complex substances which possess high viscosity. However, very sensitive criteria of ideality are available by postulating the continuity of those principles and regularities which have been revealed in the lower ranges of the scales.

It has been proved that an ideal mixture function and an ideal temperature function can be recognized as continuous and unique throughout the range of practical viscometry, from about 0.1 to about 5000 centipoises. These scale functions of viscosity are, however, different; the earlier postulate of their identity[1] has been abandoned and replaced by a quantitatively defined relationship. The pressure scale (Π) has been extended tentatively to nearly 10,000 centipoises.

The three viscosity scales (Φ, Θ and Π) are derived from experimental data on individual liquids each of which can cover only a limited range of liquid conditions. These sections of the basic viscosity functions have been joined into continuity. It is possible to define a fictitious *"ideal liquid"* capable of passing through all conceivable variations of the liquid state without limitation, in accord with the fundamental law embodied in the three scales. The latter provide the most extensive empirical evidence to test the validity of mathematical formulations of the viscosity functions.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, LEHIGH UNIVERSITY]

Studies of the Preparation and Allotropic Transformation of Lead Monoxide[*]

BY MAX PETERSEN

When measurements of the magnetic susceptibility of lead oxides were undertaken, it was found that the observed results depended on the manner of preparing the oxide. The chemical literature regarding these oxides is somewhat discordant. Lead monoxide may be prepared dry by the vacuum decomposition of hydrated lead oxide or of lead carbonate; but disagreement still persists as to which crystalline form, yellow or red, reresults from these decompositions.[1,2,3,4] Nor is it settled how the one crystal form is to be converted to the other. This paper reports some evidence on these points; the related magnetic observations will form another report.

The disagreement first mentioned has its origin in the manner of preparing the hydrate or in its consequent form; it has but one known crystal lattice. The author has used hydrates prepared as directed by (a) Pleissner[1] or Eberius,[5] (b) Hüttig,[3] (c) Kohlschütter and Roesti,[2] and (d) Müller.[6] One solution was always added to the other in a very fine vigorous jet driven by nitrogen under pressure, both having been cooled below 5°. Since the difference in the precipitates is involved in the results, it must be described.

(a) Following Eberius the barium hydroxide solution was added to the lead acetate. The former was meticulously drawn clear of suspensions from the flask in which it had been prepared and excess solids had been allowed to settle for a day or more. The hydrate so obtained is coarse, well-developed, cross-formed crystals sometimes attaining great ornateness. (b) Hüttig's preparation "$PbO/H_2O(1)$" was a fine powder which barely showed the cross-form of the crystals. (c) Kohlschütter's preparation appeared as small rudimentary crosses, coarser than (b) but not approaching (a). (d) The Müller hydrate was the finest precipitate obtained. By comparison of its Brownian movement with that of some zinc oxide of known size, the particle size of this hydrate was usually 0.2 to 0.4 μ.

Dehydration was always done in a good Hyvac vacuum, using an all-glass system save at the pump connection. The hydrate, usually about 10 g., was spread on the bottom of a 125-ml. Erlenmeyer flask. This flask was fused to a 12-mm. Pyrex tube about 50 cm. long leading to a 3.5 × 60 cm. phosphorus pentoxide drying tube, connected to the pump by a short rubber tube. An electric furnace lined with heavy copper plate maintained the desired temperature, usually be-

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[*] Original manuscript received September 12, 1940.

(1) M. Pleissner, *Arb. Kais. Gesundh.*, **26**, 304 (1907).

(2) V. Kohlschütter and H. Roesti, *Ber.*, **56**, 280 (1923).

(3) G. Hüttig and B. Steiner, *Z. anorg. allgem. Chem.*, **197**, 257 (1931).

(4) G. L. Clark and W. P. Tyler, THIS JOURNAL, **61**, 58 (1939).

(5) E. Eberius, Thesis, Leipzig, 1931.

(6) E. Müller, *Z. physik. Chem.*, **114**, 129 (1924).

tween 105 and 125°. Dehydration at 120° was nearly complete in eight hours; after forty to fifty hours the flask was cooled, flooded with nitrogen, and cut off.

The evidence of many such dehydrations and variations of them is that a very finely divided hydrate finally yields preponderantly but not purely yellow oxide when dehydrated between 100 and 140° in a vacuum. When coarse Pleissner hydrate is thus treated it yields red oxide with only a trace of yellow. When hydrates (b) and (c), intermediate in fineness, are used they yield mixed oxide, the coarser of them giving the more red. Some of the powder patterns of red oxide displayed evidence of the distorted lattice studied by Clark and Tyler.[4] The dehydration of the ornate Pleissner hydrate crystals does not wreck their gross structure, but yields red oxide replicas of the hydrate crosses. These show strained diffraction patterns and resist packing with considerable mechanical strength. They even retain much of their original form but not the mechanical strength after nearly complete conversion to minium in a heated oxygen atmosphere.

These findings regarding the oxide formed from the several hydrates differ from those of Rencker and Bassière[7] and of others who made decompositions in air; they confirm those of Eberius[5] and in part those of Hüttig and Steiner.[3] The latter made isobaric dehydrations which were sometimes continued to higher temperatures than those the author used. The fact that in such cases their final product was preponderantly red they attribute to secondary transition.

The oxide formed by decomposition of lead carbonate was found to vary with particle size in a manner similar to that resulting from dehydrations. The carbonate, very finely precipitated with thorough precaution against the formation of basic carbonate, and thoroughly dried, was decomposed at about 250° in the vacuum system described. It yielded a mixed product containing considerable yellow oxide, though not so much as that from hydrate at 120°. Preliminary heating at 80° or 125–150° did not alter the facts perceptibly. Coarser carbonates behaved like coarse hydrates in yielding but a trace of yellow oxide when similarly treated. These products, when they contained a substantial fraction of yellow oxide, were particularly unstable. If stored in a room-temperature desiccator this oxide in a few days changed its color toward brick-red, but it still showed X-ray evidence of yellow oxide after several weeks.

The circumstance that yellow oxide is formed at these temperatures has had much study. Before X-ray evidence established the recognition of the two crystal phases,[8,9,10] observations were directed to the elucidation of the difference between the two forms of oxide in terms of the state of aggregation or optical effects in the surface. Kohlschütter and Scherrer concluded from topochemical evidence that the formation of yellow oxide from the dehydration of the hydrate was a secondary process involving solution of oxide in retained water which had left its place in the crystal lattice. Hüttig and Steiner[3] were concerned with the persistence of the yellow phase formed at their lower temperatures rather than with its original formation. Clark and Tyler,[4] following ideas set forth by Bloom and Buerger,[11] attribute the stabilization of the yellow formation to foreign nuclei. Clark and Tyler's evidence was that yellow oxide is formed in their dehydrations but not in the decomposition of carbonate. Finding no evidence of lead acetate, they conclude that the agent must be the water of hydration. To accept this conclusion leads to several difficulties. First, the author finds that carbonate decomposition does yield a not inconsiderable final portion of yellow phase, which can only have been diminished during the decomposition by its instability. Further, the author finds that coarse hydrates dehydrated in the same manner as fine yield much less yellow oxide, in some cases practically none. That much may originally have been formed and subsequently converted almost entirely to red oxide, which was the final product with Pleissner hydrate, is not plausible, for the end-product varied too little with the time and speed of dehydration. These Pleissner hydrates were quite as high in water ratio as any; and their large particle size would increase the likelihood that water leaving its place in the crystal lattice could long be retained within the particle to act as a foreign stabilizing nucleus. A further difficulty for stabilization by water arises from its opposite role in the conversion of yellow oxide to red.

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(7) E. Rencker and M. Bassière, *Compt. Rend.*, **202**, 765 (1936).

(8) V. Kohlschütter and P. Scherrer, *Helv. Chim. Acta*, **60**, 337 (1924).

(9) F. Halla and F. Pawlek, *Z. physik. Chem.*, **128**, 49 (1927).

(10) J. Darbyshire, *J. Chem. Soc.*, 211 (1932).

(11) M. C. Bloom and M. J. Buerger, *Z. Kryst.*, **96**, 365 (1937).

Of the temperature above which yellow lead oxide is truly stable there are three extant statements: 587° by Jäger and Germs,[12] 489° by Cohen and Addink,[13,14] and 530° by Rencker and Bassière.[7] Not to be included with these is Tammann and Kordes'[15] "zusammen-backen" temperature of 470°, which involves no change of phase. After a great variety of experiments had shown how to convert either form of the oxide to the other, the author essayed to redetermine the stability boundary temperature so variously reported.

A tubular furnace was so wound that for some 20 cm. of its central portion a nearly uniform temperature gradient of about 8°/cm. was obtained between 400 and 600°. To a long porcelain boat were fixed four chromel–alumel couples. In it was spread a light layer of Cohen and Addink red oxide which had not before been made yellow. After three to four days of constant heating in dry nitrogen in this furnace the boat was quenched on a block of dry-ice. At the hot end the oxide had all turned yellow; at the cool end it was still red. At that intermediate point where the last yellow particle was located the oven temperature which had prevailed was determined from the couple records and their relative locations. Granting that the boat had been handled and quenched without mechanically disturbing its contents, one must still expect that the last yellow particle found would have been at a higher temperature than the true boundary point, for the really last yellow particles were in contact with the red phase when quenched, and may have turned red during the cooling. This test distinguishes itself from Cohen and Addink's in that they used spatially uniform heating, and also in that they used oxide which had been several times converted from the one phase to the other. The author made seven satisfactory runs, for which the coolest converted oxide was at 494, 490, 493, 493, 491, 492, 490°. The author concludes that Cohen and Addink's value, 489°, is the most credible and is within a degree of the true value.

The disparity of reports as to the conversion of one crystal form to the other has several causes. Conversion of red to yellow is sure at 620 ± 10° in an hour; quenching the specimen in an alcohol–dry-ice mixture seldom permits a return to red, and, if it does, a few conspicuous red colonies occur. If the temperature is held nearer the phase boundary much tolerance of superheating will be found. Red oxide such as that from Pleissner hydrate will endure 520° for sixteen hours apparently unchanged; one specimen of Cohen and Addink red oxide was held between 504 and 508° for nineteen days without evident effect.

The conversion of yellow to red oxide has been repeatedly done by the author by heating the oxide in a vacuum at 420–430° for two to three weeks. The failure of Rencker and Bassière[7] at temperatures a little below 530° is obvious. But it can be repeated even below 489°; casual admixture of red oxide "seeds" is of little effect, and "several hours" are too few. Success may be had with any finely divided yellow oxide as derived from hydrate or with a mixture derived from carbonate unless it has been fully converted to yellow by heating. If it has, it must first be rubbed to assure conversion.

Trituration induces the yellow to red conversion by subsequent heating. Large crystals of calcined yellow oxide may be kept for many months with little conversion, and will fail to turn to red oxide in a reasonable time at 420°. Cohen and Addink yellow oxide behaves likewise, but not if either has been rubbed in a mortar. Whether this is because the rubbing strains yellow crystals or because it produces small intimate intrusions of red phase nuclei it is difficult to decide. Clark and Rowan[16] have reported that red oxide made from yellow by three hours of ball-mill grinding shows lattice faults and increased catalytic action. Such evidence of faults in the yellow phase is unknown.

Disagreement as to the quantity of red phase produced by rubbing in a mortar has its source in differing degrees of caution against traces of water vapor. The author's evidence confirms that of Hüttig and Steiner[3] that the production of red phase is very slight. Rubbing was done in a nitrogen tent with extreme care to exclude water vapor; only oxides previously dried over phosphorus pentoxide in vacuum for days were used. Such rubbed oxide looks redder than X-ray evidence shows it to be. If any access of water vapor

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[12] F. M. Jäger and H. C. Germs, *Z. anorg. allgem. Chem.*, **119**, 145 (1921).

[13] N. W. H. Addink, Thesis, Utrecht, 1933.

[14] E. Cohen and N. W. H. Addink, *Z. physik. Chem.*, **168**, 188 (1934). Unfortunately this value is not accredited to its authors in Fricke and Hüttig's "Hydroxyde und Oxydhydrate," where the temperature 587° is given as due both to Cohen and Addink and to Jäger and Germs.

[15] G. Tammann and E. Kordes, *Z. anorg. allgem. Chem.*, **149**, 63 (1925).

[16] G. L. Clark and R. Rowan, THIS JOURNAL, **63**, 1302 (1941).

is permitted the results are quite different. The increase of water content in such conversions has been measured by Mr. Alex Stewart,[17] who found it to be 0.04 to 0.06%. These facts conform to the known technical procedures for converting commercial yellow to red oxide.

A previously unreported variance between yellow lead oxide crystals appeared during these studies. If one deviated from Müller's method of preparing hydrate by adding cold lead acetate solution to an excess of cold 2 *N* sodium hydroxide and left the flask undisturbed for some hours, thin flakes of yellow oxide grew in clusters on its walls. They may attain several mm. in size but even fairly large ones may be as thin as one micron. These yellow crystals differ in form from another product in hand, and have an anomalous magnetic susceptibility. This prompted a careful study of their other aspects. The latter product was prepared at the National Lead Company's research laboratory; it was twice precipitated out of sodium hydroxide solution and consisted of beautiful glistening crystals. For this material I wish to acknowledge my very great obligation. These crystals, though now several years old, show but little red phase. In this they are unlike those of my preparing, which have very poor stability.

The first obvious distinction between the National Lead crystals and the author's is that while both are diamond-shaped flakes, for the former the acute angle is 68 ± 1°, while for the latter it is 58 ± 1°. The microscopic relief of the National Lead crystals is much greater than that of the author. To an experienced crystallographer they do not seem to be the same material. The latter are bi-axial, optically positive, with axes in the plane of the plate, the higher index in the major axis. They are transparent and have a metallic greenish-gold luster. If heated briefly to 300–400° they lose their transparency, and when cooled have turned bright sulfur-yellow, evidently by numerous internal fractures.

An X-ray comparison of these two products was made, using three powder diffraction films of each product. Each film had a new specimen newly mounted, and was measured with extreme care on three separate days. The difference of one set of three from the other was two and one-half times the internal differences of either set but all were within the internal agreement of results by two authors.[9,14] The lattice dimensions derived by least squares from selected unambiguously indexed lines are tabulated with earlier data for comparison.

TABLE I

Author	*a*, Å.	*b*, Å.	*c*, Å.
Cohen and Addink[14]	5.486	4.730	5.879
Darbyshire[10]	5.459	4.723	5.859
Halla and Pawlek[9]	5.50	4.72	5.88
Author, NL crystals	5.474	4.745	5.887
Author, MP crystals	5.479	4.744	5.883

Summary

When hydrated lead oxide is dehydrated in a vacuum at about 120°, varied fractions of the resulting oxide are obtained in the yellow, orthorhombic form, depending on the original state of the hydrate. The most finely precipitated hydrates yield almost pure yellow, the coarsest nearly pure red, tetragonal oxide.

When carbonates are decomposed in a vacuum at about 250°, a similar dependence of yield of yellow oxide on particle size is found, but the proportion of yellow is less than that from hydrates, save the coarsest.

The temperature of the boundary between red and yellow stability is 489 ± 1°.

Two preparations of yellow oxide of different habit of growth give X-ray powder patterns in which only a barely measurable difference, perhaps not significant, is found. From these data the lattice dimensions are given.

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[17] The author is indebted to him for personal communication of unpublished results of work done in this matter by the National Lead Company research staff.