[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

THE SOLUBILITY OF HYDROGEN SELENIDE[1]

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Object of the Investigation

In the course of an investigation of the free energy of the reaction Ag_2Se (s) $+ H_2$ (g) $\rightleftarrows H_2Se$ (g) $+ 2Ag$ (s), it was found necessary to use data on the solubility of hydrogen selenide in hydrogen iodide solution. While planning these measurements it was found that the data for the solubility of hydrogen selenide in water were meager and open to objection. Hence it was decided to measure, in addition, the solubility of the gas in pure water, since the same apparatus would serve for both solvents.

The Existing Data

Berzelius in 1862 stated that hydrogen selenide appeared more soluble in water than did hydrogen sulfide. De Forcrand and Fonzes-Diacon[2] made several determinations by allowing hydrogen selenide to be absorbed by 0.7 cc. of water at several temperatures and observing from the buret reading the amount of gas absorbed. These results are given in Table I.

TABLE I

EXISTING DATA ON THE SOLUBILITY OF HYDROGEN SELENIDE

Temp., ° C.	4.00	9.65	13.20	22.50
Vol. of H_2Se/vol. of H_2O	3.77	3.43	3.31	2.70

These results appeared doubtful since the volume of water used was only 0.7 cc. and the volume of the hydrogen selenide absorbed ranged between the narrow limits of 2.7 and 3.77 cc. A small, absolute error of observation would mean a relatively large percentage error. No other data were found in the literature.

Experimental Procedure

Pure hydrogen selenide was passed into freshly boiled-out, distilled water and into various concentrations of freshly prepared hydriodic acid until the solutions were saturated at the temperatures desired. Samples of these saturated solutions were withdrawn and analyzed for their hydrogen selenide content.

The hydrogen selenide was prepared by the action of water on aluminum selenide made from purified (sulfur-free) selenium and aluminum powder by ignition in an assay crucible.

The hydrogen iodide was prepared by the reaction between red phosphorus and iodine in the presence of water. The volatilized hydrogen iodide was absorbed in

[1] Constructed from a thesis submitted by Ava Josephine McAmis in partial fulfilment of the requirements for the degree of Master of Arts at the University of Texas.

[2] de Forcrand and Fonzes-Diacon, *Ann. chim. phys.*, [7] **26**, 247 (1902).

conductivity water; dilutions were made from this stock solution and carefully standardized against standard alkali.

The **samples** of the saturated solutions were analyzed for hydrogenselenide content by two methods; a gravimetric (in case of water solutions) and a volumetric method. The gravimetric procedure was based upon the reaction between silver nitrate and hydrogen selenide. The volumetric method may be outlined as follows: the sample of saturated hydrogen selenide solution was added to an excess of standard iodine solution, the selenium allowed to settle, and the excess of iodine titrated with standard thiosulfate solution, using starch as an indicator. These two methods yielded results agreeing with sufficient accuracy for this determination.
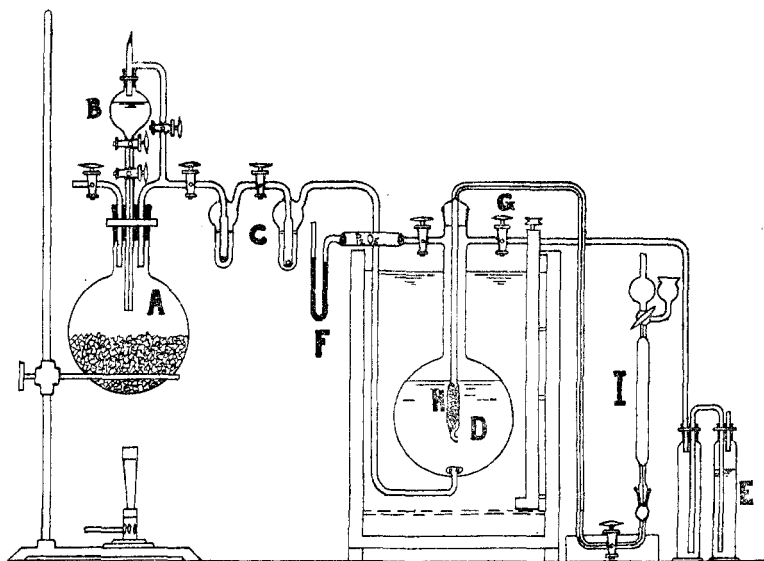

Fig. 1.

The details of the apparatus are shown in Fig. 1. After evacuation, distilled and boiled-out water was allowed to drop from B upon the solid aluminum selenide in A. The gas passed through the scrubbers C, filled with water, into the bottom of the saturating flask D, kept in a thermostat. The exit gas passed into a bottle E filled with a strong solution of sodium hydroxide. The hydrogen selenide was allowed to pass through the distilled water in D at a steady rate for a period of about six hours. This time was found, by trial, to be ample for saturation. Before withdrawing a sample of the saturated solution for analysis, the hydrogen selenide issuing at G was analyzed for purity; its purity varied between 99.5 and 99.9%, as determined by adsorption in potassium hydroxide solution. All stopcocks were then closed and the pressure of the hydrogen selenide above the solution in D was noted on the manometer F; the barometer reading,

also, was noted.   The sample was withdrawn through the filter H (to remove any crystalline selenium formed by oxidation of hydrogen selenide by the small quantities of oxygen present in the water) into the sampling tube I.   The volume of this sampling tube had been found by a mercury calibration to be 15.32 cc.   The sampling tube was withdrawn, the tip wiped off quickly, and inserted into an excess of standard iodine solution or silver nitrate.   The hydrogen selenide solution was then allowed to flow into the Erlenmeyer flask or beaker, respectively; the material adhering to the sides was washed down by means of distilled water from the funnel connected to the 3-way stopcock.   By keeping the tip of the sampling tube underneath the surface of the solutions while allowing the hydrogen selenide solution to flow out, any loss of hydrogen selenide as gas from its saturated solution was effectively prevented.   The hydrogen selenide content was then determined either volumetrically or gravimetrically by one of the methods outlined.   In case of the hydriodic acid solutions only the volumetric method was employed.

The Data Obtained

The data are presented in Tables II and III.   The following complete tabulation will serve to show how the data were treated for final presentation in the tables.

TABLE II

SOLUBILITY OF HYDROGEN SELENIDE IN WATER AT p_{H_2Se}, 760 MM.

Temp., ° C.	Moles per liter	Cc. per liter	No. of detns.	Av. devn., %
14.6	0.09789	2194	5	0.14
15.0	.09611	2154	5	.29
25.0	.08415	1886	6	.21
25.6	.08277	1855	4	.14
35.0	.07317	1640	4	.23

TABLE III

SOLUBILITY OF HYDROGEN SELENIDE IN SOLUTIONS OF HYDROGEN IODIDE AT 25° AND 760 MM.

Concn. of HI (M)	Moles per liter	Cc. per liter	No. of detns.	Av. devn., %
0.20	0.08478	1900	4	0.31
.40	.08634	1935	4	.31
2.73	.11012	2468	4	.82

Sample, 15.32 cc.   G. of H₂Se per 15.32 cc., 0.11710
Temp., 14.6°   Moles of H₂Se per liter, 0.09409
Tot. press., 742.12 mm.   Moles of H₂Se per liter (760 mm.), 0.09799
p_{H_2Se}, 729.77 mm.   Vol. of H₂Se (t = 0° C.) per liter (p_{H_2Se} =
Vol. of iodine (0.1 N), 28.83 cc.   760 mm.), 2196 cc.

Henry's law was used to calculate the solubility in moles per liter at a partial pressure of 760 mm. from the observed solubility and partial pressure.   The molal volume of the hydrogen selenide was taken identical with the ideal gas volume, 22,412 cc. (N. T. P.).

For the solubility in water the volume in cubic centimeters was plotted against temperature; a "best" curve was then drawn through the experimental points and its equation determined. This is given by

$$S = 31,940.93 - 175.37T + 0.25T^2 \qquad (1)$$

where S is solubility expressed in cubic centimeters (N. T. P.) of hydrogen selenide per liter of water when the partial pressure of the hydrogen selenide is 760 mm.

By plotting the logarithm of the solubility, expressed in moles per liter against the absolute temperature, Equation 2 is obtained

$$2.3026 \log S' = 4.8513 - 0.035267\,T + 0.000035818\,T^2 \qquad (2)$$

where S' is moles of hydrogen selenide per liter ($p_{H_2Se} = 760$ mm.).

The Heat of Solution of Hydrogen Selenide

In order to calculate the total heat of solution of hydrogen selenide, use was made of the general relation

$$d\,ln\,S'/dT = \Delta H/RT^2 \qquad (3)$$

where ΔH is heat absorbed when *one* mole of gas is dissolved to form a "dilute" solution. From Equation 2

$$d\,ln\,S'/dT = -0.035267 + 0.000071636\,T \qquad (4)$$

The substitution of this value of (4) in Equation 3 yielded the value 2431 cal. as the heat evolved when one mole of hydrogen selenide is dissolved in water at 25°.

This value does not agree with the value given by Fabre.[3] By allowing (a) hydrogen selenide gas and (b) a hydrogen selenide solution to react with potassium hydroxide and sodium hydroxide solutions, Fabre obtained a mean value of 4630 cal. as the heat evolved upon dissolving 1 mole of hydrogen selenide. This value seems quite high, and it is believed that the value derived from the solubility data is nearer the truth than Fabre's result.

Using the data at 25°, the free-energy decrease attending the reaction

$$H_2Se\ (1\ M) = H_2Se\ (760\ mm.) \qquad (5)$$
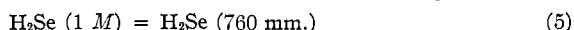
has been calculated from the measured concentrations (mean) of hydrogen selenide in pure water and in the three concentrations of hydriodic acid. The values are given in Table IV.

TABLE IV

Concn. of H₂Se Moles per liter	Solvent	P_{H_2Se}	$-\Delta F$ (for Reaction 5) Cal.
0.08017	water	723.97	1463
.08105	0.2 M HI	726.68	1460
.08231	0.4 M HI	725.46	1451
.10425	2.73 M HI	723.70	1309

[3] Fabre, *Ann. chim. phys.*, [6] **10**, 472 (1887).

Summary

1. The solubility of hydrogen selenide in water has been determined for the temperature range 15° to 35°.

2. The solubility of hydrogen selenide in aqueous hydriodic acid (concn. 0.2, 0.4 and 2.73 M) at 25° has been measured.

3. The molal heat of solution of hydrogen selenide in water has been calculated from the solubility data and found to be 2431 cal. at 25°.

4. The free-energy decrease for the reaction H_2Se (1 M) = H_2Se (760 mm.) has been calculated for several concentrations of hydrogen selenide.

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THE DETERMINATION OF URANIUM[1]

BY G. E. F. LUNDELL[2] AND H. B. KNOWLES[3]

Chief among the methods for the determination of uranium are the gravimetric method in which the element is precipitated as diammonium uranate, $(NH_4)_2U_2O_7$, and weighed as uranous uranate, U_3O_8, and the volumetric method in which uranium is reduced by zinc and then titrated with permanganate. The accuracy of the gravimetric method has often been questioned on the score that it is quite difficult to attain the theoretical composition $UO_2 . 2UO_3$, and various corrective measures such as ignition in oxygen or reduction to uranium dioxide in hydrogen have been proposed. The volumetric method is also usually described as uncertain because the reduction of uranium seldom goes to the same point, and attempts to bring its valence to a definite stage before titration have usually been unsuccessful.

It seems worth while, therefore, to record our experience as to the performance of these methods, especially as both are excellent when simple precautions are observed. In our hands the volumetric method has proved to be as accurate as any that are based on reduction in the Jones reductor, provided the reduction is made in a cool solution and the reduced solution is given sufficient exposure to the air before titration. The gravimetric method also is most excellent when macerated paper is used, and there is no need whatever for special ignition in oxygen or hydrogen.

Experimental Part

The analyses were made with a sulfuric acid solution of uranyl sulfate prepared from a sample of uranous uranate U_3O_8, that had been obtained