Solubility of Hydrogen Selenide Gas in Water

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The solubility of hydrogen selenide in water between 25° and 75° C under a partial pressure of 1 atm is reported. The enthalpy of solution and the Henry's constant are calculated.

The value of the enthalpy of solution for hydrogen selenide in water is used in calculating the thermodynamic properties of selenium compounds. It is important to know such a value precisely. Since the only two values reported in the literature (1, 3) are discordant, the measurements were repeated using more efficient equipment. The solubility of hydrogen selenide gas was measured between 25° and 75° C. The partial pressure of the gas was kept constant at 1 atm.

EXPERIMENTAL

The saturated hydrogen selenide solution is obtained by bubbling hydrogen selenide gas (from Matheson of Canada Ltd. of purity more than 98%) through previously deoxygenated demineralized water. The temperature is kept constant at the desired value at ±0.1° C. Once equilibrium is attained, the hydrogen selenide concentration is determined gravimetrically using $AgNO_3$ as precipitating agent.

A schematic drawing of the instrument is shown in Figure 1. It is composed of three major parts: the gas circuit, the reaction chamber, and the sampling system.

Gas Circuit. The nitrogen, used to expel the oxygen from the system, is admitted through three wash bottles containing an alkaline solution of pyrogallol and four wash bottles containing water. Both nitrogen and hydrogen selenide are admitted into the reaction chamber through stopcocks S_3, S_4, and S_5.

Reaction Chamber. The reaction chamber consists of a flask, F, which is immersed in a controlled temperature bath, B. The pressure inside the flask is measured with an accuracy of ±0.3 mm of Hg and controlled with a precision of ±0.16 mm of Hg by means of a manometric device M, which is connected to the flask through stopcock S_1. A stopcock, S_2, allows the gas to escape into the atmosphere. A magnetic stirrer, A, is used to stir the solution.

Sampling System. By means of a small gas overpressure in the flask, the solution is pushed into the buret, B, the end of which dips in a solution of silver nitrate. The excess of solution is pushed back by hydrogen selenide.

The purified nitrogen is bubbled into the system for a period of 48 hr to expel all traces of atmospheric oxygen. The temperature of the system is adjusted to the lowest value at which measurements are desired. The hydrogen selenide is then bubbled through the solvent for 1 hr. Then all stopcocks are closed and the system is left standing for 15 days. Such a long period is necessary to obtain a solution saturated with hydrogen selenide. Periodically, pressure checks are made to ensure that the pressure (corrected for water vapor pressure) remains constant. After the 15-day period, a 10-ml sample of the solution is obtained and analyzed gravimetrically following the standard procedure. The temperature of the system is then increased by 1° C, and 4 hr are then allowed to obtain a new
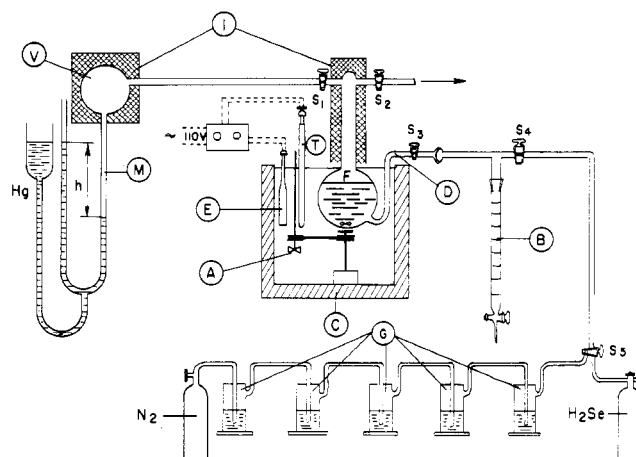
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Figure 1. Experimental system

A. Stirrer. B. Sampling buret. C. Controlled temperature bath. D. Gas circuit. E. Heater. F. Reaction chamber. G. Wash-bottles system. I. Thermal insulation. M. Manometric system. S_1, S_2, S_3, S_4, S_5. Stopcocks. T. Thermoregulator. V. Ballast

Table I. Solubility of H_2Se in Water

Temp., ° C	Solubility, mole-liter^{-1}	
	1st Sampling	2nd Sampling
25.1	0.08347	0.08289
26.6	0.08062	0.08031
28.0	0.07943	0.07909
29.5	0.07709	0.07675
31.1	0.757	0.07533
33.0	0.07091	0.07133
34.7	0.06913	0.06915
36.7	0.06647	0.06613
39.0	0.06338	0.06331
41.0	0.06097	0.06141
43.0	0.05922	0.06033
45.0	0.05833	0.05643
47.0	0.05544	0.05504
49.0	0.05361	0.05297
51.0	0.05249	0.05161
53.0	0.05079	0.05073
55.0	0.05012	0.0487
57.4	0.04672	0.04744
59.0	0.04587	0.04384
61.0	0.04465	0.04299

Table II. Solubility of H_2Se in Water

Temp, ° C	Solubility, mole-liter^{-1}		
	1st Sampling	2nd Sampling	3rd Sampling
63.0	0.04397	0.04197	. . .
65.0	0.04377	0.04214	0.04255
66.0	0.04228	0.04269	0.0440
70.0	0.04017	. . .	. . .

$$S = 1.7583 - 9.664 \times 10^{-3} \, T + 1.3572 \times 10^{-5} \, T^2 \qquad (3)$$

$$\ln S = -8.4278 + 1772.35/T \qquad (4)$$

The normalized errors for the equations are, respectively, 0.000717 and 0.000698.

Thermodynamically, the slope of the linear Equation 4 represents the enthalpy of solution divided by gas constant R (2). When the experimental values are represented by the linear Equation 4, the value of the enthalpy of solution is

$$\Delta H = -1.772.35 \times R = -3.522 \text{ kcal-mole}^{-1}$$

Since the solution is diluted, Henry's law can be applied,

$$K_h = P/X_2 \qquad (5)$$

where P is the partial pressure of hydrogen selenide expressed in atmospheres and X_2, the hydrogen selenide molar fraction in the solution.

Since the number of moles of hydrogen selenide in the solution is negligible when compared with the number of moles of solvent, the values of the constant K_h as function of the temperature can be obtained from the equation,

$$\ln K_h = 12.4425 - 1772.35/T \qquad (6)$$

DISCUSSION

The solubility values obtained are precise to within 1% for temperatures lower than 50° C. At higher temperatures, because of the larger experimental errors especially between 60° and 70° C, the precision is lowered.

On the other hand, the calculated enthalpy value of -3.522 kcal-mole^{-1} falls between the only two old values reported in the literature, namely -4.630 kcal-mole^{-1} obtained by Fabre (1) and -2.431 kcal-mole^{-1} obtained by McAmis and Felsing (3).

LITERATURE CITED

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Figure 2. Variation of hydrogen selenide solubility with temperature

equilibrium. The equilibrium is verified by leaving the system standing for 30 min and observing that the pressure remains constant.

RESULTS

The experimental results are reported in Table I. In Table II some values obtained at higher temperatures are reported. These values are highly affected by experimental errors. They are therefore ignored in the solubility calculation.

The experimental values given in Table I were used to calculate the values of the constants appearing in the following equations using a least squares method:

$$S = A + BT + CT^2 \qquad (1)$$

$$\ln S = A' + B'/T \qquad (2)$$

where S is the solubility (moles-liter^{-1}) and T is the temperature (° K). The equations obtained are:

Thermal Conductivity of Phosphoric Acid–Water Mixtures at 25° C

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A thermal conductivity cell of the transient hot-wire type, used in conjunction with an improved potentiometric measurement method, is described and shown to give reliable results for aqueous ortho-phosphoric acid–water mixtures at 25° C.

Measurements of the thermal conductivities of liquid ortho-phosphoric acid (H_3PO_4) and an 87% aqueous solution in the temperature range 20–130° C have been previously reported by this author (18). A transient hot-wire probe, consisting of an electrically heated bare platinum wire immersed in the liquid, was used. More recently, Luff and Wakefield (13) reported the thermal conductivities of aqueous phosphoric acid solutions in the concentration range 84–115% H_3PO_4 (60–83% P_2O_5) and the temperature range 25–150° C. They used a modified transient probe, consisting of an electrically heated manganin wire and copper-constantan thermocouple in a glass capillary. In the area of overlap, 87–100% H_3PO_4 and 25–130° C, the results of Luff and Wakefield (13) are 5–7% lower than those of