hydrogen peroxide is oxidized by Ce^{+4} the O–O bond is not severed. Thus a possible reaction mechanism for eq. 1 would be

$$Ce^{+4} + H_2O_2 = Ce^{+3} + H^+ + HO_2 \qquad (2)$$

followed by

$$HO_2 + Ce^{+4} = Ce^{+3} + O_2 + H^+ \qquad (3)$$

or at the electrode

$$e^- + HO_2 + H^+ = H_2O_2 \qquad (4)$$

If HO_2 is produced at the electrode by the reduction of O_2 and diffuses into the solution, it will react with the Ce^{+4} as in eq. 3. In any of the cases, eq. 3 or 4 of the production of HO_2 at the electrode, the same number of equivalents of material is being reduced. Because the O–O bond is not severed, the reaction

$$HO_2 + H_2O_2 = H_2O + O_2 + HO\cdot \qquad (5)$$

cannot take place at an appreciable rate in the body of the solution. However, since the reduction of O_2 takes place at a metal surface, it may be that there is still some mechanism by which H_2O_2 can be reduced to H_2O. Additional experiments would be necessary to determine if the non-additivity in the case of ceric and oxygen is due to reduction of the H_2O_2 to H_2O or by the replacement of the ceric by a faster diffusing O_2.

The reduction in current for mixtures of chromic and oxygen and for chromic and iodine can be explained in the same manner as the ferric–dichromate mixture. The reactions in the diffusion layer are, respectively

$$4H^+ + 4Cr^{+2} + O_2 = 4Cr^{+3} + 2H_2O$$
$$2H^+ + 2Cr^{+2} + H_2O_2 = 2Cr^{+3} + 2H_2O$$
$$2Cr^{+2} + I_3^- = 2Cr^{+3} + 3I^-$$

In these last two cases, although the current reduction is significant, it is somewhat difficult to make a residual current correction because of the rapidly rising hydrogen wave.

The hydrogen ion concentration of 1 *M* is high enough so that there will be very little change in its concentration at the surface of the electrode. Therefore these results cannot be due to precipitation of hydroxides or other compounds such as have been reported previously.[3]

A quantitative treatment of the decrease or increase in current cannot be made on the basis of a simple replacement of the oxidized form of one species by the oxidized form of another species. Thus in the dichromate–ferric case the difference in the observed current from the sum is not the fraction of the replaced ions (which cannot be determined) times the fractional difference in diffusion coefficients. An exact treatment must take into account the combined factors of diffusion and reaction kinetics. The equations describing these combined factors can be formulated readily as a system of four non-linear partial differential equations with appropriate boundary conditions. The difficulty of solving these equations is too great to permit a quantitative treatment at this time.

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[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 105–121.

The Preparation and Properties of Brown Phosphorus

BY FRANCIS OWEN RICE, RITA POTOCKI AND KENNETH GOSSELIN

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Of the various allotropic forms of phosphorus, the common white form has been most thoroughly studied. Both vapor density[1] and cryoscopic measurements,[2] as well as X-ray[3] and electron diffraction studies,[4] all indicate that the molecule is P_4. Vapor density measurements[1] show that P_4 is an extremely stable molecule that dissociates appreciably to P_2 only near 1000° even at 1 mm. pressure. A spectroscopic study[5] of the P_2 molecule indicates that the strength of the bond in P_2 is 115.5 kcal. and that any thermal dissociation at 1000° even at very low pressures, would be negligible.

Although the other common form, red phosphorous, has been studied extensively, its structure has not as yet been settled conclusively. Pauling[6] has suggested that red phosphorus is formed from from white phosphorus by rupture of one bond and formation of long chains of P_4 units, each unit consisting of two equilateral triangles with a common base. This view is consistent with the results of X-ray studies,[3] which indicate that each atom in red phosphorus has three nearest neighbors and is also consistent with the results of kinetic studies[7] on the rate of reaction of white to red phosphorus. If, however, red phosphorus actually consists of long chains of P_4 units, the results of two studies of Melville and Gray[8] are rather unexpected. They concluded that the abnormally high vapor pressure of red phosphorus in a closed system could be understood on the basis that only P_2 molecules evaporate from red phosphorus *in vacuo* and these immediately dimerize to P_4 since the equilibrium, $2P_2 \rightleftarrows P_4$, even at red heat is almost entirely on the P_4 side. Our own work helps confirm this conclusion.

Our preliminary experiments were performed with white phosphorus in an apparatus described in previous work.[9] The phosphorus was kept at a temperature of about 45° where its vapor pressure is about 0.2 mm. According to vapor density measurements, the dissociation of phosphorus vapor at 1000° is

Pressure	P_4 at equilibrium, %
1.0	3.36
0.5	1.73
0.1	0.35
0.04	0.25

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[1] (a) A. Stock, G. Gibson and E. Stamm, *Ber.*, **45**, 3527 (1912); (b) G. Preuner and J. Brockmuller, *Z. physik. Chem.*, **81**, 129 (1912).

[2] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1946, p. 161.

[3] (a) C. D. Thomas and N. S. Gingrich, *J Chem. Phys.*, **6**, 659 (1938); (b) R. Haltgren, N. S. Gingrich and B. E. Warren, *ibid.*, **3**, 351 (1935).

[4] L. R. Maxwell, S. B. Hendricks and V. M. Mosley, *ibid.*, **3**, 699 (1935).

[5] (a) G. Herzberg, L. Herzberg and G. G. Milne, *Can. J. Research*, **18A**, 139 (1940); (b) D. P. Stevenson and Don M. Yost, *J. Chem. Phys.*, **9**, 403 (1941).

[6] L. Pauling and M. Simonetta, *ibid.*, **20**, 32 (1952).

[7] T. W. DeWitt and S. Skolnik, THIS JOURNAL, **68**, 2305 (1946).

[8] H. W. Melville and S. C. Gray, *Proc. Faraday Soc.*, **32**, 271, 1026 (1936).

[9] F. O. Rice and M. J. Freamo, THIS JOURNAL, **73**, 5529 (1951).

We found that when the vapors pass through a furnace and condense on a liquid nitrogen cooled finger, only white phosphorus condenses when the furnace is below 600°. Above this temperature the condensed material is colored and when the furnace temperature is about 1000°, or higher, a dark brown deposit is obtained. The material is insoluble in propane and ethylene at their boiling points and in carbon bisulfide at −103°. A qualitative test with a powerful magnet indicated that the material is not paramagnetic. Brown phosphorus is stable indefinitely at liquid nitrogen temperatures, but on heating, changes irreversibly to a mixture of red and white phosphorus. This change occurs at a measurable rate in the range −100 to −50° but almost instantly at room temperature or higher. We analyzed the mixture by subliming off the volatile white phosphorus onto another cold finger and weighing each separately. Analysis of samples obtained by heating brown phosphorus to −80°, room temperature and 100° all gave the same result (within ±5%), namely, 20% red phosphorus and 80% white phosphorus. The non-volatile red phosphorus remaining on the finger after evaporation of the white phosphorus varied somewhat in color according to the method of preparation, a heavy coating of brown phosphorus heated to room temperature or higher giving an almost black material. We determined that the density of this almost black material was 2.05 to 2.06 by a flotation method using aqueous barium iodide of varying densities. The density at room temperature of white phosphorus is 1.83, of red phosphorus 2.04 to 2.34 (depending on the method of preparation)[10] and of the high pressure black phosphorus, 2.69. Since our black material did not conduct electricity and had a density in the range of red phosphorus, we have assumed that the polymerization of P_2 may yield substances somewhat different in color depending on the molecular weight but are all essentially "red" phosphorus.

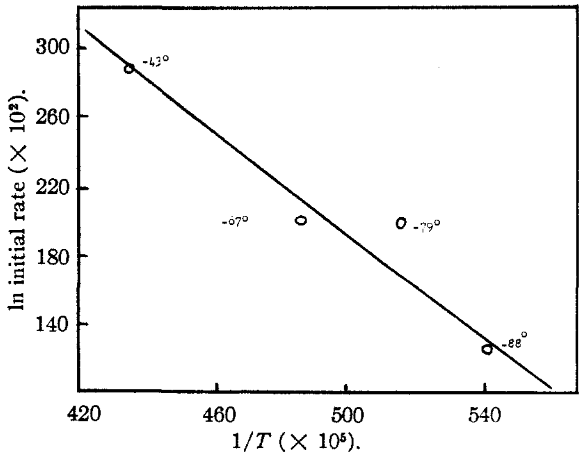

Fig. 1.

Brown phosphorus may also be prepared by heating ordinary red phosphorus in an evacuated jacket at 350–360° or higher and condensing the vapor on a liquid nitrogen cooled finger. The material prepared in this way seems to be identical in all respects with that prepared in the manner described for white phosphorus. We have also found that white phosphorus at −190° exposed to the light from a quartz mercury lamp, gradually changes to the brown form.

We tried a number of different methods for measuring the rate of change of brown phosphorus at various temperatures and finally adopted a method of distilling a thin layer of P_2 onto a liquid nitrogen cooled finger. The P_2 was produced by heating ordinary red phosphorus in a small side arm to 350° for a fixed length of time so that a layer of constant thickness would be obtained. The whole apparatus was then surrounded by a vacuum vessel containing a window and the liquid nitrogen cooled finger was rotated so that the deposit of brown phosphorus was opposite the window. Light from a tiny electric bulb in the cold finger passed through the brown phosphorus and onto a photocell attached to a galvanometer. We measured the rate of change in arbitrary units of galvanometer deflections at four temperatures obtained by filling the vacuum vessel and cold finger with ethane (b.p. −88°), hydrogen bromide (b.p. −67°), chlorotrifluoromethane (b.p. −79°) and propane (b.p. −43°). From the graphs we estimated the initial rate of change in terms of galvanometer deflection per minute and plotted the initial rate against $1/T$. The result is shown in Fig. 1 and gives an activation energy of about 3 kcal. for the change.

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[10] See E. Cohen and J. Olie, *Z. physik. Chem.*, **71**, 1 (1910); P. Jolibois, *Compt. rend.*, **151**, 383 (1910).

A Preparation of Carrier-free Sb^{125} from Neutron Irradiated Stannous Chloride[1]

BY JOSEPH D. ROBINSON AND MILTON KAHN

RECEIVED NOVEMBER 29, 1952

Only one method for the preparation of carrier-free[2] antimony has been reported.[3] This method involves the deuteron bombardment of tin followed by one precipitation and two distillations to effect the separation of the antimony. Since facilities for deuteron bombardment are often not available and the separation procedure reported requires considerable time, a search for a simpler method which would require only thermal neutron irradiation of the target was undertaken.

This communication reports a procedure for the separation of 2.7-year Sb^{125} from solutions of irradiated stannous chloride employing deposition of the antimony from halide acid solution on metallic copper without the use of external electro-

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[1] This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission and submitted in partial fullfilment of the requirements for the degree of Master of Science in the Graduate School of the University of New Mexico, August, 1952, by Joseph D. Robinson.

[2] The term carrier-free as used by the authors denotes that no isotopic carrier has been knowingly mixed with the nuclide under discussion.

[3] R. Maxwell, H. Haymond, W. Garrison and J. Hamilton, *J. Chem. Phys.*, **17**, 1340 (1949).