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HEATS OF FORMATION AND ENTROPIES OF HS^- AND $S^=$. POTENTIAL OF SULFIDE-SULFUR COUPLE.

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ABSTRACT

The heat of neutralization of H_2S solutions by NaOH was measured at 25° for various mole ratios of NaOH to H_2S. These data, with the two dissociation constants of H_2S, allow calculations of the free energies and heats of formation and the partial molal entropies of $S^=$ and HS^-. The results are for $S^=$ and HS^- respectively: ΔF^o = 20.6 and 3.00 kcal., ΔH^o = 7.8 and -4.10 kcal., and $\bar{S}^o$ = -4 and 15.0 eu. The potentials of the $S^=$ - S couple is 0.447 v.

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INTRODUCTION

The value of $\bar{S}^{\circ}_{S^=}$ found in the National Bureau of Standards tables is 5 eu.[1] This appears to be considerably too positive for a monatomic, dinegative ion.[2] The value is based on the second dissociation constant of H_2S, K^{II}, measured by Kubli[3] and on studies of the heat of H_2S neutralization by several early investigators.[4-6] Interpretation of the early thermal data is uncertain because of the high ionic strengths necessarily employed and a lack of reliable activity coefficients for $S^=$ and HS^-.

K^{II} has recently been determined spectrophotometrically over a range of low ionic strengths.[7] Thus it appeared desirable to utilize modern calorimetric techniques for a study of the heat of neutralization over a wide range of $S^=$ to HS^- mole ratios. One can then combine the results of such heat measurements with the data of Konopik and Leberl[7] and obtain more reliable values for the thermodynamic functions of $S^=$ and HS^-.

EXPERIMENTAL

The calorimeter used in this investigation has been previously described.[8,9] All heats were measured at 25.0 ± 0.5° and are reported in terms of the defined calorie (1 cal. = 4.1840 abs. joules). The uncertainty in the measured heats is ± 0.3 cal. Samples of concentrated NaOH solutions were contained in paraffin-coated, small glass bulbs and were introduced into the calorimetric solutions by shattering the bulbs with a glass rod.

A 50% stock solution of NaOH, prepared from Baker and Adamson reagent grade pellets, was filtered through glass wool to remove Na_2CO_3 and stored in a paraffin-coated container. Before each run the NaOH was filtered again through glass wool and after appropriate dilution was transferred immediately to a stoppered, waxed weight buret. A weighed portion of this solution was then added to the sample bulb. The remainder was analyzed by adding a weighed amount of the solution to a known excess of standard $HClO_4$ and titrating with standard NaOH to the brom-thymol blue end point. Tests on the calorimetric solutions with $Ba(NO_3)_2$ after several runs revealed only traces of carbonate.

An aqueous solution of H_2S was prepared before each run from purified,[10] commercial grade H_2S, and a weighed amount of this solution was added to the calorimeter. After the calorimetric run the resulting Na_2S-NaHS-NaOH solution was analyzed for total sulfide iodimetrically.[11]

The density of the calorimetric solution — necessary for the calculation of the concentrations of all species present — was measured immediately after each run with calibrated 25 and 50 ml. pipets.

Data. The experimental results are presented in Table I. (A = moles of H_2S, B = moles of water in calorimeter before breaking sample bulb, C = moles of NaOH, D = moles of water in sample bulb, Q = heat evolved in calories and d = density of the resulting solution at 25° in g./ml.)

TABLE I

Run	A x 10^2	B	C x 10^2	D x 10^2	Q	d
1	1.399	60.68	1.708	13.21	117.7	.997
2	1.593	60.07	1.909	4.40	217.6	.997
3	1.698	60.88	2.550	5.79	258.9	.997
4	1.674	60.75	2.817	6.38	272.5	.997
5	1.716	61.24	3.793	8.62	321.2	.997
6	1.818	61.44	4.257	9.67	351.1	.998
7	1.522	60.83	5.345	39.49	144.1	.998
8	1.670	60.17	7.001	49.90	168.6	1.000
9	1.069	60.50	6.657	49.95	108.4	.999
10	1.550	61.12	8.128	60.91	152.0	1.000
11	1.216	60.77	8.640	64.69	125.9	1.000

CALCULATIONS AND DISCUSSIONS

The complete equation for the calorimetric reaction is assumed to be: (1)

$$A\ H_2S + B\ OH^- + (C + D)\ H_2O = (A - E)\ HS^- + E\ S^= + (C + D + A + E)\ H_2O + (B - A - E)OH^-$$

Thus, to interpret properly the heat data it is necessary to know the concentrations of all species present after the reaction. Since there is a discrepancy in the K^{II} values reported in the recent studies by Kubli[3] and Konopik and Leberl[7], the pH measurements of both authors were critically re-examined. Both sets of data were found to be consistent upon eliminating Kubli's assumption that activity of OH^- equals concentration of OH^-. All the data were placed on an extended Debye-Hückel plot from which it was possible to obtain a pK_u^{II} ($pK_u^{II} = -\log K_u^{II}$) value for each calorimetric run. K_u^{II} is not a true equilibrium constant, but a function of ionic strength, and is defined as

$$K_u^{II} = \frac{a_{H^+} (S^=)}{(HS^-)} \qquad (2)$$

where ( ) refers to moles/liter and a_{H^+} = activity of H^+.

Since the measurements of Kubli and Konopik and Leberl were made at 20°, it was necessary to convert their results to 25°. The true equilibrium constant, K^{II}, is related to K_u^{II} by:

$$K^{II} = K_u^{II} \frac{f_{S^=}}{f_{HS^-}} \qquad (3)$$

where $f_{S^=}$ and f_{HS^-} refer to the respective activity coefficients. Assuming ΔH^o of the second dissociation step to be constant over the 5° temperature range, we can calculate K^{II} at 25° from the van't Hoff equation. Then also assuming that the activity coefficient ratio is constant over the same temperature range, we are able to calculate K_u^{II} at 25° (Table II). This calculation was done by successive approximations, using first the old heat data and then correcting with that obtained in this work.

To calculate the concentrations of all species present after reaction, we utilize equation (2), total sulfide concentration, initial NaOH concentration, and the following relationships:

$$(Na^+) = (OH^-) + (HS^-) + 2(S^=) \qquad (4)$$

$$a_{H^+} = \frac{1.008 \times 10^{-14}}{(OH^-)\, f_{OH^-}} \qquad (5)$$

The activity coefficients of OH^-, f_{OH^-}, were calculated from Kielland's equation.[12]

These values were checked against the experimental mean activity coefficients of NaOH[13] and gave very good agreement over the ionic strength range of our experiments (μ = 0.01 to 0.09).

To obtain standard state values, the experimentally observed heats were corrected to infinite dilution for all species. Utilizing the principle of ionic strength we assume, for example, the heat of dilution of NaOH at μ = 0.1 equals the heat of dilution for 0.1 M NaOH. Then neglecting the H_2S heat of dilution, approximating that of NaHS as equal to NaOH, and that of Na_2S as equal to Na_2SO_4, we define:

Q' = heat evolved for B moles NaOH in D moles of H_2O to infinite dilution (6)

Q'' = heat evolved for E moles Na_2SO_4 in ionic strength μ to " " (7)

Q''' = " " " (B-2E) moles NaOH in ionic strength μ to " " (8)

$$Q^o = Q - Q' + Q'' + Q''' \quad (9)$$

The above dilution heats were obtained from the National Bureau of Standards tables for the heats of formation of NaOH and Na_2SO_4.[1] For the most concentrated NaOH solutions, the heats of dilution were experimentally determined and were found consistent with those calculated from the Bureau of Standards data. The observed heats of formation for the concentrated solutions are:

1 mole NaOH in 2.264 moles H_2O ΔH_f = -107.409 kcal.

1 mole NaOH in 2.256 moles H_2O ΔH_f = -107.397 kcal.

In Table II are found the results of the above calculations. (E = moles of $S^=$ present after reaction, and the Q's are given in calories.)

TABLE II

Run	pK_u^{II} (25°)	$E \times 10^3$	Q'	Q"	Q'''
1	12.69	.549	4.4	.1	.9
2	12.68	.642	90.2	.1	1.1
3	12.64	1.803	122.3	.3	1.6
4	12.62	2.382	135.7	.4	1.7
5	12.57	4.287	181.9	.8	2.5
6	12.54	5.250	204.2	1.0	2.8
7	12.49	6.522	17.2	1.3	3.9
8	12.40	9.261	26.0	2.0	5.5
9	12.43	6.088	20.0	1.3	5.6
10	12.36	9.749	24.5	2.2	6.8
11	12.35	8.193	26.0	1.9	7.8

In order to obtain the standard heats of formation of $S^=$ and HS^- ($\Delta H^o_{S^=}$ and $\Delta H^o_{HS^-}$), we make use of the following equation:

$$-Q^o = (A - E)\Delta H^o_{HS^-} + E\,\Delta H^o_{S^=} + (A + E)\Delta H^o_{H_2O} - (A + E)\Delta H^o_{OH^-} - A\,\Delta H^o_{H_2S_{aq}} \qquad (10)$$

Rearranging gives:

$$\frac{-Q^o}{A-E} + \left(\frac{A}{A-E}\right)\Delta H^o_{H_2S_{aq}} + \frac{(A+E)}{(A-E)}\left(\Delta H^o_{OH^-} - \Delta H^o_{H_2O}\right) = \Delta H^o_{S^=}\left(\frac{E}{A-E}\right) + \Delta H^o_{HS^-} \qquad (11)$$

Thus, in Figure I a plot of the left hand member of (11) abbreviated as "y", vs. $\frac{E}{A-E}$ gives a straight line with slope equal to $\Delta H^o_{S^=}$ and intercept equal to $\Delta H^o_{HS^-}$. The values of $\Delta H^o_{H_2S_{aq}}$, $\Delta H^o_{OH^-}$ and $OH^o_{H_2O}$ (the standard heats of formation of H_2S_{aq}, OH^- and H_2O) were obtained from Latimer.[14]

The values obtained above for $\Delta H^{o}_{S^{=}}$ and $\Delta H^{o}_{HS^{-}}$ along with K^{I} and K^{II} for H_2S allow a calculation of the remaining thermodynamic functions. We have taken $K^{I} = 1.02 \times 10^{-7}$ (Kubli's[3] value corrected to 25°) and $K^{II} = 1.3 \times 10^{-13}$ (from the extrapolated value of pK_u^{II}[3,7] at zero ionic strength and corrected to 25°).

A summary of the results is presented in Table III. The limits of error are based on an estimated uncertainty of 0.05 pK units in pK_u^{II} and 0.1 pK units in the extrapolated value, pK^{II}.

Using our values for ΔF^{o}, the potential of the sulfide - sulfur couple is

$$S^{=} = S + 2e^{-} \qquad E^{o} = 0.447 \pm 0.004 \text{ v.}$$

TABLE III

	HS^{-}	$S^{=}$
ΔF^{o}_{kcal}	3.00	20.6 ± .2
ΔH^{o}_{kcal}	-4.10 ± .08	7.8 ± .8
$\bar{S}^{o}_{eu}$	15.0 ± .4	-4 ± 3

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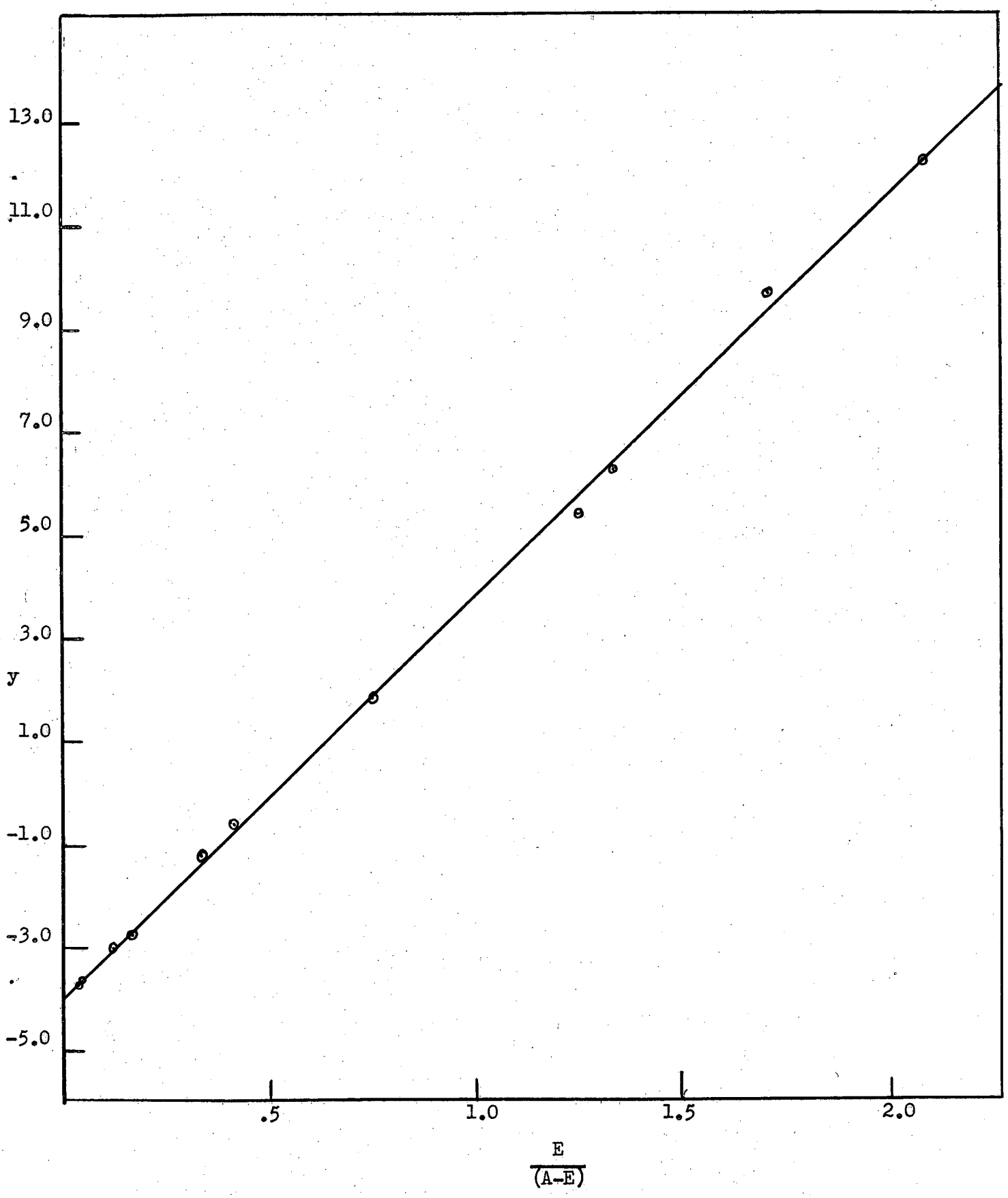
FIGURE I