cit.*) (C), and the present authors (D).

TABLE II.

	(A).	(B).	(C).	(D).
Red	9·13	9·28	9·27	9·14
Yellow	9·29	9·52	8·70	9·56

It is concluded that the value for the yellow in (C) must be in error, as all other workers are agreed that this form is denser than the red. The error is to be attributed to the incomplete removal of air from the yellow crystals which, owing to their form, occlude very readily. If 9·56 be taken as the density of the yellow form, it follows that the lower densities of the black solids cannot be explained by assuming them to be mixtures of yellow oxide and metallic lead (*d* 11·3). They may, however, be explained by assuming them to be mixtures of yellow oxide and hydrated lead oxide, *e.g.*, so-called $3PbO,H_2O$ ($d^{0°}$ 7·952; Ditte, *Ann. Chim. Phys.*, 1883, **28**, 123). Analysis of black solid from Expt. S. 8 gave Pb, 92·6 (PbO requires Pb, 92·83%). Strong heating followed by rapid cooling (to guard against carbonate formation) gave a loss of 0·18% weight. A mixture of yellow oxide and hydrated oxide in the proportion calculated from the densities requires a water content of 0·12% : the calculation is only approximate, for a small error in any of the densities causes a relatively large error in the amount of water.

On exposure of the black solid to air for a long time, its colour changed to a very light grey. A thin white deposit formed, and treatment with dilute nitric acid showed the presence of carbonate. This may be taken as further evidence of the presence of hydrated lead oxide in the black solid, since this is known to absorb carbon dioxide from the air, whereas the yellow oxide does not. It is concluded that the lower density of the black solid is due to the presence of hydrated oxide, and that the very small amount of black material has no appreciable effect.

Solubility Measurements.—Solubility measurements of lead oxide

in caustic soda solutions of various concentrations were carried out at 84° and at 20°, in electrically regulated thermostats. The alkali solution of the approximate strength required was saturated by heating it with lead hydroxide at a temperature well above 84°, and then decanted into the large tube A (Fig. 2) fitted with a mercury-sealed stirrer to exclude carbon dioxide. Oxide crystallised out, and after stirring for several hours, samples of the solution were extracted by means of the solubility pipette B (for description and method of using, see Farrow, J., 1926, 49). Calibrations of the pipette by weighing with mercury at 20° were carried out at intervals since caustic soda solutions attack the glass. Calibrations at 84° were not so accurate as at 20°, and it was therefore decided to calculate the volumes at 84° by using the coefficient of expansion of the soft glass of which the pipette was made. For sampling, the pipette, filled to a known level in the capillary and with stopper C pushed home, is removed and closed with the cap; it is washed with hot water, and the contents are extracted and titrated with sulphuric acid of appropriate strength, methyl-red being used as indicator. Both alkali and lead hydroxide are titrated. The lead is meanwhile precipitated as sulphate. Alcohol, regulated in amount so that it does not cause the precipitation of sodium sulphate, is added, and the lead sulphate recovered and weighed. A correction for the lead is applied to the titre of sulphuric acid, and the volume normality (N_v) of the sodium hydroxide found. The amount of lead present is expressed in g.-mols. per litre. The solution at 84° is transferred with or, usually, without the solid to a similar apparatus at 20°, and stirred for about 5 days. Samples can then be withdrawn and analysed as above. The results are shown for 84° in Table III, the nature of the solid deposited being indicated by initial letters (see bottom of table). In general, they represent means for two samples, the second extracted after a further hour's stirring after the first was removed. Expts. S. 11 and S. 14 were

FIG. 2.

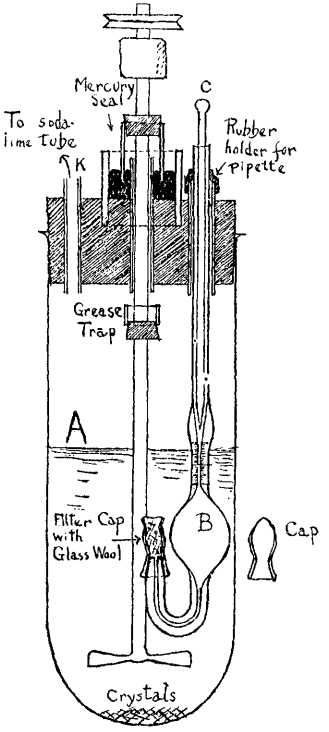


TABLE III.

Concentrations of PbO *in solutions of* NaOH *at* 84°.

Expt.	NaOH, N_v.	PbO, g.-mol. per litre.		Expt.	NaOH, N_v.	PbO, g.-mol. per litre.	
S. 2	2·048	0·1327	Y.N.-c.	S. 7	7·208	0·3835	Y.
S.21	3·103	0·2544		S. 6	8·407	0·3952	
S.10	4·067	0·2650		S.11	9·653	0·4824	
S. 4	4·199	0·2486		S.11*a*	9·818	0·4861	
S. 8	4·886	0·2936		S.14	11·42	0·5761	
S. 9	6·366	0·3629	Y.C.	S.14*a*	11·57	0·5882	
S.24	6·483	0·4492	Y.N.-c.	S.18	15·20	0·5588	
				S.19	16·28	0·5999	Y.+R. → R.
				S.20	20·65	0·8156	

Y. = Yellow. C. = Crystalline. N.-c. = Non-crystalline. R. = Red.
[In the last case, transformation to the pure red oxide was rapid.]

TABLE IV.

Concentrations of PbO *in* NaOH *solutions at* 20°.

Expt.	NaOH, N_v.	PbO, g.-mol. per litre.	Time from start of expt. (days).	
S. 1	2·102	0·1393	4	W.N.-c. PbO, aq.
S. 2	2·109	0·1327	5	
S.21	3·202	0·1715	8	
S. 4	4·334	0·2447	8	
S.10	4·235	0·1896	8	B.
	4·243	0·1826	24	
S. 8	5·046	0·2308	11	B.
S. 5	6·251	0·2454	6	S.-g.
S. 9	6·580	0·1494	9	Y. (trace B).
S.24	6·942	0·1767	6	B. + Y.
S. 7	7·524	0·1684	6	
S. 6	8·734	0·1419	5	G.-y.
S.25	8·725	0·1238	6	Y.
S.11	10·25	0·1315	8	
S.14	12·05	0·1392	5	
S.15	13·00	0·1503	14	Y. + B.
S.16	14·80	0·1614	5	Y.
	14·80	0·1585	14	Y. → R.*
	14·80	0·1576	34	
	14·70	0·1221	73	
	14·70	0·1212	90	R.
S.18	15·83	0·1619	6	R. (little Y).
	15·89	0·1388	68	R.
S.17	16·19	0·1599	5	R. (little Y).
	16·22	0·1459	102	R.
S.19	16·94	0·1609	12	R.
S.22	17·90	0·1803	6	R.

W. = White. B. = Black. S.-g. = Steel-grey. R. = Red.
* The yellow solid was gradually converted into the red as the experiment proceeded.

repeated as nearly as possible in independent determinations (11*a* and 14*a*). Table IV gives the results at 20°, which represent, in general, means for two or more samples extracted. Where no appreciable change occurred of lead oxide concentration with time,

the value in col. 4 is for the last sample extracted. The results are shown graphically on Figs. 3 and 4.

The diagrams for 84° and 20° show two main curves CD and EF for the solubilities of the yellow and the red oxide respectively. The rate of attainment of equilibrium between solid and solution is very much lower at 20° than at 84°, as would be expected. It is

FIG. 3.

Solubilities at 84°.

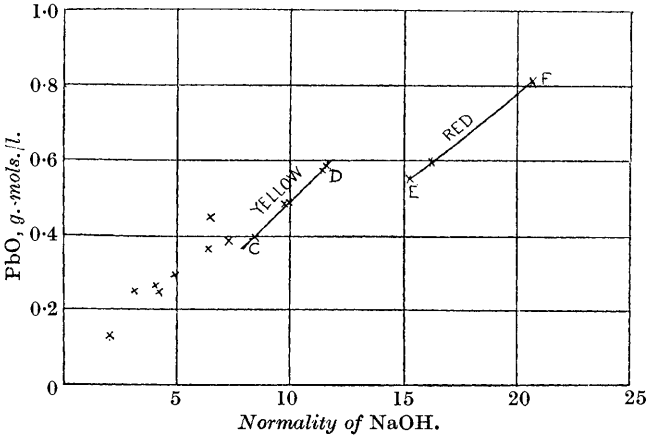
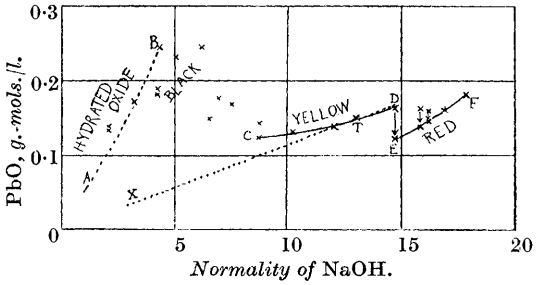


FIG. 4.

Solubilities at 20°.



also lower the smaller the alkali concentration. This is shown, for example, by the facts that only at high alkali concentrations does the more stable red form appear at all in reasonable time, and that for the lowest alkali concentrations very little fall in lead oxide concentration occurs on transference of the solution from 84° to 20°. The curve DX (Fig. 4) shows the probable true course of the solubility for yellow oxide down to the origin (the solubility in water is very small). The experimental values show greater and greater

divergence from this with decreasing alkali concentration. The random points below about 8*N*-alkali are accounted for by failure of the solution and solid to reach equilibrium. For the weakest alkali solutions, especially at 20°, the high lead concentrations are in part due to the fact that the solid phase consists wholly or partly of hydrated lead oxide. No importance is attached to the broken curve AB (Fig. 4) except as showing increased lead concentration when the solid is hydrated oxide. It is clear that the high lead concentrations are not connected with the appearance of a black solid phase, since they are observed at 84° when no black solids appear and at 20° when the solid is yellow. Further, the point T (S. 15; Fig. 4) represents a yellow–black mixture but lies well on the yellow curve. Solubility measurements, it is concluded, provide no evidence of a black modification of lead oxide.

The Black Colour of Certain Specimens of Lead Oxide.—Black oxide specimens, obtained either from potash solutions or by the action of light on the yellow crystals, do not show definite evidence of peroxide content on treatment with dilute nitric acid. When dissolved in air-free lead acetate solutions in evacuated tubes, they do not definitely give a black residue of metallic lead.

Action of Heat.—When heated in air or in a vacuum, a black unstable modification might be expected to change, *e.g.*, to the yellow. Blackness due to metallic lead should be unaffected by heating in a vacuum, but destroyed owing to oxidation by heating in air. Some greenish-yellow specimens were first used. Heated in a vacuum for a short time at about 250°, they were blackened. A similar blackening occurred with the pure yellow crystals, but the degree of blackening varied for different samples with identical treatment. Treatment with lead acetate solution in the absence of air left a black cloud of metallic lead; on admission of air, this was converted into white hydroxide, which then dissolved, leaving a small brownish residue. The black cloud also dissolved in dilute nitric acid, leaving a similar brown residue, which dissolved on being warmed after addition of little oxalic acid. It is concluded that this was lead peroxide. The action of heat on other specimens was as follows:

(*a*) Yellow oxide from heating carbonate: no blackening.

(*b*) The same as (*a*), but washed with sodium hydroxide solution, then with water and dried over sodium hydroxide: in a vacuum turned greenish-black; in air no blackening.

(*c*) Yellow crystalline oxide from potash solution: on gentle heating in air, first blackened and then on further heating became yellow again.

(*d*) Red crystalline oxide from potash solution: in a vacuum,

blackened; in air, first blackened and then on further heating became red again.

It is concluded that the action of heat is a simultaneous oxidation and reduction of sodium plumbite to give metallic lead and plumbate and hence peroxide (compare stannite, which gives tin and stannate). It is dependent on the presence of alkali incompletely washed out from the crystals. In the crystalline specimens, alkali is partly occluded, and the blackening can be observed on gentle heating in air. On further heating oxygen penetrates and oxidises the lead, thereby destroying the black colour. When the alkali is added afterwards to lead oxide originally free from it, the action is not so pronounced, and owing to the alkali being on the surface, the blackening is not produced on heating in air.

Action of Light.—Ordinary litharge is acted upon by light in presence of air to give triplumbic tetroxide (Becquerel, "La Lumière," 1868, Vol. 2, p. 54). The action does not take place in hydrogen or in a vacuum. Applebey and Reid found blackening of yellow crystalline oxide in air or in a vacuum. The following oxide specimens were exposed to sunlight.

(*a*) Yellow crystalline (from potassium hydroxide): blackened in air or in a vacuum (some samples blackened on a single day's exposure, others only after some months).

(*b*) Yellow oxide (by heating the carbonate): unaffected in a vacuum; rapidly turned orange in air.

(*c*) Oxide as in (*b*), washed with caustic soda solution, then with water, and dried over caustic soda: in a vacuum, very uneven blackening; in air, a slight darkening followed by change to orange—if water is present, there is a rapid change to green (due to a trace of lead), followed by production of intense orange colour (Pb_3O_4).

(*d*) Bright red crystals (from caustic potash): in air, after prolonged exposure, showed darkening. The crystals changed to dull purple and the uniaxial interference figure became indistinguishable. The products from blackening by light were not present in sufficient quantity for identification as lead and peroxide, but from the parallelism of the results it is concluded that the effect of light is to bring about the same reaction as occurs on heating, and that this is again due to the presence of alkali in the crystalline specimens. The different behaviour of ordinary alkali-free litharge is thus explained.

General Conclusions on the Colours of Lead Monoxide.—There are two polymorphic forms only, the red and the yellow. Black forms obtained from solution or by action of heat or light on the red or the yellow form owe their colour to the presence of metallic lead, though only by the action of heat is enough lead produced to be detected

satisfactorily. Green forms observed by numerous workers likewise owe their colour to small amounts of lead in the yellow form. The variation in colour of the red form down to purple and the dullness of the crystal faces of these dark varieties are due to the lead present.

Summary.

1. Crystallographic measurements of the red form of lead oxide are given.

2. Densities, solubilities in sodium hydroxide solutions of concentrations up to 20*N* at 84° and at 20°, and microscopic examination of various preparations of lead monoxide fail to show definite evidence for a black modification.

3. The black colour of certain lead oxide specimens is shown to be due to the presence of metallic lead, and its production by the action of heat or light on the red or the yellow form is peculiar to specimens prepared by contact with alkali.

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