Theoretically, the compounds described here can be used as indicators. With the knowledge of the value of the equilibrium constant and of the concentration of indicator, the concentration of base can be calculated from measured values of I_0/I. From these data, the ionization constants of colorless compounds may be found. Benzamide, *p*-nitrobenzamide, lauryl mercaptan and glycerol were added to solutions of 2,4-dinitrodiphenylamine of constant ethoxide concentration in an attempt to determine their dissociation constants. Benzamide had no effect on the value of k' and has therefore a pK_a greater than 20. *p*-Nitrobenzamide shows a small effect on the value of k' and the pK_a may be estimated to be about 19. Lauryl mercaptan on the other hand is too strong an acid to be measured by this method, and must have a pK_a less than 15. The pK_a of glycerol was found to be 18.4 in ethanol. The titration curve is shown in Fig. 5.

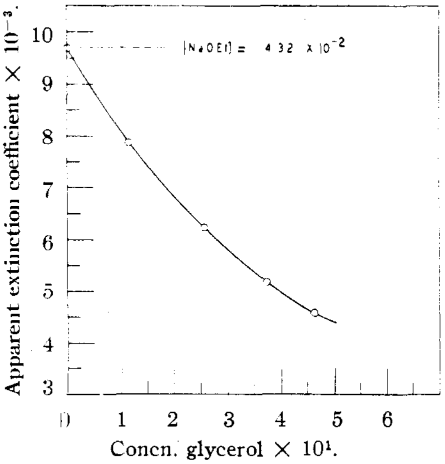

Fig. 5.—Use of 2,4-dinitrodiphenylamine as an indicator at 5000 Å. to determine the dissociation constant of glycerol in ethanol.

Summary

A precise spectrophotometric method is described whereby the ionization constants of weak acids may be determined provided there is a shift in the absorption maximum on ionization. The ionization constants of 4,4',4''-trinitrotriphenylmethane, 2,4-dinitrodiphenylamine, 2,4-dinitroaniline, 4-nitrodiphenylamine and glycerol in alcohol, and of *p*-nitrobenzyl cyanide in water were determined.

CHICAGO, ILLINOIS RECEIVED MARCH 20, 1947

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Observations on the Stability of the Barium–Hydrogen and Zirconium–Hydrogen Systems[1]

BY W. C. SCHUMB,[1a] E. F. SEWELL[1a] AND A. S. EISENSTEIN[1b]

Introduction.—The need for quantitative information about the formation and thermal dissociation of barium hydride arose during the development of the hydrogen thyratron[2] in the Radiation Laboratory, Massachusetts Institute of Technology. A major problem encountered in this development was the maintenance within certain limits of an adequate hydrogen pressure in the tube, and a primary cause of loss of hydrogen pressure was found to be the formation of barium hydride as free barium was liberated from the oxide cathode. As indicated below, the literature contained only fragmentary data on the dissociation pressures of barium hydride at various temperatures and the present investigation was undertaken to supply the desired information. In addition, it was decided to measure the equilibrium gas pressures in the zirconium–hydrogen system, for which some earlier data were available, as this hydride gave promise of use as a hydrogen reservoir, when employed with an auxiliary temperature control circuit.

Observations on the Barium-Hydrogen System.—Aside from the early work of Guntz[3] and of Gautier[4] on the interaction of hydrogen with barium amalgam[3] or with barium–cadmium alloy,[4] and the later observations of Dafert and Miklauz[5] on the preparation of barium hydride from hydrogen and metallic barium (reduced from the oxide by aluminum powder), the only careful study of the dissociation of barium hydride appears to be that of Ephraim and Michel,[6] who employed metallic barium prepared from the oxide by reduction with excess of magnesium.

Guntz[3] had reported the reaction of barium and hydrogen to be far from complete at 1200°, he therefore heated several hundred degrees higher; Gautier[4] found absorption of hydrogen to be noticeable even at 350°; while Dafert and Miklauz[5] observed absorption of hydrogen by finely divided barium in a heated porcelain tube to begin

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[1] This paper is based on work done for the Office of Scientific Research and Development under Contract OEMsr-262 with the Massachusetts Institute of Technology. The paper was presented at the Hydride Symposium of the Chicago meeting of the American Chemical Society, September 10, 1946.

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[2] Tube types 3C45, 4C35, 5C22.

[3] Guntz, *Compt. rend.*, **132**, 963 (1901).

[4] Gautier, *ibid.*, **134**, 1109 (1902).

[5] Dafert and Miklauz, *Monatsh.*, **34**, 1685–1712 (1913).

[6] Ephraim and Michel, *Helv. Chim. Acta*, **4**, 900–924 (1921).

at 120° and to proceed very vigorously at 170–180°, the reaction being complete in a short time with no further absorption at higher temperatures. They also found the reaction product to possess a composition closely conforming to the theoretical for the compound, BaH_2.

Ephraim and Michel[6] gave an approximate curve representing what they believed the dissociation pressures of the pure hydride should be over the range 620 to 740°. They found that the dissociation pressures of alkali and alkaline earth metal hydrides are displaced by the presence of excess metal; that a physical absorption of hydrogen precedes the chemical formation of hydride, as well as running parallel with it; and that whereas the hydride formation of alkali metals is slow, that of the alkaline earth metals is rapid and may be accompanied by incandescence.

The measurements of these latter investigators were carried out under conditions wherein coating of the barium metal with hydride and solution of the metal in the hydride were inevitable. The temperature range covered by these authors is above that employed in the present work and the dissociation pressures (200 to 500 mm.) are far above the maximum reached in our measurements, 0.16 mm.

The barium hydride used in the present work was prepared by two methods. In the earlier experiments, barium metal, obtained as a crust in a nickel boat (by decomposition of barium azide by heating to 325° *in vacuo*) was caused to react with purified hydrogen at a pressure of about 600 mm., the temperature being gradually raised to about 440° before cooling and pumping down the system. This method was later abandoned in favor of the second in which a very thin coating of the metal was provided so that the chance for incomplete reaction and solution in the hydride was minimized. A coil of getter wire[7] was inserted into the reaction tube, where it could be heated electrically to about 700° in an atmosphere of hydrogen at about 2.4 mm. pressure. Barium metal was vaporized from the coil and reacted immediately with the hydrogen to form a thin layer of hydride, with possibly some metal, on the surrounding walls of the glass reaction tube. The pressure on a McLeod gage measured as quickly as possible thereafter had dropped to a very small value, showing that union of the barium with hydrogen had been rapidly accomplished. Heating with the surrounding electric sleeve then made it possible to take pressure–temperature readings on the dissociation of barium hydride, and it became evident that equilibrium was set up very promptly between the film on the glass and the gas phase. Readings were taken up to about 550°. These data are shown in the accompanying graph (Fig. 1). A plot of log *p* *vs.* $1/T_K$ shows a linear relationship above 470°, indicating a true equilibrium state.

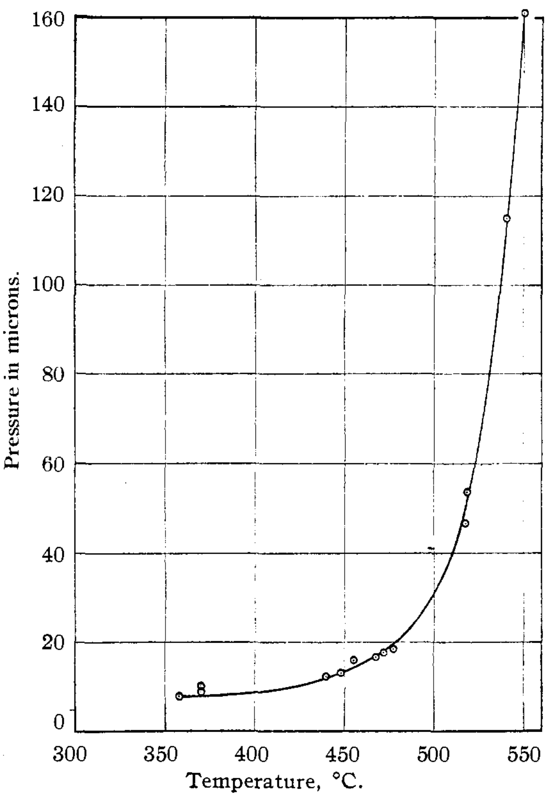

Fig. 1.—Dissociation pressure of barium hydride as a function of temperature; external heating furnace.

In order to secure readings at higher temperatures (the readings above being limited by the softening point of the glass), the procedure just described was modified as follows. The external electric sleeve was dispensed with, and instead a bulb was sealed to the end of the original reaction tube, containing a cylindrical nickel sleeve heated by a spiral molybdenum heater, and, centrally disposed within this sleeve, a barium–nickel spiral coil. A small thermocouple junction was welded to the inside wall of the heating cylinder. In this way the barium–nickel coil when heated electrically could be flashed so as to produce a film of barium and barium hydride on the inner surface of the heated shield, where the thermocouple junction was located, so that a measure of the temperature at this point could be obtained.[8]

With this apparatus it was possible to measure the dissociation pressure of barium hydride at much higher temperatures than in the previous trials, measurements being made up to about 600°. The values observed by this method were, in general, higher than those obtained by the previous method, and it is believed the cause of this difference lies in the fact that a white coating, believed to be the hydride, was formed on the glass walls at one point during the course of the experi-

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[7] So-called "kick" getter, pure barium enclosed in a nickel sleeve.

[8] In this arrangement, provision was not made for a cold-junction outside the reaction tube (compare Fig. 3). The temperature of the junctions of the thermocouple with the sealed-in wires was approximated by means of a mercury thermometer with the bulb brought as close to these points outside the tube as possible.

ment. This deposit was extensive enough to have adsorbed hydrogen in appreciable quantities, so that when the glass walls later became heated sufficiently, the adsorbed gas was released and caused high pressures to develop.

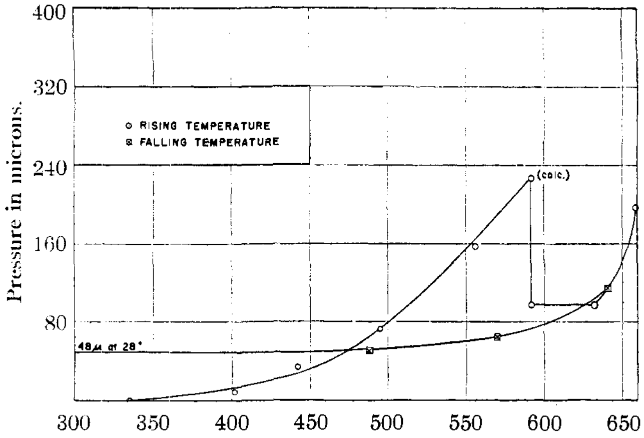

Fig. 2.—Dissociation pressure of barium hydride as a function of temperature; internal heating furnace. Break in curve attributed to evaporation of barium.

Two trials were made with this arrangement of the apparatus. During the first trial, pressure–temperature readings were taken with both rising and falling temperatures over the range of 330–660°, as shown in Fig. 2. When the temperature reached about 590° a sudden drop in pressure from about 225 to 97μ (mercury pressure) occurred, and at the same time a copious white hydride coating was deposited on the glass walls of the reaction bulb. From 600 to 660°, the pressure again climbed to 193μ. As the temperature was allowed to fall, however, the pressure fell off more slowly than it had risen, leaving a residual pressure of 48μ at 28°, showing clearly that some adsorbed gas had been set free during the run.

Repetition of this trial, with more barium "flashed" from the spiral, gave somewhat higher values, both with rising and falling temperatures, a residual pressure on cooling of about 160μ being formed. It seems clear that any measurements made at temperatures of upwards of 550° will be affected by the volatility of metallic barium, which will distill away from the heated zone and combine with hydrogen in the cooler adjacent parts of the apparatus.[9]

Observations on the Zirconium–Hydrogen System.—Various aspects of the zirconium–hydrogen system have been studied by a number of investigators and the literature contains some quantitative data on the dissociation of zirconium hydride at different temperatures, including especially the work of Wedekind,[10] of Sieverts[11] and his associates, of de Bohr and Fast[12] and of Hall, Martin and Rees.[13] Although the propriety of designating the hydride as a chemical compound may be open to question, since it is not a saline type hydride but rather an interstitial solid solution approximating in composition the formula $ZrH_{1.98}$, nevertheless definite equilibrium pressures of hydrogen are indicated when the metal in a thin film is exposed to hydrogen at definite temperatures, and these pressures under proper conditions may be duplicated with rising and falling temperature. Because of the possible usefulness of this substance as a hydrogen reservoir, as mentioned above, it was considered desirable to determine the equilibrium gas pressures developed in the zirconium–hydrogen system by a technique similar to that used in the latter part of the work on barium hydride.

The starting material was a thin layer of zirconium hydride powder, held by means of an organic binder on the inside surface of a heated nickel cylinder in a glass reaction bulb (see Fig. 3). When the tube was evacuated and the nickel cylinder heated to about 800°, the hydride and binder were decomposed so that a thin coating of metallic zirconium remained, the temperature of which, as before, was indicated by means of a thermocouple, the hot junction being welded to the wall of the heating cylinder. The zirconium metal was then converted to hydride by heating in hydrogen; the dissociation pressures were observed, after cooling to room temperature and pumping out the excess hydrogen, by raising the temperature in a uniform manner and reading the pressure at regular time intervals in the reaction system by means of a McLeod gage. The pressures were observed with temperatures rising to 600°, and then with falling temperatures.

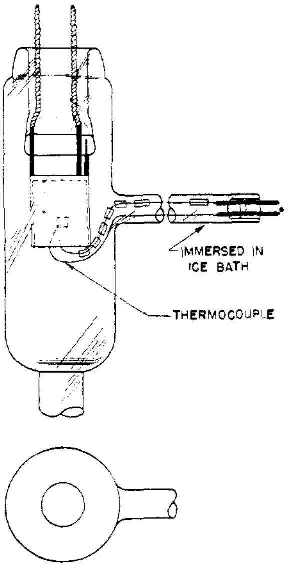

Fig. 3.—Reaction tube for measuring the dissociation pressure of zirconium hydride.

It was found possible, in a given run, to reproduce the observed readings reasonably well with rising and falling

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[9] In this connection, J. A. M. van Leimpt. *Rec. trav. chim.*, **55**, 468 (1936), has furnished data on the vapor pressure of barium which indicate that at 627° the vapor pressure is about one micron, while at 727° it becomes 12.7μ, the corresponding rates of evaporation of the metal being 2.45×10^{-6} and 2.82×10^{-4} g. per sq. cm. per sec. These amounts are significant and may be considered as additional evidence in support of the above statement.

[10] Wedekind, *Ann.*, **371**, 378 (1910); **395**, 149 (1913).

[11] (a) Sieverts and Roell, *Z. anorg. allgem. Chem.*, **153**, 289 (1926); (b) Sieverts and Gotta, *ibid.*, **172**, 1 (1928); (c) Sieverts, Gotta and Halberstadt, *ibid.*, **187**, 155 (1930).

[12] de Boer and Fast, *Rec. trav. chim.*, **55**, 350 (1936).

[13] Hall, Martin and Rees, *Trans. Faraday Soc.*, **41**, 306 (1945).

temperatures, except as regards the following phenomenon. When finely divided zirconium was heated in an atmosphere of hydrogen for the first time, the pressure rose in a regular manner for a while due to the thermal expansion of the gas, but in the neighborhood of 400° a sudden drop in pressure occurred, followed by a renewed climb. Thereafter the *P–T* curve could be reproduced, without the break referred to, with both rising and falling temperatures.

A second run, using the same hydride sample as in the first case but exposed to a fresh atmosphere of excess hydrogen, showed a similar behavior, except that the pressures observed were higher throughout than in the first trial. A break was noted, as before, followed by a fairly reproducible curve with rising and falling temperatures.

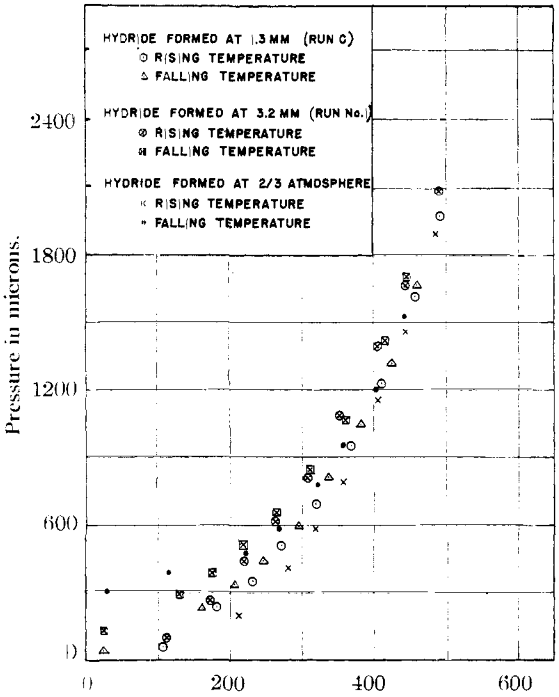

Fig. 4.—Dissociation pressure of zirconium hydride as a function of temperature; note independence of curves on pressure used in formation of the hydride.

In a third run, after exposure again to an atmosphere of excess hydrogen, a still higher set of pressure values was obtained but no break in the curve was noted. Reproducibility of the values with rising and falling temperatures was again fairly satisfactory, indicating that equilibrium had been attained in the system. Furthermore, holding the temperature constant for sixteen hours, or in one case for forty-five hours, did not appreciably alter the observed pressure in the system, a fact which further strengthened the belief that equilibrium values were being obtained. It appeared that each hydride formation produced a slightly different composition of zirconium and hydrogen; but when once formed, each gave a specific and reproducible dissociation curve.

An investigation was next made to find which variables affect the combination of zirconium and hydrogen and must be controlled if the same hydride is to be formed. The variables of temperature, pressure, and time were considered. To find the optimum temperature for combination at a given pressure, the temperature was lowered at regular intervals, from a value too high to permit reaction and the time required to reach an equilibrium state was recorded. Pressures of 3.2 and 1.3 mm. for the formation of the hydride were chosen, as these values were readily obtainable when the hydrogen was being supplied by means of a palladium tube.

In a typical run (no. 1 of Fig. 4) the hydride and the binder were decomposed as before, by heating to about 750° with pumping until a good vacuum was obtained. Hydrogen was then admitted from a flask reservoir to a pressure of 3.2 mm. and the addition was continued at this pressure until no appreciable drop in pressure occurred in five minutes. The temperature was then lowered about 50–75° and held until the pressure again reached equilibrium at 3.2 mm. This method was repeated down to room temperature, whereupon the residual gas was pumped out. The same technique was used when the formation of the hydride was carried out at 1.3 mm. pressure. The pressure was then measured at five-minute intervals following a rise in temperature produced by an increase in the heater current. This time interval had previously been found by experiment to be sufficiently long for equilibrium to be reached.

The pressure–temperature curves (Fig. 4) for zirconium hydride formed at 1.3 and 3.2 mm. pressure are seen to be very similar. Runs A and B, which are not shown, were carried out on the same day upon hydride formed at 1.3 mm., whereas Run C was made the following day, and there is no appreciable difference in the resulting curves. Run D, which also is not shown, was made following a weekend of standing at room temperature but followed the general curves on cooling. Runs no. 1 and 2 (hydride formed at 3.2 mm.) were made on the same day. The resulting curve was identical with that given by the hydride formed at 1.3 mm. The above data indicate that the dissociation curve was independent of formation pressure, but to confirm this, the hydride was next formed at two-thirds of an atmosphere of hydrogen with slow continuous cooling from 750°. The dissociation curve obtained is shown to be of the same general character as the curves of the hydrides formed at the lower pressures, except that slightly higher residual pressure was found on cooling to room temperature. This residual always disappeared on several hours of standing at room temperature.

In a separate experiment, a tube was used to simulate the type of reservoir proposed for gas tubes. The filament consisted of a tungsten coil about 3.5 cm. long, with a coil diameter of 0.8 cm. The coil was coated with a layer of zirconium hydride mixed with an organic binder.

The hydride and binder were decomposed on the coil by heating slowly to 750°, and pumping to obtain a good vacuum. Hydrogen was added until a pressure of 3.2 mm. was obtained holding the temperature constant at 700° until equilibrium was established. Then the temperature was lowered 50° and again held until no more pressure drop occurred. This procedure was repeated to room temperature where a residual pressure of 0.097 mm. resulted, showing that zirconium had taken up practically all of the initial 3.2 mm. of hydrogen on cooling. The volume of the system was in this case approximately 1500 cc.

A dissociation curve was run on this zirconium hydride as shown in Fig. 5, run no. 1, with a residual pressure of 0.773 mm. on cooling. Upon pumping out this residual gas, similar curves could be obtained with rising and falling temperature, as shown by run no. 2.

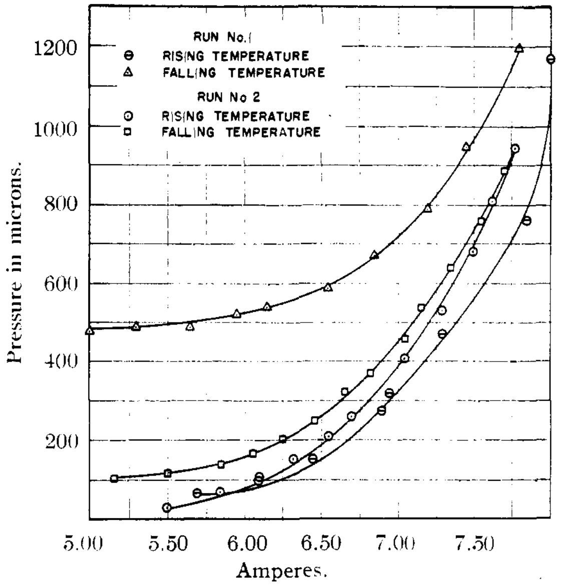

Fig. 5.—Pressure–heater current characteristics of zirconium hydride reservoir for hydrogen thyratron.

Summary

1. In order to provide information concerning the equilibrium conditions of metallic hydrides in hydrogen thyratrons, the equilibrium gas pressures in the barium–hydrogen and zirconium–hydrogen systems have been measured up to 600 and 650°, respectively. Combination of hydrogen with metallic barium occurs readily when the metal is finely divided or in thin layers. The dissociation pressure of barium hydride at 600° appears not to exceed 0.24 mm., which is low in terms of hydrogen thyratron requirements. At this temperature barium metal begins to evaporate rapidly, rendering its use as a hydrogen reservoir impractical.

2. The equilibrium gas pressure in the zirconium–hydrogen system rises from 0.16 mm. at about 150° to 2.1 mm. at 500°. The variation of the pressure with temperature was found to be relatively independent of the pressure at which the hydride was formed initially. The pressures were reproducible with rising and with falling temperature if an excess of hydrogen present was avoided when the hydride was cold.

CAMBRIDGE, MASSACHUSETTS
RECEIVED NOVEMBER 15, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WESTERN AUSTRALIA]

The System Potassium Sulfate–Sodium Sulfate–Magnesium Sulfate–Water at 35°

BY N. S. BAYLISS, A. R. H. COLE,(1) W. E. EWERS(2) AND N. K. JONES(1)

Introduction

Previous work on this quaternary system and its three associated ternary systems has been summarized by D'Ans(3) with the exception of Bozza's later investigation(4) of the system K_2SO_4–$MgSO_4$–H_2O at 35°. D'Ans points out that the data on the quaternary system were all obtained before 1915, and furthermore they are confined almost exclusively to the points (invariant at constant temperature and pressure) that represent equilibrium between the solution and three solid phases. The present work was undertaken because the results of another investigation in this Laboratory showed that the previous data needed revision, particularly with respect to the glaserite field.

As well as redetermining the "invariant" points, we have added measurements of a number of points along the "univariant" lines (equilibrium between the solution and two solid phases) and on the "bivariant" surface representing equilibrium between glaserite and saturated solutions. In order to round off the investigation, we found it convenient to re-examine the three related ternary systems K_2SO_4–Na_2SO_4–H_2O, K_2SO_4–$MgSO_4$–H_2O, and Na_2SO_4–$MgSO_4$–H_2O, including measurements of a number of points on the "univariant" lines not hitherto determined.

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(1) Hackett Research Scholar.

(2) Assistant Research Officer, Council for Scientific and Industrial Research.

(3) J. D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Kali-Forschungs-Anstalt, Berlin, 1933, pp. 108, 130, 151, 165.

(4) G. Bozza, *Giorn. chim. Ind. Applicata*, **16**, 109 (1934).