when $(D - D_0) \times a_{H}^{+}/[Cu^{++}]$ was plotted against D and led to values of log K_1 = 7.15, 7.19 and 7.14 for the 1:1 copper adenine-N-oxide complex, which agree with the constant obtained by potentiometric titration.

Any tendency for the neutral molecules to coördinate with metal ions must be very slight because at pH 4 a solution 0.4 μM in adenosine (which can coördinate in only this way) and 0.01 M in copper nitrate has an ultraviolet absorption spectrum close to that obtained by summing the spectra of the individual species. Similarly, Harkins and Freiser[3] found the titration curve of adenosine plus copper to be practically identical with the hydrolysis curve of copper(II), except that in sufficiently alkaline solution there was evidence of weak complex formation with the ribose group of adenosine.

Both series of complexes fit the Irving–Williams stability sequence, Mn < Fe < Co < Ni < Cu > Zn. Values of log K_1 for adenine-N-oxide complexes are less than for the corresponding adenine complexes, differences from reported[3] figures being about 1 log unit for nickel and cobalt and 0.2 unit for copper. This reduced stability is in line with the greater acidity of the N-oxide. In the same way, the greater stabilities by about 2–3 units of the metal complexes of adenosine-N-oxide relative to o-aminophenol[13] reflect the difference of 2.9 in their pK_a values.

Acknowledgments.—Dr. D. I. Magrath is thanked for suggesting this investigation and providing the adenine-N-oxide. The author is also indebted to Dr. G. B. Brown for a generous sample of adenosine-N-oxide and for his interest in this work.

[13] P. Sims, *J. Chem. Soc.*, 3648 (1959).

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

The Barium–Barium Hydride Phase System[1]

BY DAVID T. PETERSON AND M. INDIG

The Ba–BaH_2 phase diagram was established by thermal analysis and chemical analysis of equilibrated phases. The m.p. of barium is raised to a peritectic at 950° and 66 mole % BaH_2. A phase transformation in BaH_2 was found at 550°. The m.p. of BaH_2 obtained by extrapolation of the liquidus curve was 1200°. The solubility of BaH_2 in solid barium at 370° was 9.8 mole %.

Introduction

Barium hydride is a typical saline hydride, and the current interest in metal–salt equilibria and in metal–hydrogen systems made an investigation of the barium–barium hydride system seem worthwhile. Barium was chosen as the first of the alkaline earth group to be investigated because the metal undergoes no allotropic changes.[2] In addition, the Ba–$BaCl_2$ system shows larger solubilities than the other alkaline earth metal–halide systems,[3–5] and it was hoped that the Ba–BaH_2 system would also show easily measured solubilities. The equilibria were investigated by thermal analysis and chemical analysis of equilibrated phases rather than by measuring equilibrium hydrogen pressures because of the narrow temperature ranges over which this measurement can be made. Also, the interpretation of pressure–composition measurements can be difficult in the absence of any knowledge as to what phases are present in the system.

Experimental

Materials.—The Ba metal used for this investigation had been purified by double distillation under 10 mm. argon pressure. After distillation, the metal was handled in a glove box filled with argon to reduce contamination by reaction with the atmosphere. An analysis of a typical batch of this metal is given in Table I. Spectrographic analyses indicated that Al, Cu, Ca, Mg, Si and Sr were below 50 p.p.m. The m.p. was 729° and the thermal arrest was flat as expected for a pure material.

TABLE I

ANALYSIS OF BARIUM METAL

	Nitrogen, p.p.m.	Carbon, p.p.m.	Iron, p.p.m.	Manganese, p.p.m.
Crude barium	430	500–800	53	50
Distilled barium	73	35	23	80

Thermal Analysis.—The thermal analysis capsules were type 304 stainless steel cylinders 6.5 cm. long, 2.2 cm. diameter with 1.5 mm. walls and ends. A 5 mm. diameter with 1.5 mm. walls and ends. A 5 mm. diameter thermocouple well extended 8 mm. into the capsule from the bottom. A weighed charge of barium was placed in the capsule in the glove box. The loaded capsule was placed in a Vycor tube one end of which was closed and the other had a standard taper. A stopper with a stopcock was sealed to the standard taper with Apiezon W. The tube assembly was removed from the glove box and attached to the charging system. The sample tube was evacuated and a known volume of hydrogen introduced and allowed to react with the barium. The tube was heated to 250° to increase the rate of reaction. After the desired hydrogen concentration was reached, the tube assembly was returned to the glove box and the thermal analysis capsule closed by arc welding a cover plate in place.

The loss of hydrogen from the capsule by diffusion through the walls of the capsule during the thermal analysis was reduced by placing the capsule in a close-fitting quartz tube which was evacuated and closed. The amount of hydrogen which escaped was determined by measuring the pressure with a manometer. In all cases, the change in composition was negligible. A differential thermal analysis was used to give greater sensitivity in detecting small heat effects. The sample thermocouple was calibrated at the m.p. of an N.B.S. standard aluminum sample and a sample of

---

[1] (a) Contribution No. 855. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) Based in part on the thesis submitted by M. Indig to Iowa State University in partial fulfillment of the requirements for the master of science degree.

[2] R. G. Hirst, A. J. King and F. A. Kanda, *J. Phys. Chem.*, **60**, 302 (1956).

[3] H. Schäfer and A. Niklas, *Angew. Chem.*, **64**, 610 (1952).

[4] D. D. Cubicciotti and C. D. Thurmond, THIS JOURNAL, **71**, 2149 (1949).

[5] D. T. Peterson and J. A. Hinkebein, *J. Phys. Chem.*, **63**, 1360 (1959).

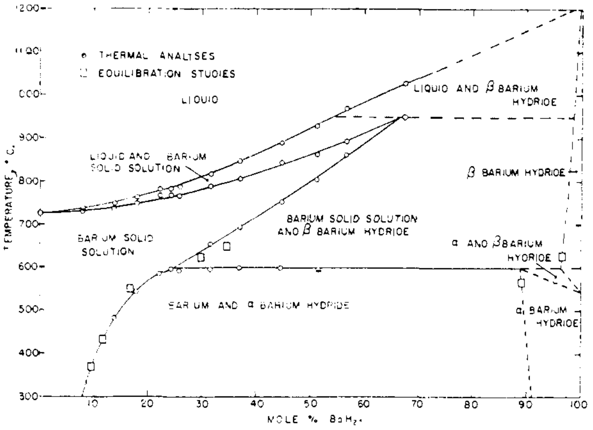

Fig. 1.

electrolytic silver. A rather rapid heating and cooling rate (10° per min.) was used above 800° to minimize the loss of hydrogen by reducing the time at elevated temperatures.

Equilibration and Analysis.—The composition of the coexisting phases in the two solid phase region was determined by equilibration and analysis of the two phases. Barium was cast into a 2 cm. diameter rod, and sections of this rod were reacted with hydrogen until a considerable layer of BaH_2 had formed on the outside. The specimen was then held at a constant temperature until equilibrium was established. Complete equilibration was indicated by the absence of concentration gradients in the core. The BaH_2 layer was chipped off in the glove box and samples taken for analysis. The core of barium saturated with BaH_2 was turned down in a lathe in the glove box until all of the surface BaH_2 had been removed and then cut into sections for analysis. The samples were analysed for hydrogen by reacting them with water and collecting and measuring the hydrogen produced. The accuracy of the method was ± 0.4% for the solid metal samples, but the analysis of BaH_2 was less accurate because the samples consisted of a number of pieces, and the larger surface area resulted in more reaction with the atmosphere. In addition, the BaH_2 samples occasionally contained some powdered material which could not be transferred quantitatively into the analysis apparatus.

Results

The phase diagram for the Ba–BaH_2 system is shown in Fig. 1. The diagram was constructed principally from the results of thermal analyses but the interpretation of the thermal arrests was verified by equilibration experiments and X-ray diffraction examination. The barium phase was studied by X-ray diffraction at room temperature to determine whether allotropic modifications of barium were stabilized by hydrogen as has been reported by Smith[6] for calcium. In all of the specimens, including compositions above and below the solubility limit, the barium phase was body-centered-cubic. All of the lines in the diffraction patterns of the barium hydride phase in equilibrium with barium metal were coincident with lines reported for BaH_2 by Zintl and Harder.[7] Some of the weak lines reported for BaH_2 were not observed but this was probably because the diffraction patterns had a high background.

The thermal arrest at 598° was rather puzzling and, after the absence of a phase transformation in barium had been established, indicated that barium hydride underwent a solid state transition. This was confirmed by X-ray diffraction examination of a sample of BaH_2. A portion of the hydride layer of an equilibration sample was ground in a glove box to −200 mesh and loaded into a quartz capillary. The remainder of the hydride layer was analysed and found to contain 89 mole % BaH_2. The capillary was evacuated and sealed off. X-ray diffraction patterns of this specimen were obtained in a high temperature camera of the type described by Buerger.[8] The diffraction patterns at room temperature, 400 and 500°, were from alpha BaH_2. The pattern at 600° was completely different and was tentatively indexed on the basis of a body-centered-cubic unit cell with a lattice constant of 9.465Å. This diffraction pattern, which was taken with filtered copper radiation had peaks at these values of θ; (11.83, v.s.) (13.65, s.) (18.05, m.) (20.55, m.) (23.80, w.) (24.82, m.) (27.72, v.w.) (29.37, v.w.) (32.22, w.) (33.02, w.) (35.47, v.w.) (36.97, v.w.) (37.52, v.w.) (39.37, v.w.) (40.12, v.w.) (43.92, v.w.) (44.72, v.w.) (46.97, w.) (49.27, v.w.) (51.62, v.w.) (53.17, v.w.) (53.97, v.w.). The diffraction pattern obtained after cooling to room temperature was identical to the original pattern. This showed that the phase change was reversible and not due to contamination or a change in composition.

Discussion

The outstanding characteristic of the Ba–BaH_2 system is the very large solid solubility range in barium metal. This is quite different from the limited solubility, even in the liquid state, of LiH in Li and the very limited solid solubility[9] of $BaCl_2$ in Ba. This extensive solid solubility is similar to that observed in the Zr–ZrH_2[10] and Ti–TiH_2[11] systems in the b.c.c. metal phase. BaH_2 is a typical ionic, saline hydride and the similarity of these systems adds support to the hypothesis that TiH_2 and ZrH_2 are compounds of principally ionic character as postulated by Libowitz and Gibb.[12] The fact that the solubility of BaH_2 is higher in the solid than in the liquid metal at the same temperature indicates that the hydrogen in solution prefers to be closely surrounded by metal atoms, and the more open structure of the liquid is less favorable for extensive solubility.

---

[6] J. F. Smith and B. T. Bernstein, *J. Electrochem. Soc.*, **106**, 448 (1959).

[7] E. Zintl and H. Harder, *Z. Elektrochem.*, **41**, 33 (1935).

[8] M. J. Buerger, N. W. Buerger and F. G. Chesley, *Am. Mineralogist*, **28**, 285 (1943).

[9] C. E. Messer, E. B. Damon, P. C. Maybury, J. Mellor and R. A. Seales, *J. Phys. Chem.*, **62**, 220 (1958).

[10] D. A. Vaughan and J. R. Bridge, *Trans. AIME*, **206**, 528 (1956).

[11] G. A. Lenning, C. M. Craighead and R. I. Jaffee, *ibid.*, **200**, 367 (1954).

[12] G. G. Libowitz and T. R. P. Gibb, Jr., *J. Phys. Chem.*, **60**, 510 (1956).