

come prominent because the anion and cation of potassium chloride have approximately the same mobility, but it is not sufficient to explain the case of sodium chloride, in which the mobilities of anion and cation are quite different. We believe that the apparent decrease in cation transference numbers in sodium chloride solutions with rise in temperature is due to the inaccurate conductivity data given in "International Critical Tables." Thus if we use the more recent value, $\Lambda_0 = 126.42$, for sodium chloride at 25° , the calculated value of t_+° for aqueous solution of sodium chloride at 25° will be 0.3963 in agreement with the value found from direct transference data and in agreement with the above generalizations in that the limiting transference number at 25° is higher than at 15° . However, since the recent accurate conductivity data have been determined for 25° only, all the values given in Table IV for the four different temperatures are taken from the paper by Brescia, LaMer and Nachod which is based on the values given in "International Critical Tables." The older value

for Λ_0_{NaCl} at 25° is 125.63, which is only 0.79 unit different from the new value. This illustrates the immense importance and need of obtaining accurate conductivity data at different temperatures, in order to obtain limiting ionic mobilities and limiting transference numbers with a high degree of accuracy.

Summary

Tables are given of the limiting mobilities of potassium and chloride ions at 15, 25, 35 and 45° , based on conductance data given by Li and Fang and transference data given by Allgood, LeRoy and Gordon. Approximate values for the limiting ionic mobilities of sodium and acetate as well as the limiting transference numbers in aqueous solutions of sodium chloride and sodium acetate for these temperatures are also given. The transference numbers calculated for sodium chloride solutions illustrate the necessity of obtaining accurate conductivity data not at one temperature, 25° , only, but at different temperatures.

PEIPING, CHINA

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Studies of Lead Oxides.¹ VI. The Effect of Grinding on the X-Ray Diffraction Patterns of Mixtures Containing Lead Oxides

BY GEORGE L. CLARK AND STANLEY F. KERN

Of all the variables which are known to affect the nature of materials used in the lead storage battery, grinding, especially of mixtures, has been studied the least. Leblanc and Eberius² report, "A hard stroke with a spatula, leaving a brown-red trail in the yellow oxide, suffices for the conversion of Y-PbO (yellow, orthorhombic) into R-PbO (red, tetragonal), while the conversion of Pb_3O_4 (black) into Pb_3O_4 (red) proceeds only under the hardest grinding and crushing on the roughest surfaces." Clark and Rowan³ have shown that the R-PbO obtained on grinding Y-PbO is different from the normal R-PbO in that it gives an X-ray diffraction pattern identical with a distorted R-PbO formed by the vacuum decomposition of lead carbonate, basic carbonate or white lead, or lead oxide hydrate, and in that

it exhibits an abnormal chemical activity toward hydrogen peroxide and an increased heat of solution in perchloric acid over that of the normal R-PbO.

It has been observed previously in this Laboratory that intense grinding of normal R-PbO caused a slight broadening of some lines on the X-ray diffraction pattern. This non-uniform broadening is indicative of distortion.

Brown, Cook and Warner⁴ have reported the effect of grinding upon the apparent density of Pb_3O_4 samples obtained by oxidation of three different lead oxides.

Procedure

Seven binary mixtures involving the lead oxides were investigated using six to eight different percentage compositions of each. These mixtures were ground with a rubbing or shearing action and in identical manner in an agate mortar and samples reserved after various times of

(1) For the fifth paper of this series, see Clark and Rowan, *THIS JOURNAL*, **63**, 1305 (1941).

(2) M. Leblanc and E. Eberius, *Z. physik. Chem.*, **A160**, 69 (1932); see also M. Petersen, *THIS JOURNAL*, **63**, 2617 (1941).

(3) Clark and Rowan, *ibid.*, **63**, 1302 (1941).

(4) O. W. Brown, S. V. Cook and J. C. Warner, *J. Phys. Chem.*, **26**, 477 (1922).

grinding for X-ray diffraction studies. In this manner, twenty to thirty patterns were obtained to describe each of the following mixtures

Y-PbO-PbO ₂	PbSO ₄ -PbO ₂
Y-PbO-SiO ₂	R-PbO-PbI ₂
R-PbO-PbO ₂	Y-PbO-PbI ₂
R-PbO-PbSO ₄	

The grinding was carried out manually and in contact with the atmosphere in all cases except for a few samples of the PbO-PbO₂ system. Some of these were ground in an atmosphere of nitrogen and the rest in a vacuum. The same results could be obtained in times three times as long by grinding in the rod mill described by Clark and Rowan.³

Through holes bored in the sides of an air-tight box, rubber gloves were inserted and attached to the box in such a manner that these connections were also air tight. The gloves were used to operate the mortar and pestle inside the box. Nitrogen which previously had been passed through sulfuric acid and ascarite was passed through the box forming the nitrogen atmosphere used in these experiments.

For the vacuum grinding the mortar was placed in a glass jar having a flat brass cover. A rubber gasket was used between the brass cover and the glass jar to give a vacuum-tight contact. In the center of the cover was a hole fitted with a collar through which the pestle was operated. A length of rubber tubing fitting tightly around the collar and the pestle constituted the vacuum-tight connection at this point and allowed ample movement of the pestle to effect the grinding. Two smaller holes were on either side of the large central opening. One was connected to a Cenco-Hyvac pump and the other to a glass tube, one end of which was drawn into a capillary and sealed.

The sample of PbO was heated for several hours at 3 mm. pressure and 450° previous to grinding to ensure complete removal of any carbon dioxide present. A small amount of this PbO was mixed with an equal amount of PbO₂, the mixture placed in the mortar and the system evacuated within a minute after the PbO had been removed from the vacuum furnace. The sample was ground for twenty minutes and transferred to the capillary which was sealed off and used for X-ray diffraction studies.

All materials used were C. P. chemicals or made from C. P. reagents.

The X-ray diffraction patterns were registered in a cylindrical camera using a wedge-shaped sample holder for mounting the samples.⁵ For the samples ground in vacuum the capillaries containing the sample were mounted directly. Radiation from a copper target X-ray tube was used throughout the investigation.

Results and Discussion

The description of some typical patterns will illustrate the phenomena observed when these mixtures were ground.

PbO-PbO₂ Mixtures.—For a mixture of 67% PbO₂ and 33% Y-PbO, after twenty minutes of

grinding, the speckled lines of Y-PbO, easily observed for a mixture before grinding, are completely missing from the pattern, indicating that the Y-PbO has completely disappeared. Nor is there any evidence of R-PbO to which the yellow modification ordinarily is transformed on grinding. Other patterns were obtained from the following mixtures after they had been ground twenty minutes: 50% PbO₂-50% Y-PbO, 33% PbO₂-67% Y-PbO, 10% PbO₂-90% Y-PbO, 5% PbO₂-95% Y-PbO. *In each case both the Y-PbO and R-PbO patterns are completely missing.* On the other hand, corresponding mixtures ground with fine sand (SiO₂) as an abrasive invariably showed broad interferences of R-PbO.

The patterns of corresponding mixtures of PbO₂ and R-PbO up to a mixture of 10% PbO₂ and 90% R-PbO under the same conditions of grinding for twenty minutes disclosed only the pattern of PbO₂ with one extra line which could be attributed to 2PbCO₃·Pb(OH)₂.

In attempting to determine what happened to the PbO on grinding, the following theories were proposed. First, the distorted (activated) PbO, formed on grinding, may have absorbed oxygen from the atmosphere and was oxidized to PbO₂. The high oxidation potential needed for such a reaction made this theory rather doubtful. Active oxygen analysis on the sample before and after grinding showed that there was no increase in active oxygen, as determined by the method of Diehl and Topf and recommended by Mrgudich and Clark.⁶

The second theory claimed that the PbO was incorporated into the PbO₂ lattice, giving either an interstitial solid solution of PbO in PbO₂ or a type of substitutional solid solution where the PbO₂ lattice remains but the ratio of oxygen to lead is less than two. The formation of an interstitial solid solution was immediately discounted as no parameter changes were observed on the PbO₂ pattern and because packing considerations would make this situation impossible.

The existence of an "oxygen-deficient" lattice of PbO₂ is well known. Clark and Rowan¹ have shown that sulfamic acid, although a very good solvent for PbO, is incapable of increasing the ratio of oxygen to lead in an oxygen-deficient lattice. However, after the ground mixture of PbO₂-PbO has been treated with sulfamic acid, an ac-

(5) G. L. Clark, "Applied X-Rays," 3rd ed., McGraw-Hill Book Co., 1940, p. 269.

(6) J. N. Mrgudich and G. L. Clark, *Ind. Eng. Chem., Anal. Ed.*, **9**, 256 (1937).

tive oxygen analysis on the residue showed that the residue was PbO_2 and therefore the PbO must have been removed. A precipitate of lead sulfate was obtained when sulfuric acid was added to the sulfamic acid extraction solution, thereby substantiating the conclusion that the divalent lead was removed from the ground mixture. In the light of these facts, there could be no appreciable incorporation of PbO into the PbO_2 lattice.

The final theory is a combination of two effects. It is known that grinding, in general, decreases the particle size of a crystalline material and in some cases introduces distortion. As mentioned previously, it has been observed in this Laboratory that R- PbO , as well as Y- PbO , when ground produces an X-ray diffraction pattern of distorted R- PbO . It is possible that grinding these mixtures decreases the particle size of the PbO and introduces such a large amount of distortion that Bragg scattering can no longer result. Thus, even a mixture of 90% PbO ground with 10% PbO_2 fails to produce the slightest diffraction evidence of PbO .

It has also been shown that this distorted PbO is highly active. In this highly distorted or activated state, some of the PbO could react rapidly with the carbon dioxide and water of the atmosphere to form a basic carbonate of lead. To substantiate this theory both R- PbO and Y- PbO were ground alone in air under the same conditions used for the mixtures, and the X-ray diffraction patterns obtained from the ground samples compared with the patterns of the basic carbonates. The patterns obtained from ground R- PbO , Y- PbO and the ground mixtures of PbO_2 - PbO which contain a large percentage of R- PbO or Y- PbO always show one or more interferences characteristic of $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and thus indicate that this carbonate is being formed. Chemical analysis showed that the amount of carbon dioxide present in the ground samples was about 80% of that required for the complete conversion, of the PbO present, into $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. These facts indicate that the effect of grinding on these mixtures is the activation of the PbO which then reacts with the carbon dioxide and water of the atmosphere to give $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. However, the intensity of the diffraction interferences from this basic carbonate is far too small to account for 80% conversion of the PbO to the basic carbonate. Hence, we must conclude that either not all of the carbon dioxide in the mixture is in

molecular union with the PbO or that the basic carbonate remains in a state of great dispersion and distortion. Since the diffraction interferences of the basic carbonate are very diffuse, it was more logical to accept the latter conclusion.

From these experiments, it was possible to conclude only that the absence of the PbO lines on patterns obtained from ground mixtures of PbO_2 - PbO was accompanied by a large increase in carbon dioxide content of the sample. Whether the abnormal absorption or incorporation of the carbon dioxide into the mixture was a cause of the disappearance of the PbO pattern, or a result of the high activity introduced into the PbO on grinding, could not be ascertained from these experiments. To attempt to find facts favoring either explanation it was decided to grind the mixtures in an atmosphere as nearly free from carbon dioxide as possible.

The first attempt toward this goal was grinding in an atmosphere of nitrogen. The experimental procedure has been described above. X-Ray diffraction patterns taken of the samples after being ground in the nitrogen atmosphere were similar to those obtained from samples ground in air. Chemical analysis of these samples showed that they had absorbed some carbon dioxide, but to a far less degree than the samples ground in air. Although this experiment was unsuccessful in completely removing carbon dioxide from the atmosphere, it did indicate that the disappearance of the diffracting power of PbO was not primarily dependent on the amount of carbon dioxide absorbed.

Samples ground in vacuum gave X-ray patterns completely devoid of all PbO lines. Chemical analysis of the samples showed that there was less than 0.1% of carbon dioxide present in the ground sample. Hence, we are forced to conclude that the disappearance of the lines characteristic of PbO is not necessarily a function of the carbon dioxide absorbed.

Clark and Rowan¹ have shown that distorted PbO when annealed at a temperature above 300° was converted to the normal PbO . It was believed that if the PbO was present as a distinct phase annealing should restore it to the original form. A sample of PbO_2 - PbO after being ground was annealed at 300° and an X-ray pattern taken of the product. The pattern showed the presence of a *large amount of the PbO* and a small amount of Pb_3O_4 , as well as PbO_2 , indicating that the PbO

was present in the ground sample in a form easily converted to the normal crystalline PbO.

These experiments prove that it is impracticable to place limits on the amount of PbO detectable in PbO₂ by the powder diffraction method, as too much depends upon the previous history of the sample.

R-PbO-PbSO₄ Mixtures.—Grinding experiments on these mixtures, followed by the X-ray method and chemical analysis, indicate that the PbO was converted into a poorly diffracting and, therefore, a highly distorted PbO.

In the unground mixture approximately 10% is the limit of detection of PbO in lead sulfate. This same limit can be said to hold for lead sulfate in PbO.

PbSO₄-PbO₂ Mixtures.—Grinding decreases the particle size of the lead sulfate but in no other way alters the pattern. The limit of detection of one component in the presence of the other is less than 5%.

PbO-PbI₂ Mixtures.—In direct opposition to the findings in the previous experiments it was found that grinding PbO in the presence of lead iodide does not destroy the PbO pattern. However, grinding does have an effect in that the pattern obtained from lead iodide tends to disappear. Chemical analysis of these samples before and after grinding shows no appreciable absorption of carbon dioxide on grinding.

In order to explain the apparent resistance of the PbO to reaction with carbon dioxide when ground with lead iodide, it is necessary to consider the differences between lead iodide and PbO₂. The PbO₂ lattice is made up of oxygen octahedra with a lead ion in the center of each octahedron. These octahedra are held together by shared corners and edges giving rise to strong bonding energies in each of the three directions. On the other hand, lead iodide exhibits a layer lattice composed of two layers of iodide ions to one layer of lead ions. The bonding force between the adjacent layers of iodine ions is weak and, as a result, the lead iodide crystal is easily sheared in this direction.

On grinding these mixtures, PbO₂-PbO and PbI₂-PbO, there is a tendency to set up a stress in the materials of the mixtures. In the PbO₂-PbO mixture there is a competition between the strong bonding forces between the octahedra in the PbO₂ lattice and the forces tending to keep the PbO lattice in the undistorted form as to which

will yield to the applied stress. It is supposed that these forces for the latter are the weaker and, as a consequence, the PbO lattice is distorted by the stress of grinding. In the distorted form the PbO lattice is active and reacts with the carbon dioxide and moisture of the air and is partly converted into the basic carbonate. The PbO₂ seems to have more than a simple abrasive effect since silicon dioxide ground with PbO is not effective in destroying the PbO pattern or in producing a highly active oxide.

In the PbI₂-PbO mixtures the competition is between the forces of PbO and the relatively weak forces between the adjacent layers of iodide ions in the lead iodide lattice. In this case, we find that it is the bonds between these layers of iodine ions that yield to relieve the stresses introduced on grinding and thereby protect the PbO from distortion and the accompanying activation and reaction with carbon dioxide.

Summary

1. Grinding mixtures of PbO₂ with either R-PbO or Y-PbO results in the disappearance of the X-ray diffraction lines characteristic of PbO. This is not the case when PbO is ground with an abrasive like silicon dioxide. A. Active oxygen analysis on the samples before and after grinding showed that there was no increase in oxygen content in the mixture during grinding and, consequently, no oxidation of the PbO to PbO₂. B. The formation of a solid solution of PbO in PbO₂ or compound formation between them is improbable as the PbO is easily extracted from the ground mixture with sulfamic acid, no new lines indicative of compound formation are present on the pattern and, on annealing the ground sample, the PbO is restored to normal R-PbO. C. There is an abnormally high absorption of carbon dioxide by the PbO when ground with PbO₂. The absorption of carbon dioxide is not necessarily the cause of the disappearance of the PbO pattern as the PbO lines do not appear on patterns of samples ground in a vacuum and containing less than 0.1% carbon dioxide. D. The high absorption of carbon dioxide by the mixture when ground in air is further evidence of the increased activity of PbO when formed in the distorted form.

2. Lead oxide loses its diffracting power when ground with other compounds such as lead sulfate, although these are not so effective as PbO₂.

3. Grinding mixtures of lead iodide and PbO

results in the disappearance of the pattern of the lead iodide while the PbO pattern remains. The lead iodide acts as a lubricant and thereby protects the PbO from distortion. This lubricating

action of the lead iodide arises from the weak forces existing between layers of iodide ions in the lead iodide crystals.

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Reproducible Contact Angles on Reproducible Metal Surfaces. III. Contact Angles of Saturated Aqueous Solutions of Different Organic Liquids on Silver and Gold

BY F. E. BARTELL AND PAUL H. CARDWELL

Recent communications from this Laboratory have presented the results obtained in studies of water-air contact angles on silver and gold,¹ and of organic liquid-water interfacial contact angles on these same solids.² For each of these systems explanations were suggested for the "hysteresis" of the contact angles. The system solid-saturated aqueous organic liquid solution-air reported upon in this paper is even more complex than the two types of systems previously discussed, and though angles can be reproduced readily by controlled procedures, the factors which may contribute to the "hysteresis" of these contact angles are more numerous and more complex than those encountered in the other systems.

The liquids used in this investigation were "conductivity" water, isoamyl alcohol, normal butyl acetate, benzene, α -bromonaphthalene and heptane. The organic liquids were of the same high degree of purity as those previously used. The procedure for the formation and measurement of contact angles and the method for preparing reproducible surfaces of silver and gold have been described in a previous paper.¹

Three different groups of solution contact angles were measured. Angles formed by solution drops on initially fresh and clean surfaces of silver and gold comprised the first group, angles formed by solution drops on solids which had stood in air saturated with water and organic liquid vapors comprised the second, and angles formed by air bubbles on solids in saturated aqueous organic liquid solutions comprised the third group. The contact angles reported for both drop and bubble systems are the angles measured through the aqueous solution phase.

When a drop of saturated aqueous organic liquid

solution was placed upon a fresh and clean solid surface, in a cell with air saturated with water vapor alone, the angle measured immediately after formation of the drop was not reproducible. Initial air adsorption upon the metal surface was so rapid that exact duplicates could not be obtained for these initial angles. When the solution drop was left stationary on the solid for a short period of time and was then caused to advance by adding solution to increase the volume of the drop, the value of the contact angle of the advanced drop was not the same as that of the original drop. This change in the contact angle appeared to be much greater than would have been caused by further adsorption of air by the solid during the short period of time that the solution drop was allowed to stand on the solid, since after the initial rapid air adsorption the rate of air adsorption appears to decrease.¹ It was concluded that organic liquid must have evaporated from the solution drop into the air of the closed cell and subsequently have been adsorbed by the solid and that this adsorbed organic liquid caused part of the change.

Reproducible contact angles of solution drops on silver and gold surfaces could be obtained when these metal surfaces were exposed for sufficient periods of time to air saturated with the vapors of the given aqueous organic liquid solution. Values obtained for angles measured in air saturated with the vapors of the given solutions are shown in Table I. The advancing angles of Table I are the angles measured immediately after the drops were formed upon the surfaces which had been allowed to stand in contact with the vapors. The receding angles were obtained by immediately withdrawing the solution-drop once it was formed. On solids exposed to the vapors for a few seconds only, the receding angles were smaller than the

(1) Bartell and Cardwell, *THIS JOURNAL*, **64**, 494 (1942).

(2) Bartell and Cardwell, *ibid.*, **64**, 1530 (1942).