held the slide firmly enough to prevent movement of the assembled apparatus. The results given above were obtained with a 10× micrometer eyepiece and a $^2/_3$ in. objective. The microscope was first focussed on the upper edge of the tube, the position of which was read on the micrometer scale, then focussed down to the bottom of the meniscus, which should be so illuminated as to show as a bright line, and the body inclined until the upper edge of the bright line broadened and touched the scale mark, which from the first reading indicated the position of the upper edge of the tube. If a micrometer eyepiece is not available, one with cross-hairs will serve to locate the edge of the tube, although the difficulty of adjustment is somewhat increased. It is obvious that tubes with their ends ground accurately at right angles and polished would give better results than those used in this work. The determinations can be made very rapidly.

The fact that these results are uniformly low is striking. This may be due in part to a slight change in the length of the column arising from the flattening of the meniscus, the actual length being slightly greater than the distance as measured between the bottoms of the two menisci. A correction factor is indicated.

The writer is indebted to Dr. W. B. Harkins for his kind suggestions relative to the testing of this instrument.

## Summary.

A device is described, by means of which the surface tension of a liquid may be determined when only a drop or two is available, and which may be used as an aid in identifying organic liquids.

ALLIANCE, OHIO.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 120.]

# A THERMODYNAMIC INVESTIGATION OF REACTIONS INVOLVING SILVER SULFIDE AND SILVER IODIDE.

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## 1. Outline of the Investigation.

This research consists on the experimental side primarily in a determination of the equilibrium at 25° of the reaction

$$Ag_2S(s) + 2H^+I^- \text{ (in water)} = 2AgI(s) + H_2S \text{ (in water)}.$$

It was undertaken with two distinct objects in view. The first of these objects was to determine how the activity coefficient (or effective ionization) of the acid varies with its concentration. The second object was to determine the free-energy change attending the reaction.

This reaction is especially well adapted for determining the variation of the activity coefficient $\alpha$ of hydriodic acid with its concentration $c$, in the respect that a small change in the ion-concentration $c\alpha$ causes a very much larger change in the hydrogen sulfide concentration, as will be seen from the mass-action expression

$$K = (H_2S)/(H^+)^2(I^-)^2 = (H_2S)/(c\alpha)^4.$$

This fact carries with it, however, the disadvantage that the study can be extended over only a small range of acid concentration. Thus our experiments had to be confined to concentrations of hydriodic acid between 0.024 to 0.116 normal.

The free-energy decrease ($-\Delta F$) attending the change in state

$$Ag_2S(s) + 2H^+(1\ M) + 2I^-(1\ M) = 2AgI(s) + H_2S\ (1\ M)$$

can be computed by the familiar thermodynamic equation

$$-\Delta F = RT \log K,$$

using the equilibrium constant $K$ derived from the experiments and making the most reasonable assumption as to the ionization. By combining with this free-energy decrease the previously determined free energies of silver iodide and of hydrogen iodide in dilute solution we may derive the free-energy change attending the reaction

$$Ag_2S(s) + H_2(g) = 2Ag(s) + H_2S(g).$$

To confirm these results these free energies were also determined by measuring the electromotive force at 25° of the cells

$H_2$ ($p$ atm.), HCl (0.1 $f$.), HCl (0.1 $f$.) + $H_2S$ ($p$ atm.), $Ag_2S$ + Ag.

$H_2$ ($p$ atm.), HI (0.030 or 0.098 $f$.), AgI + Ag.

Finally, to determine the heat effect attending the reaction, the electromotive force of the first of these cells was measured at other temperatures.

## 2. Description of the Equilibrium Experiments.

The substances used in the experiments were prepared as follows: The water was redistilled from alkaline permanganate, rejecting the first fourth of the distillate. The hydrogen sulfide was made by treating ferrous sulfide with hydrochloric acid and washing the gas with a small quantity of barium hydroxide solution. The silver iodide was prepared by adding hydriodic acid solution to an excess of silver nitrate solution and thoroughly washing the precipitate by decantation in blackened bottles. The hydriodic acid solution was made from iodine sublimed from a mixture of it with potassium iodide and then resublimed alone.

This iodine was added to water, and hydrogen sulfide was passed in, the liquid being decanted from the sulfur after several days and filtered through an alundum filter. It was kept under an atmosphere of hydrogen sulfide.

The equilibrium mixtures were prepared as follows: To the silver iodide in blackened bottles hydriodic acid of various concentrations was added. A rubber stopper carrying 3 glass tubes, each with a glass stopcock, was then inserted in the neck of each bottle. Two of these tubes extended beneath the liquid in the bottles. One of these served to pass hydrogen sulfide into the mixture; and the other, provided with an alundum filter, to withdraw samples of the solution for analysis. The third tube extended only into the gas space above the liquid and served to regulate the gas pressure inside the bottles. Hydrogen sulfide was then passed into the mixture until the silver iodide began to darken. To approach the equilibrium from the opposite side hydriodic acid was added to mixtures already approximately at equilibrium. The necks of the bottles and the protruding tubes were well coated with paraffin to prevent leakage. The bottles were placed on a horizontal shaft in a thermostat at 25° and rotated for several days.

The bottles were then hung upright in the thermostat and the solid allowed to settle. Two samples of the solution were withdrawn, one for the determination of the hydrogen sulfide, the other for that of the hydriodic acid, at the same time nitrogen being allowed to draw into the bottle. The first sample was caused to suck up into an evacuated weighed bulb containing a known quantity of iodine dissolved in potassium iodide solution; whereupon the bulb was reweighed and the excess of iodine unconsumed by the hydrogen sulfide was titrated with standard sodium thiosulfate solution with the aid of starch or (in case of the more dilute solutions) of carbon disulfide. The other sample, consisting of about 15 cc., was weighed, diluted with 75 cc. of water, boiled to expel the hydrogen sulfide, and titrated with standard sodium hydroxide solution with the aid of phenolphthalein. These analytical methods were tested in advance and found to give results accurate within 0.2%.

## 3. The Data of the Equilibrium Measurements and the Activity Coefficients Calculated from Them.

In the following table is given in the first column the number of the experiment; in the second column, the number of days the mixture was rotated; in the third column, a letter *l* or *r* showing whether the equilibrium was being approached from the left or right hand side of the reaction $Ag_2S + 2HI = 2AgI + H_2S$; in the fourth and fifth columns, the concentrations $c_{HI}$ and $c_{H_2S}$, expressed in formula weights per liter, of the hydriodic acid and hydrogen sulfide in the equilibrium mixtures; in the sixth column, the equilibrium constants $K$ calculated from them by the equation $K = c_{H_2S}/(c_{HI}\gamma)^4$ with the aid of values of the ionization $\gamma$ given in the seventh column derived from the equivalent conductance measurements of Strachan and Chu;[1] and in the eighth column the values of the activity coefficient $\alpha$ of the hydriodic acid calculated by the equation $\alpha = \gamma(K)^{0.25}/5.558$, which is derived from the theoretical expression $c_{H_2S}/(c_{HI}\alpha)^4$ = const., under the arbitrary assumption that at 0.025 $N$ (where $K^{0.25} = 5.558$) the activity coefficient $\alpha$ and the ionization $\gamma$ have the same value, 0.924.

Table I.—The Equilibrium Data and the Equilibrium Constants and Activity Coefficients Calculated from Them.

| Expt. | Days rotation. | Direction. | Concentration. | | Equil. const. $K$. | Ionization $\gamma$. | Activity coeff. $\alpha$. |
|---|---|---|---|---|---|---|---|
| | | | $c_{H_2S}$. | $c_{HI}$. | | | |
| 1 | 7 | *r* | 0.0002522 | 0.02426 | 996 | 0.924 | 0.935 |
| 2 | 7 | *r* | 0.0002944 | 0.02580 | 915 | 0.923 | 0.914 |
| 3 | 7 | *r* | 0.0003424 | 0.02655 | 951 | 0.923 | 0.922 |
| 4 | 3 | *l* | 0.001002 | 0.03478 | 966 | 0.918 | 0.920 |
| 5 | 3 | *l* | 0.002807 | 0.04526 | 981 | 0.912 | 0.918 |
| 6 | 7 | *r* | 0.004058 | 0.05023 | 932 | 0.910 | 0.905 |
| 7 | 3 | *l* | 0.005029 | 0.05252 | 968 | 0.909 | 0.912 |
| 8 | 7 | *r* | 0.006801 | 0.05678 | 967 | 0.907 | 0.910 |
| 9 | 2 | *l* | 0.01971 | 0.07450 | 974 | 0.900 | 0.905 |
| 10 | 2 | *l* | 0.03298 | 0.08506 | 974 | 0.897 | 0.902 |
| 11 | 2 | *l* | 0.03349 | 0.08551 | 969 | 0.896 | 0.900 |
| 12 | 3 | *l* | 0.06330 | 0.1008 | 971 | 0.892 | 0.896 |
| 13 | 3 | *l* | 0.07695 | 0.1061 | 966 | 0.890 | 0.893 |
| 14 | 3 | *l* | 0.1108 | 0.1162 | 973 | 0.889 | 0.893 |
| | | | | Mean, | 964 | | |

## 4. Discussion of the Activity Coefficients Derived from the Equilibrium Measurements.

In the first place, the fact may be pointed out that there is no regular difference between the equilibrium constants obtained in approaching the equilibrium in the two opposite directions, showing that equilibrium was in reality attained.

Next it may be noted that the equilibrium constants exhibit only a very slight variation with the concentration, and that correspondingly the activity coefficients change with the concentration at nearly the same rate as the ionization values derived from the conductance ratios. It is to be remembered, however, that the range of concentration here involved (0.025 to about 0.12 formal) is relatively small, and that this may not be true in general.

Finally, the results may be compared with those obtained for hydrochloric acid by Noyes and Ellis.[2] Between the concentrations 0.025

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[1] This Journal, 36, 818 (1914).

[2] *Ibid.*, **39**, 2543 (1917).

and 0.12 the activity coefficient of hydrochloric acid decreases 8.3%, while that of hydriodic acid decreases only 4.5%.

It is to be noted that these values of the activity coefficient are only relative, as they are based on the arbitrary assumption that the value is identical with that of the ionization at 0.025 formal, and that, for example, values 3.8% smaller result if the activity coefficient be taken as identical with that of hydrochloric acid at 0.025 formal, for which 0.889 was found by Noyes and Ellis (instead of 0.924).

### 5. The Electromotive Force of Hydrogen Silver-Sulfide Cells.

We determined the electromotive forces at 5° or 10°, at 25°, and at 35°, of the cells

$$H_2\ (p\ \text{atm.}),\ \text{HCl}\ (0.5\ \text{or}\ 0.1\ f.),\ \left\{\begin{matrix}\text{HCl}\ (0.5\ \text{or}\ 0.1\ f.)\\ H_2S\ (p\ \text{atm.})\end{matrix}\right\},\ Ag_2S(s) + Ag(s).$$

The apparatus used consisted of 2 tubes connected by a siphon provided with a stopcock. Two separate platinized-platinum electrodes, prepared by M. Chow, of this laboratory, as described by Ellis,[1] were placed in one tube, and electrolytic hydrogen was continuously bubbled through it. This hydrogen was washed with alkaline pyrogallate and acid potassium dichromate; and, before entering the cell, it was passed through a bulb containing hydrochloric acid of the same strength as was present in the cell and having the same temperature. Four separate silver sulfide electrodes were placed in the other tube. These were made by coating silver-plated platinum spirals with a paste of silver oxide, and heating them until the oxide was decomposed, leaving a rough pure white mass of metallic silver. In case of the cell with the 0.1 formal acid the electrodes were dipped in a hydrogen sulfide solution, thus covering them with a thin coat of silver sulfide. In the cell with 0.5 formal acid they were previously coated with silver iodide, and later the iodide was converted to sulfide with a hydrogen sulfide solution. Solid silver sulfide, prepared by passing hydrogen sulfide into a silver nitrate solution and thoroughly washing the precipitate, was added to the acid solution in the tube containing the silver-sulfide electrodes. Through the tube containing these electrodes hydrogen sulfide was slowly bubbled. This hydrogen sulfide was made by heating a magnesium hydrosulfide solution prepared by passing ordinary hydrogen sulfide (made from ferrous sulfide and hydrochloric acid) into a cold suspension in water of carbonate-free magnesium oxide. In this way with 300 g. of magnesium oxide there could be obtained for many hours a steady stream of hydrogen sulfide easily controllable by the amount of heat applied.

The hydrogen and hydrogen sulfide gases both escaped at atmospheric pressure. Their partial pressures were, therefore, less than that of the

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[1] This Journal, 38, 742 (1916).

atmosphere by the vapor pressure of water in the hydrochloric acid solution at the temperature of the measurement. They were equal to each other and consequently the electromotive force was independent of the pressure.

The observed data are given in the following table. The first and second columns show the temperature and concentration in formula weights of per liter of solution. The third gives the number of hours that elapsed between the setting up of the cell and the first measurements. In the fourth column is recorded the mean result of these first measurements, this mean being the average of the 8 observations made with the 8 different combinations of the 2 hydrogen electrodes and the 4 silver sulfide electrodes. In the fifth and sixth columns are given the corresponding mean results obtained one hour and two hours later than the first measurement. The seventh column shows the average deviation from the mean result of the 8 observations from which it was derived.

TABLE II.—THE OBSERVED ELECTROMOTIVE FORCES OF THE HYDROGEN SILVER-SULFIDE CELLS.

| Temp. °. | Formal acid conc. | Elapsed time in hours. | Observed electromotive forces. | | | Average deviation. |
|---|---|---|---|---|---|---|
| 25 | 0.1 | 13 | —0.03670 | —0.03669 | —0.03670 | 0.00003 |
| 35 | 0.1 | 3 | —0.03586 | —0.03582 | —0.035 4 | 0.00004 |
| 10 | 0.1 | 3 | —0.03781 | —0.03779 | . . . . . | 0.00003 |
| 35 | 0.5 | 6 | —0.03569 | —0.03569 | —0.03570 | 0.00003 |
| 5 | 0.5 | 4 | —0.03794 | —0.03794 | —0.03791 | 0.00010 |
| 35 | 0.5 | 4 | —0.03583 | —0.03574 | —0.03572 | 0.00003 |

The following table contains the mean values derived from the foregoing observations for the cells formulated at the beginning of this section, together with values (within parentheses) interpolated for the temperatures at which measurements were not made:

TABLE III.—MEAN VALUES OF THE ELECTROMOTIVE FORCE OF THE HYDROGEN SILVER-SULFIDE CELLS.

| | Cell with. | | |
|---|---|---|---|
| Temp. °. | 0.1 *f*.HCl. | 0.5 *f*.HCl. | Final value. |
| 5 | (—0.3 18) | —0.03 93 | —0.03805 |
| 10 | —0.03779 | (—0.0 756) | —0.03767 |
| 25 | —0.03670 | (—0.03645) | —0.03658 |
| 35 | —0.03584 | —0.03571 | —0.0357 |

Reversing the sign of the numbers given in the last column of the table, we get the values of the specific electrode potential $\left\{\begin{matrix}\mathrm{Ag}\\ \mathrm{Ag_2S}\end{matrix}\right\}, \left\{\begin{matrix}\mathrm{H_2S}\ (1\ \mathrm{atm.})\\ \mathrm{H^+}\ (1\ M)\end{matrix}\right\}$.

## 6. The Electromotive Force of Hydrogen Silver-Iodide Cells.

The cells studied were $H_2$ ($p$ atm.), HI (0.030 or 0.098 *f*.), AgI + Ag. The apparatus employed was the same as that used for the silver silver sulfide cells. The silver silver-iodide electrodes were prepared in several ways. The first ones (denoted by A in the table below) were made by dipping silver silver-sulfide electrodes into a hydrogen iodide solution. Others (denoted by B) were made by electrolyzing silver-iodide on to the electrodes A just described with a current of 0.002 ampere for 2 hours. The final electrodes (denoted by C) were made by pasting precipitated silver-iodide on to these electrodes B, and heating them for 2 hours at a temperature of 120° to convert any amorphous silver iodide to the crystalline state. The pressure of the hydrogen was always equal to the barometric pressure diminished by the vapor pressure of water in the solution.

The observed data are given in Table IV. The first and second columns show the temperature and the concentration in formula weights of hydrogen iodide per liter of solution. The third column contains letters representing the electrodes prepared in the different ways indicated above. The fourth column gives the number of hours that elapsed between the setting up of the cell and the first constant measurements; and the fifth shows the barometer reading at the time of these measurements. In the sixth and seventh columns are recorded the mean results of these electromotive-force measurements and the average deviations of the 8 observations made with the 8 different combinations of the 2 hydrogen electrodes and the 4 silver silver-iodide electrodes. In the eighth column are given these electromotive forces corrected to a hydrogen pressure of one atmosphere. In the last column, headed Specific E. M. F., is given the electromotive force of the cell $H_2$ (1 atm.), $H^+$ (1 *M.*) || $I^-$ (1 *M.*), AgI + Ag, as calculated from the electromotive forces in the eighth column by the logarithmic formula with the aid of the activity coefficients (0.921 and 0.897) for 0.0300 and 0.0980 formal hydrogen iodide solutions, obtained by interpolation from the values given in Table I. These last values with sign reversed are the values of the specific electrode potential Ag + AgI, $I^-$ (1 *M.*).

TABLE IV.—THE ELECTROMOTIVE FORCES OF THE HYDROGEN SILVER-IODIDE CELLS.

| Temp. °. | HI. conc. | Electrodes. | Elapsed Time. Hrs. | Bar. press. | Observed E. M. F. | Av. dev. | Corrected E. M. F. | Specific E. M. F. |
|---|---|---|---|---|---|---|---|---|
| 25 | 0.0980 | A | 2 | 756 | —0.02329 | 0.00002 | —0.02282 | —0.14775 |
| 2 | 0.0980 | B | 4 | 766 | —0.02326 | 0.00007 | —0.02297 | —0.14790 |
| 25 | 0.0980 | C | 10 | 753 | —0.02336 | 0.00008 | —0.02285 | —0.14778 |
| 25 | 0.0300 | C | 6 | 761 | +0.03640 | 0.00014 | +0.03678 | —0.14764 |
| 25 | 0.0300 | C | 7 | 761 | +0.03645 | 0.00018 | +0.03683 | —0.14759 |
| | | | | | | | Mean, | —0.14773 |

## 7. Free-Energy Changes Attending the Reactions.

The free-energy decrease attending the reaction whose equilibrium we studied is found by the equation

$$-\Delta F = RT \log K$$

(adopting the mean value of $K$ given in Table I) to be 4070 cal. at 25°. This result is expressed by the equation[1]

$$(F_{298}) \quad Ag_2S(s) + 2H^+(1\ M.) + 2I^-(1\ M.) = 2AgI(s) + H_2S\ (1\ M.) + 4070\ \text{cal.}$$

From Pollitzer's[2] determination that the solubility of hydrogen sulfide at 25° is 0.1004 molal when its partial pressure is 737 mm. we find with the aid of the usual logarithmic expression

$$(F_{298}) \quad H_2S\ (1\ M.) = H_2S\ (1\ \text{atm.}) + 1325\ \text{cal.}$$

Adding these two equations we get:

$$(F_{298}) \quad Ag_2S(s) + 2H^+\ (1\ M.) + 2I^-\ (1\ M.) = 2AgI(s) + H_2S\ (1\ \text{atm.}) + 5400\ \text{cal.}$$

Jones and Hartman[3] found that the electromotive force at 25° of the cells Ag + AgI, KI (0.05*f.* and 0.1 *f.*), $I_2(s)$, after correcting for the tri-iodide concentration at the iodine electrode and for the liquid potential arising from it, is +0.6847 volt. This corresponds to the following equation:

$$(F_{298}) \quad 2AgI(s) = 2Ag(s) + I_2(s) - 31600\ \text{cal.}$$

Lewis and Randall[4] have reviewed the data on the electrode potential of iodine, and on the basis of the measurements of Farragher find for the cell $I_2\ (1\ M.)$, $I^-\ (1\ M.) \,||\, KCl\ (0.1\ N)$, $KCl\ (1\ N)$, $Hg_2Cl_2 + Hg$ at 25° the value —0.3407 volt. Adding to this the value —0.2828 volt recently derived by Lewis, Brighton and Sebastian[5] for the cell Hg + $Hg_2Cl_2$, KCl (1 $N$), KCl (0.1 $N$) $||$ $H^+\ (1\ M.)$, $H_2$ (1 atm.) at 25°, we get for the cell $I_2\ (1\ M.)$, $I^-\ (1\ M.) \,||\, H^+\ (1\ M.)$, $H_2$ (1 atm.), or for the electrode potential of dissolved iodine, the value —0.6235 volt. The corresponding free-energy equation is

$$(F_{298}) \quad H_2\ (1\ \text{atm.}) + I_2\ (1\ M.) = 2H^+(1\ M.) + 2I^-(1\ M.) + 28780\ \text{cal.}$$

Lewis and Randall[6] have also derived the equation

$$(F_{298}) \quad I_2(s) = I_2\ (1\ M.) - 3930\ \text{cal.}$$

Adding the last 3 equations we get

$$(F_{298}) \quad 2AgI(s) + H_2\ (1\ \text{atm.}) = 2Ag(s) + 2H^+\ (1\ M.) + 2I^-\ (1\ M.) - 6750\ \text{cal.}$$

Adding this equation to the one preceding the last 3 equations we get

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[1] Throughout this article the symbols $F_{298}$ and $H_{298}$ prefixed to equations indicate that they are free-energy equations or heat-content equations, respectively, and that they refer to 25° C. or 298° A. In general, the conventions employed are those adopted by Lewis (THIS JOURNAL, **35**, 1–30 (1913); **36**, 1969–1993 (1914)).

[2] *Z. anorg. Chem.*, **64**, 121 (1909).

[3] THIS JOURNAL, **37**, 752 (1915).

[4] *Ibid.*, **36**, 2264 (1914).

[5] *Ibid.*, **39**, 2259 (1917).

[6] *Ibid.*, **36**, 2262 (1914).

$(F_{298})$ $Ag_2S(s) + H_2$ (1 atm.) $= 2Ag(s) + H_2S$ (1 atm.) — 1350 cal.

We may derive other values of the free-energy decrease attending these reactions with the aid of the equilibrium measurements of Danneel,[1] who studied at 13° the reaction

$$2AgI(s) + H_2 \text{ (1 atm.)} = 2Ag(s) + 2HI \text{ (in water)}.$$

Danneel approached the equilibrium from both sides, using platinum black as a catalyzer, and found the equilibrium concentration of the hydrogen iodide to be 0.0430 formal. Since, when the change takes place under equilibrium conditions, the free energy change is zero, we may write the following free-energy equation:

$(F_{286})$ $2AgI(s) + H_2$ (1 atm.) $= 2Ag(s) + HI$ (at 0.043 *f.*) + 0 Cal.

To calculate the free-energy change at 25° we need the value of the heat content attending the reaction. This is obtained by combining the following thermochemical equations:

$(H_{291})$ $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) = HI(g)$ — 6170 cal.

$(H_{291})$ $HI(g) + \infty Aq = HI\infty Aq$ + 19350 cal.

$(H_{291})$ $AgI(s) = Ag(s) + \frac{1}{2}I_2(s)$ — 14960 cal.

Thomsen[2] and Berthelot[3] measured the first and second of these reactions with fairly concordant results (6040 and 6300, 19200 and 19500). For the heat of formation of 1AgI(s) the best values are evidently those (14820 and 15100 cal.) recently determined by Fischer[4] and Braune and Koref.[5] The means of these values have been adopted in the foregoing equations.

Adding together these 3 thermochemical equations and multiplying the result by 2 we get

$(H_{291})$ $H_2(g) + 2AgI(s) + \infty Aq = 2Ag(s) + 2HI\infty Aq$ — 3560 cal.

Substituting in the general free-energy equation

$$\frac{(-\Delta F_2)}{T_2} - \frac{(-\Delta F_1)}{T_1} = \Delta H\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

for $\Delta H$ the value —3560 and for $-\Delta F$, the value 0 at $T_1 = 286$, we find that at 25° ($T_2 = 298$) the free-energy decrease $-\Delta F_2$ for the same change in state has the value 149 cal. This result is expressed by the equation

$(F_{298})$ $2AgI(s) + H_2$ (1 atm.) $= 2Ag(s) + HI$ (at 0.0430 *f.*) + 149 cal.

Taking the activity coefficient of 0.043 *f.* hydrogen iodide as 0.918, as given in Table I, we derive from the preceding equation by the usual logarithmic formula the following:

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[1] *Z. phys. Chem.*, **33**, 429 (1900).

[2] *J. prakt. Chem.*, [2] **12**, 289 (1875); "Thermochemische Untersuchungen," **3**, p. 380.

[3] *Ann. chim. phys.*, [5] **29**, 243 (1883); Berthelot's "Thermochimie," **2**, 370 (1897).

[4] *Z. anorg. Chem.*, **78**, 41 (1912).

[5] *Ibid.*, **87**, 185 (1914).

($F_{298}$) $2AgI(s) + H_2$ (1 atm.) =
$2Ag(s) + 2H^+$ (1 *M.*) $+ 2I^-$ (1 *M.*) — 7516 cal.

Adding this to the third equation in this Section we get

($F_{298}$) $Ag_2S(s) + H_2$ (1 atm.) = $2Ag(s) + H_2S$ (1 atm.) — 2116 cal.

We may also derive the free-energy change attending this last reaction from the equilibrium measurements of Danneel and of ourselves, without making any assumption as to the activity coefficient, as follows:

We find by interpolation that the concentration of hydrogen sulfide which is in equilibrium with a 0.0430 formal hydrogen iodide solution when silver-iodide and -sulfide are also present is 0.002293 formal. At these concentrations the free-energy decrease will be zero, as expressed by the equation

($F_{298}$) $Ag_2S(s) + 2HI$(0.0430*f.*) = $2AgI(s) + H_2S$(0.002293 *f.*) + 0 cal.

Adding the two preceding equations we get

($F_{298}$) $Ag_2S(s) + H_2$(1 atm.) = $2Ag(s) + H_2S$ (0.002293 *f.*) + 149 cal.

Now the data of Pollitzer[1] shows that, when the partial pressure of the hydrogen sulfide is one atmosphere, the concentration of hydrogen sulfide in 0.0430 formal hydrogen iodide solution is 0.1041 formal. From the relation

$$-\Delta F = RT \log_e \frac{0.002293}{0.1041},$$

we get

($F_{298}$) $H_2S$ (0.002293 *f.*) = $H_2S$ (0.1041 *f.*) — 2262 cal.; or

($F_{298}$) $H_2S$ (0.002293 *f.*) = $H_2S$ (1 atm.) — 2262 cal.

By combining the last of these two equations with the one preceding them, we get

($F_{298}$) $Ag_2S(s) + H_2$ (1 atm.) = $2Ag(s) + H_2S$ (1 atm.) — 2113 cal.

Finally, we may derive directly from the electromotive-force measurements given in Tables III and IV the free-energy decrease attending the two main reactions under consideration. Namely, multiplying the electromotive forces (—0.14773 and —0.03658 volt) of the hydrogen silver-iodide cell and of the hydrogen silver-sulfide cell at 25° by 193,000 and dividing by 4.182, we find the result expressed by the following equations:

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[1] *Z. anorg. Chem.*, 64, 121 (1909). By plotting Pollitzer's values of the solubility of hydrogen sulfide in hydrogen iodide solutions, when the total pressure of the gas is one atmosphere, against the concentration of the hydrogen iodide, the equation of the most representative straight line through the points is found to be $c_{H_2S} = 0.1004 + 0.01248c_{HI}$. This gives for the value of $c_{H_2S}$ when $c_{HI}$ is 0.043 formal the value 0.10094 formal. This refers, however, to a partial pressure of the hydrogen sulfide of 737 mm., the vapor pressure of the water in the 0.043 *f.*HI solution being 23 mm. Hence, for a partial pressure of one atmosphere, $c_{H_2S} = 0.10094 \times 760/737 = 0.1041$ formal.

($F_{298}$) $2AgI(s) + H_2$ (1 atm.) =
$2Ag(s) + H^+$ (1 *M.*) + $I^-$ (1*M.*) — 6817 cal.

($F_{298}$) $Ag_2S(s) + H_2$ (1 atm.) = $2Ag(s) + H_2S$ (1 atm.) — 1688 cal.

For the last of these reactions we can derive another value from the electromotive forces of the hydrogen silver-iodide cell (without using the activity coefficient of hydriodic acid) by combining them with the results of our equilibrium measurements. Namely, multiplying the electromotive forces (—0.02288 and +0.03680 volt) of the cells with 0.0980 and 0.0300 formal hydrogen iodide solutions by 193,000 and dividing by 4.182 we get the results expressed by the two following equations:

($F_{298}$) $2AgI(s) + H_2$ (1 atm.) = $2Ag(s) + 2HI$ (0.0980 *f.*) — 1056 cal.

($F_{298}$) $2AgI(s) + H_2$ (1 atm.) = $2Ag(s) + 2HI$ (0.0300 *f.*) + 1698 cal.

Now we find from our equilibrium measurements by interpolation that with 0.0980 formal hydrogen iodide the corresponding hydrogen sulfide concentration is 0.0562 formal, and that with 0.0300 formal hydrogen iodide the hydrogen sulfide concentration is 0.000550 formal. And by treating these results as we did those of Danneel, we get the following two groups of free-energy equations:

($F_{298}$) $Ag_2S(s) + 2HI$ (0.0980 *f.*) = $2AgI(s) + H_2S$ (0.0562 *f.*) + 0 cal.

($F_{298}$) $H_2S$ (0.0562 *f.*) =
$H_2S$ (0.1048 *f.* or 1 atm. over 0.0980 *f.* HI) — 369 cal.

($F_{298}$) $2AgI(s) + H_2$ (1 atm.) = $2Ag(s) + 2HI$ (0.0980 *f.*) — 1056 cal.

($F_{298}$) $Ag_2S(s) + 2HI$ (0.0300 *f.*) = $2AgI(s) + H_2S$ (0.000550 *f.*) + 0 cal.

($F_{298}$) $H_2S$ (0.000550 *f.*) =
$H_2S$ (0.1039 *f.* or 1 atm. over 0.0300 *f.* HI) — 3107 cal.

($F_{298}$) $2AgI$ (s) + $H_2$ (1 atm.) = $2Ag(s) + 2HI$ (0.0300 *f.*) + 1698 cal.

Adding the equations in each of these two groups, we get for the free-energy decrease —1425 and —1409 cal., respectively. Adopting the mean (—1417 cal.) we may write

($F_{298}$) $Ag_2S(s) + H_2$ (1 atm.) = $2Ag(s) + H_2S$ (1 atm.) — 1417 cal.

### 8. Summary of the Free-Energy Values.

The results of the preceding calculations may be summarized as follows:

We have found for the free-energy decrease attending the reaction

$2AgI(s) + H_2$ (1 atm.) = $2Ag(s) + 2H^+$ (1 *M.*) + $2I^-$ (1 *M.*) at 25°

the following values:

(*a*) —6750 cal. from the e. m. f. data of Jones and Hartman on iodine silver-iodide cells and the electrode-potential calculations of Lewis and Randall relating to hydrogen iodide.

(*b*) —6817 cal. from our e. m. f. data on hydrogen silver-iodide cells.

(*c*) —7516 cal. from the measurements of Danneel on the equilibrium of the reaction at 13°, and the available thermochemical data.

We have found for the free-energy decrease attending the reaction

$$Ag_2S(s) + H_2 \text{ (1 atm.)} = 2Ag(s) + H_2S \text{ (1 atm.) at } 25°$$

the following values:

(*d*) —1350 cal. from our equilibrium results and result (*a*) above.

(*e*) —1417 cal. from our equilibrium results (*b*) above.

(*f*) —1688 cal. from our e. m. f. data on hydrogen silver-sulfide cells.

(*g*) —2116 cal. from our equilibrium results and result (*c*) above.

(*h*) —2113 cal. from our equilibrium results and those of Danneel directly.

It will be seen that the results (*c*), (*g*), and (*h*), which involve Danneel's equilibrium measurements, are much larger numerically than results (*a*) and (*b*) and results (*d*), (*e*), and (*f*), which are based on the electromotive force data. As the latter results are fairly concordant and come from 2 or from 3 independent series of electromotive-force measurements, it seems best to adopt as final values the averages of these results, which are expressed by the following equations:

$$(F_{298})\ 2AgI(s) + H_2 \text{ (1 atm.)} = 2Ag(s) + 2H^+ \text{ (1 } M.) + 2I^- \text{ (1 } M.) - 6885 \text{ cal.}$$

$$(F_{298})\ Ag_2S(s) + H_2 \text{ (1 atm.)} = 2Ag(s) + H_2S \text{ (1 atm.)} - 1485 \text{ cal.}$$

We have attempted to formulate a temperature function that would bring this last free energy value into relation with those determined by Keyes and Felsing[1] for the same reaction at 470–630°, but have become convinced that the values of the heats of reaction and of the heat capacities available at present are not accurate enough to enable this to be done satisfactorily.

By combining the first of the last two equations with the free energy of formation of iodide ion, as determined by Lewis and Randall[2] and expressed by the equation

$$(F_{298})\quad H_2 \text{ (1 atm.)} + I_2(s) = 2H^+ \text{ (1 } M.) + 2I^- \text{ (1 } M.) + 24608 \text{ cal.}$$

we get the equation

$$(F_{298})\quad 2Ag(s) + I_2(s) = 2AgI(s) + 31493 \text{ cal.}$$

Half this quantity, or 15750 cal., is the free-energy decrease attending the formation of one AgI(*s*) from its elements at 25°.

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[1] THIS JOURNAL, **42**, 246, 251 (1920).

[2] *Ibid.*, **36**, 2264 (1914).