[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 119.]

THE EQUILIBRIUM CONDITIONS OF THE REACTION BETWEEN SILVER SULFIDE AND HYDROGEN.

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Received November 29, 1919.

1. Purpose of the Investigation.

The equilibrium of the reaction $Ag_2S + H_2 = 2Ag + H_2S$ has already been studied by Pelabon[1] at 360 and at 700°. In connection with the systematic investigation of the free energy of formation of the halides, oxides, and sulfides of the elements, mercury, silver, lead, copper, and bismuth, now being carried out in this laboratory, it seemed, however, desirable to make a new series of equilibrium measurements with the view of securing more accurate results than was possible by Pelabon's procedure, and of obtaining reliable values at temperatures far enough apart to enable the heat effect attending the reaction to be calculated by the van't Hoff equation. We have, therefore, carried out a series of determinations in 3 temperature regions having average temperatures of about 750°, 811° and 890° A.

2. The Apparatus.

The apparatus employed was the same in principle as that used by Keyes[2] in his study of the dissociation pressures of sodium and potassium hydrides. It is shown in Fig. 1. The reaction tube *J* was made of quartz, and was connected by means of a quartz capillary and ground joint to a glass capillary. Hydrogen was prepared in *C* and stored in the reservoir *B*. The whole system could be evacuated by means of the mercury pump *D;* and the analyses of the gaseous phase were made in the water-jacketed gas burets *E* and *F*. The differences in the mercury levels in determining the pressure-volume relations of the gases were read by means of a cathetometer. The furnace used was the same as that used by Keyes. In order to provide a uniform temperature throughout the furnace, the air was vigorously stirred by a fan placed at the bottom of the furnace. The temperature of the furnace was measured by means of a platinum resistance thermometer sensitive to 0.01°.

3. Preparation of the Materials.

The silver sulfide was prepared by precipitating it from silver nitrate solution with hydrogen sulfide. The precipitate was washed by decanta-

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[1] *Compt. rend.*, 126, 1864 (1898).

[2] THIS JOURNAL, 34, 779 (1912).

tion with hot distilled water, collected on a filter, washed, and dried. In order to remove any mechanically adhering sulfur, the finely powdered silver sulfide was heated at 500° in a current of nitrogen.

The hydrogen was prepared by the method used by Keyes; namely, by adding water, free from air and carbon dioxide, to a 5% sodium amalgam.

The hydrogen sulfide was prepared in an apparatus like that used in the preparation of hydrogen by adding a magnesium chloride solution slowly to solid aluminum sulfide. The aluminum sulfide was prepared by heating together lead sulfide and powdered aluminum in a muffle furnace. The magnesium chloride solution was used to prevent the possible introduction of carbon dioxide.

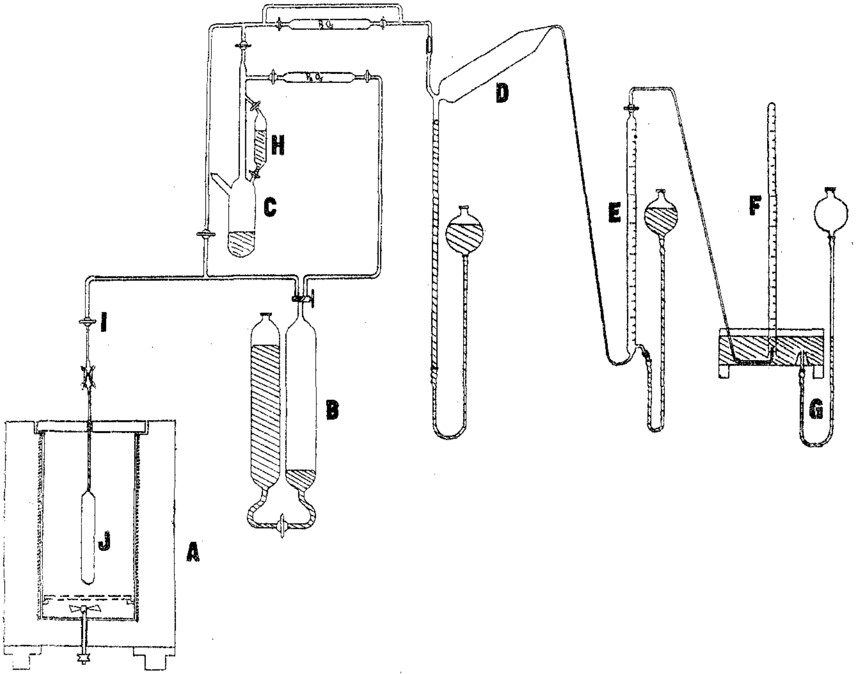

Fig. 1.

Silver in a finely divided state was made by the reduction of an ammoniacal silver nitrate solution by formaldehyde. The precipitated silver was washed repeatedly by decantation, boiled with distilled water, collected on a filter, and dried. It was again dried in a vacuum in the reaction tube at about 450°, thus removing any trace of moisture or of silver oxide.

4. The Method of Determining the Equilibrium.

The method employed will be more clearly understood by referring to the figure. The amalgam was placed in *C*, and water freed from air and carbon dioxide in *H*. The apparatus, including the gas reservoir *B*, was thoroughly exhausted by means of the pump *D*. The stop cock at the upper end of the water chamber was opened during the exhaustion for the purpose of removing the last traces of dissolved air and carbon dioxide. A few drops of water were then admitted through the lower stop cock to the amalgam, and the whole apparatus was again exhausted. The water was then admitted to the amalgam, and the evolved hydrogen, dried by passing it slowly through the phosphorus pentoxide tube, was collected in the gas reservoir *B*.

After the reaction tube *J* had been exhausted, a little hydrogen from the reservoir was admitted, and the reaction tube was again exhausted. Hydrogen was then admitted to the reaction tube, which contained the silver sulfide; and the stop cock *I* was closed. The temperature of the furnace was adjusted by an outside resistance, and the mixture given time to attain equilibrium. Samples of the gas mixture were withdrawn from the reaction tube after different intervals of time, and analyzed to determine whether equilibrium was attained. These time intervals ranged from about 12 hours to a week. The procedure in withdrawing the gas mixture was to exhaust the whole apparatus back of stop cock *I*. The stop cock was then opened, allowing the mixture of gases to rush into the exhausted space and cool instantly. The gases were then transferred to the gas buret *E*, and the volume, pressure and temperature were noted. The gaseous mixture was transferred finally to the gas buret *F*, where the hydrogen sulfide was absorbed by a 23% potassium hydroxide solution; and the residual volume of hydrogen was measured. These measured volumes were reduced to standard conditions of 0° and one atmosphere. In all cases correction was made for the water vapor pressure of the potassium hydroxide solution on the basis of the data given by Bunsen; and the corrections for temperature, height above sea level, and latitude were applied to the observed barometric reading.

Since the partial pressures of the two gases in the equilibrium mixture are proportional to their volume at 0° and one atmosphere, the equilibrium constant for the reaction is given by the expression

$$K = p_{\mathrm{H_2S}}/p_{\mathrm{H_2}} = v_{\mathrm{H_2S}}/v_{\mathrm{H_2}}.$$

5. The Experimental Results.

Table I presents the actually observed data, the corresponding volumes of the two gases reduced to the standard conditions of 0° and one atmosphere, and the computed values of the equilibrium constant. The results of Expts. 1 to 19 were obtained by approaching the equilibrium from the hydrogen silver sulfide side; those of Expts. 20 to 22 were obtained by approaching it from the other side.

TABLE I.

The Observed Data and the Equilibrium Constants Computed from them.

		Measurements of gas mixture. ($H_2S + H_2$).			Measurements of gas not absorbed by KOH($H_2 + H_2O$).			Vapor-pressure KOH at t_2.	Calc. volume at 0° and 760 mm. of		Equil. constant
Expt.	Equil. temp. t°C.	t_1.	p_1.	v_1.	t_2.	p_2.	v_2.	p_{H_2O}.	H_2S(v_{H_2S}.)	H_2(v_{H_2}.)	$K = v_{H_2S}/v_{H_2}$.
1	478.8	23.20	443.82	23.60	21.80	504.62	15.65	15.80	3.38	9.32	0.3634
2	479.6	24.50	321.45	14.05	24.20	491.08	7.00	18.00	1.45	4.00	0.3631
3	478.8	18.60	371.80	21.00	18.60	508.88	11.60	12.80	2.53	7.09	0.3568
4	468.0	21.40	362.90	19.40	21.80	510.72	10.50	15.20	2.23	6.35	0.3513
5	544.6	26.35	562.72	46.35	26.00	702.33	28.40	19.80	8.01	23.29	0.3440
6	543.5	25.00	548.03	42.40	24.60	688.49	26.95	18.40	6.19	21.81	0.2882
7	540.5	24.20	580.59	45.58	23.75	725.25	28.60	18.55	7.52	24.46	0.3073
8	524.2	22.00	516.39	39.90	22.20	650.68	24.60	16.60	6.09	19.00	0.3205
9	617.2	23.80	529.90	40.20	23.80	687.90	25.25	17.00	5.10	20.48	0.2491
10	616.0	25.12	504.26	39.90	24.60	649.85	23.75	18.40	4.93	18.10	0.2722
11	609.5	23.40	502.96	37.70	22.90	658.59	23.20	16.70	4.96	18.08	0.2745
12	606.1	24.00	493.50	34.60	23.50	647.85	21.40	17.20	4.30	16.35	0.2631
13	629.6	23.20	520.15	38.90	23.40	666.64	24.55	17.20	5.21	19.32	0.2696
14	614.0	24.60	499.70	37.20	23.90	640.91	23.30	17.70	4.87	17.57	0.2771
15	625.0	23.80	541.54	39.85	23.80	691.17	25.15	17.60	5.60	20.50	0.2733
16	633.0	25.80	533.18	40.30	25.20	682.36	25.45	19.00	5.49	20.33	0.2702
17	604.9	22.80	509.65	39.38	23.15	653.48	24.45	16.95	5.49	18.87	0.2909
18	626.4	23.95	536.76	39.50	23.75	680.07	24.60	17.55	5.91	19.73	0.2998
19	616.0	23.00	534.55	38.40	23.15	677.03	23.60	16.95	5.89	18.89	0.3120
20	454.5	25.90	488.78	31.55	26.10	631.01	18.35	19.90	5.06	13.46	0.3761
21	509.9	28.35	538.17	38.45	28.10	678.12	23.90	21.90	5.95	18.71	0.3183
22	557.8	30.08	444.83	24.55	29.35	587.77	14.80	23.15	3.01	9.93	0.3031

6. Values of the Equilibrium Constant Reduced to Uniform Temperatures.

The experiments in which the equilibrium was approached from the hydrogen silver sulfide side are grouped in 3 temperature regions; namely, Expts. 1 to 4 in a region which will be designated Region 1, whose average temperature is 749.15° A., Expts. 5 to 8 in Region 2, whose average temperature is 811.25° A.; and Expts. 9 to 19 in Region 3, whose average temperature is 889.63° A. All the separate values of $\log_{10} K$ were plotted against $1/T$, and the best representative line drawn through them. Indeed, it was found possible to draw a single straight line that well represented the points in all 3 regions. To show the concordance of the separate observations, each one was corrected, by taking into account its relation to this line, so as to correspond to one of the 3 average temperatures named above.

The so-reduced values of the equilibrium constant (p_{H_2S}/p_{H_2}), together with their means, are given in the last column of Table II.

TABLE II.

Values of the Equilibrium Constant Reduced to Uniform Temperatures.

Expt.	Absolute temperature.	Equilibrium constant.
1	749.15°	0.3652
2		0.3660
3		0.3590
4		0.3450
		Mean, 0.359
5	811.25°	0.3480
6		0.2910
7		0.3310
8		0.3319
		Mean, 0.325
9	889.63°	0.2478
10		0.2722
11		0.2711
12		0.2593
13		0.2750
14		0.2762
15		0.2770
16		0.2779
17		0.2850
18		0.3055
19		0.3119
		Mean, 0.278

7. Increase in Heat Content Attending the Reaction and Expression of the Equilibrium Constants as a Temperature Function.

The increase in heat content attending the reaction at the mean temperature (820° A) of the equilibrium measurements may be calculated by substituting the average values of T and K for Regions 3 and 1 given in Table II in the integrated form of the van't Hoff equation, as follows:

$$\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_3}\right) = \log_e \frac{K_3}{K_1} - \frac{\Delta H}{1.9885}\left(\frac{1}{749.15} - \frac{1}{889.63}\right) =$$

$$2.303 \log_{10} \frac{0.2780}{0.3588}$$

The value of ΔH is thus found to be —2410 cal. This result is expressed by the equation

$$(H_{820})\quad Ag_2S(s) + H_2(g) = 2Ag(s) + H_2S(g) + 2410 \text{ cal.}$$

With the aid of this value we may express the equilibrium constant as a function of the temperature between the limits 750° and 890° A. covered by the experiments. Namely, by substituting in the above given form of the van't Hoff equation the found values of K, T, and ΔH, and writing in place of K_3 and T_3 the general values K and T, we get

$$\log_{10} K = \frac{525.8}{T} - 1.1470.$$

The corresponding expression for the free-energy decrease $-\Delta F$ in calories attending the reaction $Ag_2S + H_2 = 2Ag + H_2S$ at any temperature T between 750° and 890° A. is

$$-\Delta F = RT \log_e K = 2408 - 5.253\ T.$$

With respect to the concordance of these equations with the observations it may be stated that the first equation, which is derived from the average values of the equilibrium constant at 749.15° and 889.63°, gives for that constant at the intermediate temperature 811.25° the value 0.317, while the average value derived from the observations in that temperature region is 0.325. It may also be mentioned that the results of the 3 experiments (20 to 22 in Table I) in which the equilibrium was approached in the direction opposite to that in which the values on which the equation is based were obtained are in fair agreement with the results computed by the equation; namely, these three experiments gave for the equilibrium constant the values 0.376 at 727.6° A., 0.318 at 783.0° A., and 0.303 at 830.9° A., while those computed from the equation for these temperatures are 0.376, 0.335, and 0.306.

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THE DETERMINATION OF CHLORINE WITH THE NEPHELOMETER.

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Received December 1, 1919.

In the study of the concentration of the vapor of "mustard gas" and similar non-volatile toxic liquids over areas sprayed with them, large samples of the contaminated air were collected, the toxic gas absorbed therefrom in alcohol, and after special treatment the chlorine was liberated as chloride and determined as such. These "war gases" are so very toxic that extremely minute quantities are significant, and in spite of the large samples of air which were collected (13 liters) it was necessary not only to detect but to measure amounts of chlorine as small as a few thousandths of a milligram.

For the rapid and approximate estimation of these amounts the copper flame test[2] gave useful results, as did also the selenious acid method of Yablick, Perrott and Furman,[3] but before these methods had been developed, and indeed afterwards when a more quantitative determina-

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[1] Published by permission of Maj.-Gen. W. L. Sibert, Director, Chemical Warfare Service, U. S. A.

[2] Lamb, Carleton, Hughes and Nichols, THIS JOURNAL, **42**, 78 (1920).

[3] *Ibid.*, **42**, 266 (*seq.*) (1920).