Annual Reports in Inorganic and General Syntheses – 1974

Edited by

Kurt Niedenzu

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（内部交流）

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PREFACE

This third volume of the "Annual Reports in Inorganic and General Synthesis" is organized along the lines used for the two preceding volumes. Again we have encouraged the authors to use synthetic aspects as their primary guideline for the arrangement and preservation of the information; however, an occasional deviation to include structural or mechanistic features seemed to be justified in order to reflect the particular features of a given element's chemistry.

The second edition also was received favorably by the scientific community. Again the reviewers stressed the need for an index. Consequently, a brief index without cross-referencing is provided. Since a very large number of new compounds are described, only an attempt to list representative compounds of a given type of species was made. Ms. Anita Wojtowicz assisted in preparing this index. Dr. Phyllis Kaplan and Dr. John Wasson deserve my special appreciation for agreeing on an extremely short notice to prepare the chapters on Pt-metals and Lanthanides, respectively. The chapter on nitrogen did not arrive in time to be included in this volume.

Professor Niedenzu spent 1974-1975 abroad on a sabbatical leave, consequently, I am solely responsible for this, the third issue, of ARIGS.

Hans Zimmer

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SIMPLE AND COMPLEX METAL HYDRIDES OF MAIN GROUPS I, II and III

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SODIUM HYDRIDE

The reaction of magnesium turnings with molten NaOH at 400°C occurs along two different paths (1):

1) $Mg + NaOH \longrightarrow MgO + NaH$

or

2) $Mg + 2NaOH \longrightarrow MgO + Na_2O + H_2$

Under the conditions of this experiment approximately 80% of the magnesium is consumed according to equation 1), the rate of consumption proceeds according to a psuedo zero order. A concentration of up to 0.41 wt.% of NaH in NaOH is observed. The possible effect of the presence of 0.4% Na_2CO_3 in the molten NaOH is not taken into consideration by the author.

A Czechoslovakian group of hydride researchers reports further progress in the direct synthesis of NaH. Ullrych (2) uses a two liter stirred laboratory autoclave containing up to 400 steel balls of 8 mm diameter. The temperature range explored is 230° to 330°, the hydrogen pressure is varied from 5 to 25 Kp/cm^2. The comparison between hydrogen, hydrogen containing 0.5 vol.% CO and hydrogen with the addition of 1.5 to 2.2 m mole of methanol per gram atom of sodium shows a substantial initial increase in the rate of reaction with CO and methanol. Carbon monoxide has superior thermal stability. As expected, the ratio increases with higher temperature and increasing H_2 pressure. Reaction rate studies show that the process is controlled by diffusion through the NaH_S/Na_L interphase, rather than by the activation energy.

The usefulness of CO as a catalyst is demonstrated by the large, specific surface of the NaH obtained (3). The reaction rate and the purity of the NaH decrease with further increasing CO amounts. A 96% conversion of Na to NaH can be obtained in eight hours at about 320°C and H_2 pressures of 120 atmospheres.

The role of CO as a catalyst is described (4) through the constants of the Arrhenius equation. The rate of the reaction is zero