[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Quantitative Oxidation of Gaseous Ammonia to Nitrate

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Gaseous ammonia and oxygen were found to react with Ba_2PbO_4 at 300 to 350° in a vacuum system to quantitatively produce barium nitrate. The nitrate product could be isolated by leaching with water, or alternatively oxides of nitrogen recovered by heating the reacted catalyst absorbent in a stream of oxygen at 750°.

Introduction

In the course of experimentation with N^{15}-enriched ammonia it was found that there is no accepted method in the literature for its quantitative conversion to nitrate. Even the 90% yield commonly attained by the Ostwald process is unattractive when highly expensive 99% N^{15} ammonia is to be converted.

This paper describes methods represented by eq. 1 whereby the oxidative absorption of gaseous ammonia by metal oxide catalyst absorbents was carried out in a vacuum system. The static system employed allows a higher precision and use of smaller amounts of material than is usual with a flow system.

$$Ba_2PbO_4 + 2NH_3 + 4O_2 = BaPbO_3 + Ba(NO_3)_2 + 3H_2O \quad (1)$$

Materials.—Barium orthoplumbate (Ba_2PbO_4) was prepared by mixing thoroughly in a mortar 33.87 g. (0.200 mole) of barium peroxide and 22.32 g. of lead monoxide. The mixture was heated to 550° in a vacuum with evolution of oxygen. The mixture was allowed to cool, removed and ground again in a mortar with subsequent heating under vacuum at 550°. After a third grinding, the mixture was heated in an oxygen atmosphere at 550° and then removed to a desiccator containing potassium hydroxide to protect it from carbon dioxide absorption. Assurance of freedom from higher oxides in the lead monoxide was achieved by heating C.P. material under vacuum at 550°, with subsequent cooling under vacuum. Barium peroxide was freshly prepared by addition of hydrogen peroxide to a filtered solution of barium hydroxide. The precipitate was dried under vacuum at 110° with use of phosphorus pentoxide in the last stages.

Barium plumbate–barium manganate mixture was prepared by grinding in a mortar manganese dioxide and barium orthoplumbate in molar proportion indicated by eq. 2. The mixture was placed in an electrically heated silica combustion tube and heated for two hours at 550° while a slow stream of carbon dioxide free air was passed over the mixture. The reaction is

$$Ba_2PbO_4 + MnO_2 + {}^1/_2O_2 = BaPbO_3 + BaMnO_4 \quad (2)$$

The mixture was removed from the furnace, reground and reheated twice more. Further quantities of barium peroxide were added to this with reheating to 550° before using as described below, so as to produce desired proportions of barium orthoplumbate in the sample.

Ammonia Oxidation by Plumbate–Manganate.—Kassner[1] described a flow system method whereby ammonia-air mixtures could be oxidatively absorbed by a mixture of barium manganate. Preliminary experiments using the static system described below showed that pure $BaPbO_3$–$BaMnO_4$ mixtures would not give good yields of nitrate, but that the mixture must contain barium orthoplumbate in molar amount greater than the moles of ammonia to be oxidized. Kassner's[1] data for low temperature absorption also reflect this behavior.

A sample of 18 g. of $BaPbO_3$–$BaMnO_4$ was ground in a mortar with 2.8 g. of barium peroxide (0.0164 mole) and then calcined at 550° in a stream of carbon dioxide-free air. The ammonia oxidation apparatus consisted of a 30 mm. i.d. tube centered in an electric furnace. Both ends of the tube were accessible by means of ground glass joints one of which terminated in a faraday tube with legs in the plane perpendicular to the axis of the tube. A stopcock allowed removal and injection of gas to the system. The absorbent was placed in a nickel boat in the heated area. A 10% excess of potassium hydroxide was placed in one leg of the Faraday tube and $N^{15}H_4NO_3$ (0.5299 g., 0.00662 mole) was placed in the other leg. Sufficient water was then added to each leg to effect solution. An asbestos thimble containing solid potassium hydroxide was placed in the 30 mm. tube close to the faraday tube. Some potassium hydroxide was placed in the other end of the apparatus to help take up water from the reaction of the ammonia and oxygen with the absorbent. The outlet to the apparatus was connected to a pump, the legs of the faraday tube cooled in Dry Ice, and the system evacuated. After warming, the potassium hydroxide solution was poured slowly onto the ammonium nitrate solution. The water remaining after evolution of the ammonia was distilled over into the potassium hydroxide contained in the asbestos thimble. Oxygen from a commercial cylinder was admitted to the system in amount corresponding to slightly greater than 2 moles of oxygen per mole of ammonia. The temperature was then brought to 300° and maintained until the manometer indicated the completion of the reaction. After five hours, the reaction was 70% complete. Heating was continued another 18 hours at which time the reaction would progress no further. The apparatus was allowed to cool before removing the boat.

Ammonium nitrate ($NH_4N^{15}O_3$) was isolated by transfer of the contents of the nickel boat to a mortar and grinding. The powder was then transferred to a sintered glass filter crucible of medium pore size. Two 35-ml. portions of cold distilled water followed by eight 35-ml. portions of boiling water were used to wash the powder. In each case the mixture was stirred with a glass rod before applying a vacuum to the filter flask. The last three filtrates had a pink color indicating the presence of some permanganate. The filtrate in a 500-cc. Erlenmeyer flask was treated with Dry Ice to form a carbonate precipitate. The solution was boiled for a short time to coagulate the precipitate and to evaporate down the solution to about 250 ml. The solution was allowed to cool slowly to prevent the formation of a finely divided filterable precipitate, and filtered on a buchner funnel. The precipitate was washed several times with cold water. The precipitate had a cream color, so was not pure barium carbonate. The filtrate containing barium nitrate and a small amount of permanganate was treated with a pinch of barium peroxide to ensure conversion of the permanganate to the +2 oxidation state which could form insoluble carbonate. Only an amount of peroxide insufficient to make the solution basic was added since, as discussed by Hillebrand, *et al.*,[2] peroxide must be acidic to convert manganese salts to the +2 oxidation state. The solution was then boiled for 90 minutes to decompose the excess peroxide so as to prevent any possibility of oxidation of subsequently added ammonia. Dry Ice was added to precipitate remaining barium and manganese and the solution was filtered. The filtrate now contained very pure barium nitrate which was analyzed by precipitation of the barium as follows. Dry Ice and excess concentrated aqueous ammonia were added to precipitate barium carbonate. The solution was warmed to 50° in a water-bath to coagulate the precipitate, and then allowed to cool slowly to room temperature. The solution was filtered on a sintered glass crucible. This final precipitate of barium carbonate

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[1] G. Kassner, *Z. angew. Chem.*, **37**, 373 (1924).

[2] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analyses," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 186

weighed 0.645 g. corresponding to a 98.7% yield of nitrate. The filtrate was concentrated to about 15 cc. at which point an additional trace of barium and manganese carbonate precipitate was filtered off with washing. The solution was then evaporated to dryness on a watch glass, and the ammonium nitrate product scraped off and weighed; yield 0.527 g. of $NH_4N^{15}O_3$, 99.7% of theory.

Ammonia Oxidation by Orthoplumbate.—It was found that BaO_2, $BaPbO_3$ and $BaMnO_4$ would not effectively oxidize ammonia under the conditions described above. However, Ba_2PbO_4 when used by itself proved to be just as quantitative and had the same kinetic behavior as its mixture with plumbate and manganate. Although Kassner[1] found the presence of barium manganate to be necessary for high temperature ammonia oxidation in which the mixture acts only as a catalyst with the nitrogen oxides not being absorbed, the present research indicates its presence to be unnecessary for low temperature oxidative absorption.

A sample of barium orthoplumbate (20 g., 0.037 mole) was placed in a nickel boat in the heated portion of the apparatus described above. Boats of potassium hydroxide were at either end of the heater to absorb the water formed by the reaction. A mixture of 0.00932 mole of ammonia gas and slightly greater than double this molar amount of oxygen which had previously been prepared in a large steel tank was admitted to a pressure of 890 mm. at room temperature. The heater was turned on and the course of the reaction followed by observing the pressure change as shown by the manometer. The temperature of the heater was kept at 350°. The observed pressures and elapsed times in hours, respectively, were 1165, $^1/_2$; 925, 1; 665, 2; 387, 4; 275, 5; 135, 7; 2, 17.

The product in this case was removed from the absorbent by passing a slow stream of oxygen over the nickel boat containing the barium orthoplumbate, barium plumbate and barium nitrate while the boat was in a silica tube at 750°. The effluent gas was absorbed in a gas washing bottle containing a standardized solution of sodium hydroxide. An excess of standardized acid was added in the presence of hydrogen peroxide to convert nitrite to nitrate and the solution back titrated. This analysis indicated the formation of 0.00931 mole of nitrate, corresponding to a 99.9% yield which confirms the pressure change results.

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Free Energies and Entropies of Formation of KCl–KBr Solid Solutions at 25°[1,2]

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Free energies of formation of KCl–KBr solid solutions at 25° are evaluated from the known solubilities of the pure salts and the solid solutions in water and the recently measured activity coefficients in the saturated aqueous ternary systems. Results are used to obtain entropies of formation of the KCl–KBr solid solutions for comparison with entropies of formation computed from Wasastjerna's theory of alkali halide solid solutions. Calculated and observed entropies are in poor agreement. From the free energy and entropy data one estimates the critical mixing temperature of KCl and KBr in the solid state to be 190 ± 15°K.

Several years ago Wasastjerna presented[3] an elegant statistical thermodynamic treatment of alkali halide solutions which makes possible the calculation of most of their equilibrium properties from a few readily available properties of the component salts. Wasastjerna's procedure consisted essentially in using the well-known treatment of strictly regular solutions after skillfully instituting the modifications necessary to take into account the important long range coulombic contribution. This theory has been conspicuously successful in accounting for the heats of formation of these solutions from their component salts. For example, for KCl–KBr or NaCl–NaBr the computed and observed heats of formation agree within about 10 cal./mole of ion pairs.[3–6] Since the heat of formation represents the difference between the lattice energy of the solid solution and that of the equivalent mixture, each of which is of the order of 175,000 cal., the successful calculation of this difference is truly a remarkable achievement. The theory achieves, in fact, greater quantitative success than might have been anticipated.

In developing his theory, Wasastjerna has postulated the existence of some local order in the alkali halide solid solutions and has evaluated a local order parameter by straightforward methods of statistical mechanics. Hovi has tabulated[7] values of the order parameter σ for KCl-KBr solid solutions at various compositions for a number of temperatures. He finds, for example, that σ for the equimolal solution at 0° is 0.322, which means that there are 32.2% more ClKBr configurations in the solution than one would find if the distribution of the two anions were random. This, of course, means that the configurational contribution to the entropy of formation will be significantly less than for a random distribution. Since the theory neglects non-configurational entropies entirely, it predicts significant negative departures from random mixing entropies.

As one can compute the entropy of formation of alkali halide solid solutions from theory, it is obviously of interest to measure these quantitites to see if the theory is as effective here as it is in accounting for energies. The first instance in which such a comparison was made was reported in a paper published some months ago from this Laboratory.[8] The system under discussion there was

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[1] From a thesis submitted by W. H. McCoy to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[2] This work was supported by a grant from the Research Corporation.

[3] J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **15**, 1 (1949).

[4] N. Fontell, V. Hovi and A. Mikkola, *Ann. Acad. Sci. Fennicae, Math.-Phys.*, AI, No. 54, 1 (1949).

[5] V. Hovi, *Soc. Sci. Fennicae, Commentationes Phys.-Math.*, **15**, 1 (1950).

[6] V. Hovi, *Arkiv Fysik*, **5**, 61 (1952).

[7] V. Hovi, *Soc. Sci. Fennicae, Commentationes Phys.-Math.*, **15**, 1 (1950).

[8] W. T. Barrett and W. E. Wallace, THIS JOURNAL, **76**, 370 (1954).