with hydrogen by electrolysis show no difficulty at 300° (which is above the critical solution temperature) and not too much at 200°. This work seems to close the question and to make it unnecessary to discuss the indirect evidence.

Summary

The isotherms of Gillespie and Galstaun for palladium and hydrogen at 250 and 280° have been confirmed.

A series of isotherms for deuterium and palladium black has been obtained from 200 to 300°, including a critical solution point. A difficulty due to reluctance to formation of the second solid phase was overcome by first forming the beta phase of hydrogen–palladium by pretreatment with hydrogen.

After such pretreatment the isotherms of deuterium are thoroughly reproducible, and after prolonged treatment of palladium with deuterium the hydrogen isotherms are again reproducible.

For a given temperature and pressure, the absorption of deuterium is less than that of hydrogen, but at all the temperatures studied there is not much difference in the maximum absorption of the two gases at the highest practicable pressures after the second solid phase has been formed. Horizontal lines appear in the deuterium isotherms at pressures about 2.3 to 2.5 times the pressures of the corresponding hydrogen horizontals.

The critical solution temperature for deuterium and palladium is found to be 276°, the critical pressure 35 atm., and the critical composition 0.25 atom D per atom Pd.

The heat of solution per mole of deuterium increases regularly with increasing deuterium content and is 7760 cal. per mole for the conversion of the first to the second solid phase.

The phase diagram is given. The locus of the compositions of coexistent solid solutions is smooth and continuous without rising steeply at any simple atomic ratio. This indicates that no palladium deuterides exist in the region above 200°. As the composition of the second solid phase is practically that of Pd_2D at 200° (like the H_2 system), further work at lower temperatures will be required to determine the possible existence of this compound.

The palladium black was prepared by reduction of palladosammine chloride and studied at once.

The Reduction of Metal Oxides in Liquid Ammonia.
I. Preliminary Communication

BY GEORGE W. WATT[1] AND W. CONARD FERNELIUS

Recent studies have shown that bismuth oxyiodide is reduced completely by solutions of sodium and potassium in liquid ammonia.[2] The removal of oxygen from the oxyiodide appears to involve the formation of alkali monoxide and its subsequent ammonolysis to alkali hydroxide and alkali amide. These experiments suggest that some oxides, like almost all halides,[3] may be reduced by liquid ammonia solutions of the alkali metals.

There have been recorded in the chemical literature certain observations which suggest that mercurous oxide,[4] zinc oxide,[5] ferric oxide,[6] and cobaltous-cobaltic oxide[6b] may be reduced under similar conditions. In none of these cases, however, has it been proved that oxygen may be removed *quantitatively* from a heavy metal oxide by means of these reducing agents.

Experimental[7]

Bismuth Trioxide.—One-half gram of bismuth trioxide in the presence of 15 cc. of liquid ammonia[8] was treated with a solution containing 0.25 g. (six equivalents) of potassium in a like volume of ammonia. The characteristic blue color of the potassium solution was discharged immediately and the yellow trioxide was reduced to a gray

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(2) Watt and Fernelius, THIS JOURNAL, 61, 1692–4 (1939).

(3) For primary references see Fernelius and Watt, Chem. Rev., 20, 211–13, 226–32 (1937).

(4) Weyl, Ann. Physik, 121, 601 (1864); 123, 350 (1864); 131, 524 (1867).

(5) Weyl, ibid., 123, 353 (1864).

(6) (a) Bergstrom, THIS JOURNAL, 53, 3037 (1931); (b) Burgess and Kahler, ibid., 60, 191 (1938).

(7) The experimental methods employed were those developed by Franklin and co-workers. All reactions were carried out in Faraday tubes at or near room temperature. For details see: Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corporation, New York, N. Y., 1935, pp. 317–30; Johnson and Fernelius, J. Chem. Educ., 6, 447–50 (1929).

(8) All of the oxides studied appeared to be insoluble in and unreactive toward liquid ammonia. However, there appears to be some evidence to indicate that cuprous and cupric oxides are slightly soluble; see Franklin and Kraus, Am. Chem. J., 20, 827 (1898).

metallic solid. At the same time there appeared a small quantity of a white flocculent precipitate (potassium hydroxide). The insoluble reaction product was washed ten times with liquid ammonia. The solvent was vaporized, the tube was evacuated, weighed, opened for analysis, and the insoluble product (0.5795 g.) was washed with water to remove potassium hydroxide.

Anal. Found: Bi, 0.4385 g.

The above weight of bismuth corresponds to 97.7% of the bismuth (as bismuth trioxide) used in the reaction and to 98.4% of the ammonia-insoluble reaction product after allowance is made for the presence of potassium hydroxide.

The aqueous washings were analyzed for potassium hydroxide and nitrogen.

Anal. Found: KOH, 0.1339 g.; N, trace.

The ammonia-soluble product was analyzed for potassium and nitrogen.

Anal. Found: K, 0.1688 g.; N, 0.0415 g.

The weight of nitrogen found in the soluble product is equivalent to 0.16 g. of potassium amide as compared to the 0.18 g. of potassium amide calculated on the assumption that one-half of the potassium used in the reaction should be converted to the amide. The combined analyses for potassium (results from analysis of both soluble and insoluble products), account for a total of 0.26 g. as compared to the 0.25 g. of potassium used in the reaction.

Cuprous Oxide.—One-half gram of cuprous oxide was treated with 0.27 g. (two equivalents) of potassium. After a few minutes a non-adherent copper mirror formed on the walls of the reaction tube. Within one-half hour the blue color was discharged and the liquid ammonia was colored pale yellow (due to dissolved potassium amide). There was no marked change in the color of the oxide. After washing the insoluble material several times with ammonia, the tube was opened and a sample (0.3820 g.) taken for analysis.

Anal. Calcd. for Cu_2O: Cu, 88.8%. Found: KOH, 0.0873 g.; Cu, 0.2628 g. or 89.2% after allowance is made for potassium hydroxide present in the insoluble product.

Cupric Oxide.—One-half gram of cupric oxide was treated with 0.49 g. (two equivalents) of potassium. The black color of the oxide was replaced immediately by the color characteristic of cuprous oxide and after a few minutes a non-adherent copper mirror formed on the walls of the tube. After washing five times with ammonia, a sample (0.1264 g.) was taken for analysis.

Anal. Calcd. for CuO: Cu, 79.9%; for Cu_2O: Cu, 88.8%. Found: KOH, 0.0415 g.; Cu, 0.0732 g. or 86.2% after allowance is made for potassium hydroxide.

Silver Oxide.—One-half gram of silver oxide was treated with 0.17 g. (two equivalents) of potassium. The black oxide was immediately converted to a gray solid. After removal of ammonia- and water-soluble materials, a sample (0.4518 g.) was taken for analysis.

Anal. Found: Ag, 0.4505 g. or 99.7%.

Germanic Oxide.—One-fourth gram of germanic oxide was treated with 0.37 g. (four equivalents) of potassium. The alkali metal was converted to the amide in ten hours. After allowing the apparently unchanged oxide to stand in the presence of the liquid ammonia solution of potassium amide for several hours, the white solid was washed thoroughly with liquid ammonia and analyzed.

*Anal.* Calcd. for GeO_2: Ge, 69.4. Found: Ge, 68.0.

Other Oxides.—Preliminary studies of the possibility of reduction of the following oxides have also been made: zinc oxide, cadmium oxide, stannous oxide, stannic oxide, lead monoxide, lead dioxide, arsenic trioxide, antimony trioxide. *In every case, reduction has been found to occur.* The reduction products appear to include the elemental metals and (or) soluble or insoluble intermetallic compounds of potassium. These reactions are being investigated further.

Discussion

The results of this investigation show that some metal oxides are reduced by solutions of potassium in liquid ammonia. The primary action involved in such reduction is undoubtedly the removal of oxygen. Subsequently, the resulting alkali monoxide is ammonolyzed to potassium amide and potassium hydroxide.

The formation of potassium hydroxide, which is insoluble in liquid ammonia, prevented the isolation of a single insoluble reduction product. Accordingly it was necessary to correct the analytical data for the heavy metal in the light of results of analyses for potassium hydroxide. This difficulty was obviated in the cases of bismuth trioxide and silver oxide since in these instances the metal formed in the reduction reaction was unreactive toward water and the hydroxide could be removed by washing with water prior to analysis.

When a liquid ammonia solution of an alkali or alkaline earth metal is brought into the presence of a metal oxide, the oxide *may* act as a catalyst[9] for the reaction

$$K \rightleftharpoons K^+ + e^-$$
$$e^- + NH_3 \longrightarrow NH_2^- + 1/2 H_2$$
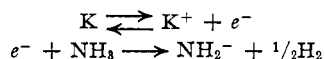
Thus, in the presence of a limited quantity of potassium, an oxide having a marked catalytic activity toward the foregoing reaction might not be reduced to any appreciable extent because of the rapid conversion of potassium to potassium amide; or, more properly, because of the elimination of electrons by virtue of the concomitant formation of molecular hydrogen. The reduction of cupric oxide, for example, appears to be a two-step process. The rate of reduction to cuprous oxide is greater than the rate of interaction between potassium and ammonia. Hence, cupric

(9) For primary references see Fernelius and Watt, *Chem. Rev.*, **20**, 198 (1937).

oxide is reduced to cuprous oxide and it follows that cupric oxide is a relatively poor catalyst for the foregoing reaction. Cuprous oxide, on the other hand, seems to be a very good catalyst and is therefore only slightly reduced when only an equivalent quantity of potassium is used. The ease of reduction of bismuth trioxide and silver oxide precludes the possibility of their exerting any appreciable catalytic effect. Germanic oxide exhibits no marked catalytic effect toward the reaction between potassium and ammonia.

The formation of insoluble or soluble intermetallic compounds of potassium (by the interaction of potassium and the metal liberated from the oxide in the reduction reaction) might have been anticipated, particularly in the case of bismuth.[2] Such reactions were suppressed by the utilization of only that quantity of potassium

required for the removal of oxygen, and by the fact that the velocity of the reduction reaction proved to be much greater than that of intermetallic compound formation.

Summary

1. A study of the action of liquid ammonia solutions of potassium on certain metal oxides has shown that: (a) cupric oxide is largely reduced to cuprous oxide; (b) cuprous oxide is reduced to elemental copper to a slight extent; (c) silver oxide and bismuth trioxide are reduced quantitatively to the corresponding elemental metals; and (d) germanic oxide is not reduced.

2. Germanic oxide is not acted upon by a liquid ammonia solution of potassium amide at room temperature.

The Partial Pressure of Hydrogen Chloride from its Solutions in Ethylene Glycol and Other Solvents at 25°

By S. James O'Brien, Christopher L. Kenny and Robert A. Zuercher[1]

It has been pointed out by Rodebush and Ewart[2] that the measurement of the partial pressure of a volatile acid solute provides a means of estimating the extent of the acid–solvent base reaction. More recently, Zellhoefer and co-workers[3] have shown that measurements of the solubility of halogenated hydrocarbons at various pressures in a number of solvents may be interpreted in terms of a solute–solvent reaction, involving the formation of a hydrogen bond, and in terms of the association of the medium. It would seem, then, that a similar study employing a solute like hydrogen chloride, which is at the end opposite to that of the halogenated hydrocarbons, on the scale of hydrogen activity, should be interesting from this point of view. Data of this kind for hydrogen chloride solutions, however, are quite limited. With the exception of a few measurements of the solubility at pressures of about one atmosphere the only direct measurements of the partial pres-

sure of hydrogen chloride from its solutions recorded in the literature are those from water at 25°,[4] glacial acetic acid at the same temperature,[2] and benzene at 30°.[5] Additional information of this kind is also indirectly available for benzene and nitrobenzene solutions at 25° from distribution studies.[6] It is believed that further studies of this kind would be worth while.

Since the work of Zellhoefer and co-workers[3b,3c] shows the solubility of monofluorodichloromethane to be less in ethylene glycol than in nitrobenzene and in acetic acid, while it is to be expected that the solubility of hydrogen chloride in ethylene glycol is greater than that in either of these two solvents, considering the high solubility of hydrogen chloride in alcohols in general, it was decided to make a study of the partial pressure of hydrogen chloride from its ethylene glycol solutions in order to provide concrete evidence concerning this point. It is the purpose of this paper, then, to report the results obtained in this study, and to discuss the available data in terms of the acid–solvent base reaction.

(1) Taken in part from a thesis submitted by R. A. Zuercher to the graduate school of The Creighton University in partial fulfilment of the requirements for the M.S. degree, June, 1939.

(2) Rodebush and Ewart, This Journal, **54**, 419 (1932).

(3) (a) Zellhoefer, Ind. Eng. Chem., **29**, 584 (1937); (b) Zellhoefer, Copley and Marvel, This Journal, **60**, 1337 (1938); (c) ibid., p. 2666; (d) ibid., p. 2714. See also Copley and Holley, ibid., **61**, 1599 (1939), on similar work with acetylenic compounds.

(4) Randall and Young, ibid., **50**, 1001 (1928).

(5) Saylor, ibid., **59**, 1712 (1937).

(6) Wynne-Jones, J. Chem. Soc., 1064 (1930).