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HEATS OF FORMATION AND ENTROPIES OF HS- AND S- POTENTIAL OF SULFIDE-SULFUR COUPLE

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Authors
Kury, J.W.
Zielen, A.J.
Latimer, W.L.

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POTENTIAL OF SULFIDE-SULFUR COUPLE.

J. W. Kury, A. J. Zielen and W. L. Latimer

February 12, 1953

Berkeley, California
HEATS OF FORMATION AND ENTROPIES OF HS⁻ AND S²⁻.

POTENTIAL OF SULFIDE-SULFUR COUPLE.

J. W. Kury, A. J. Zielen and W. L. Latimer
Department of Chemistry and Chemical Engineering
Radiation Laboratory, University of California
Berkeley, California

February 12, 1953

ABSTRACT

The heat of neutralization of H₂S solutions by NaOH was measured at 25⁰ for various mole ratios of NaOH to H₂S. These data, with the two dissociation constants of H₂S, allow calculations of the free energies and heats of formation and the partial molal entropies of S²⁻ and HS⁻. The results are for S²⁻ and HS⁻ respectively: ΔF° = 20.6 and 3.00 kcal., ΔH° = 7.8 and -4.10 kcal., and S° = -4 and 15.0 eu. The potentials of the S²⁻ - S couple is 0.447 v.
HEATS OF FORMATION AND ENTROPIES OF HS⁻ AND S²⁻.

POTENTIAL OF SULFIDE-SULFUR COUPLE.

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INTRODUCTION

The value of $S_g$ 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 H₂S, $K_{II}$, measured by
Kubli³ and on studies of the heat of H₂S neutralization by several early investiga-
gors.⁴⁻⁶ Interpretation of the early thermal data is uncertain because of the
high ionic strengths necessarily employed and a lack of reliable activity co-
efficients for S²⁻ 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 S²⁻ to
HS⁻ mole ratios. One can then combine the results of such heat measurements
with the data of Konopik and Leberl⁷ and obtain more reliable values for the
thermodynamic functions of S²⁻ and HS⁻.

EXPERIMENTAL

The calorimeter used in this investigation has been previously described.⁸,⁹
All heats were measured at 25.0 ± 0.5⁰ 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 Na₂CO₃ 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 HClO₄ and titrating with standard NaOH to the brom-thymol blue end point. Tests on the calorimetric solutions with Ba(NO₃)₂ after several runs revealed only traces of carbonate.

An aqueous solution of H₂S was prepared before each run from purified, commercial grade H₂S, and a weighed amount of this solution was added to the calorimeter. After the calorimetric run the resulting Na₂S-NaHS-NaOH solution was analyzed for total sulfide iodimetrically.

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 H₂S, 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

<table>
<thead>
<tr>
<th>Run</th>
<th>A x 10^2</th>
<th>B</th>
<th>C x 10^2</th>
<th>D x 10^2</th>
<th>Q</th>
<th>d</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>1.399</td>
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<td>1.708</td>
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<td>.997</td>
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<td>2</td>
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<td>3</td>
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<td>60.88</td>
<td>2.550</td>
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<td>.997</td>
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<td>4</td>
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<td>1.716</td>
<td>61.24</td>
<td>3.793</td>
<td>8.62</td>
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<td>.997</td>
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<tr>
<td>6</td>
<td>1.818</td>
<td>61.44</td>
<td>4.257</td>
<td>9.67</td>
<td>351.1</td>
<td>.998</td>
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<tr>
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<td>1.522</td>
<td>60.83</td>
<td>5.345</td>
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<td>144.1</td>
<td>.998</td>
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<tr>
<td>8</td>
<td>1.670</td>
<td>60.17</td>
<td>7.001</td>
<td>49.90</td>
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<td>1.069</td>
<td>60.50</td>
<td>6.657</td>
<td>49.95</td>
<td>108.4</td>
<td>.999</td>
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<tr>
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<td>1.550</td>
<td>61.12</td>
<td>8.128</td>
<td>60.91</td>
<td>152.0</td>
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<tr>
<td>11</td>
<td>1.216</td>
<td>60.77</td>
<td>8.640</td>
<td>64.69</td>
<td>125.9</td>
<td>1.000</td>
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</tbody>
</table>

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 \( pK_{II}^u \) (\( pK_{II}^u = -\log K_{II}^u \)) value for each calorimetric run. \( K_{II}^u \) is not a true equilibrium constant, but a function of ionic strength, and is defined as
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 $K^u$ by:

\[ K^{II} = K^u \frac{f_{S^\equiv}}{f_{HS^-}} \]  

where $f_{S^\equiv}$ and $f_{HS^-}$ refer to the respective activity coefficients. Assuming $\Delta H^o$ 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 $K^{II}$ 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:

\[ (Na^+) = (OH^-) + (HS^-) + 2(S^\equiv) \]  
\[ a_{H^+} = \frac{1.008 \times 10^{-14}}{(OH^-) f_{OH^-}} \]

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 ($\mu = 0.01$ 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 $\mu = 0.1$ equals the heat of dilution for 0.1 M NaOH. Then neglecting the H$_2$S heat of dilution, approximating that of NaHS as equal to NaOH, and that of Na$_2$S as equal to Na$_2$SO$_4$, we define:

\[ Q' = \text{heat evolved for } B \text{ moles NaOH in } D \text{ moles of } H_2O \text{ to infinite dilution} \quad (6) \]

\[ Q'' = \text{heat evolved for } E \text{ moles Na}_2\text{SO}_4 \text{ in ionic strength } \mu \text{ to } \mu \quad (7) \]

\[ Q''' = (B-2E) \text{ moles NaOH in ionic strength } \mu \text{ to } \mu \quad (8) \]

\[ Q^0 = Q - Q' + Q'' + Q''' \quad (9) \]

The above dilution heats were obtained from the National Bureau of Standards tables for the heats of formation of NaOH and Na$_2$SO$_4$. 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$_2$O \[ \Delta H_f = -107.409 \text{ kcal.} \]

1 mole NaOH in 2.256 moles H$_2$O \[ \Delta H_f = -107.397 \text{ kcal.} \]

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.)
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:

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

(10)

Rearranging gives:

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

(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 $\Delta H^o_{H_2O}$ (the standard heats of formation of $H_2S_{aq}$, $OH^-$ and $H_2O$) were obtained from Latimer.14
The values obtained above for $\Delta H_{S}^{\circ}$ and $\Delta H_{\text{HS}}^{\circ}$ along with $K^I$ and $K^\text{II}$ for $\text{H}_2\text{S}$ 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 $K^\text{II} = 1.3 \times 10^{-13}$ (from the extrapolated value of $pK_u^{\text{II}}$ 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 $pK_u^{\text{II}}$ and 0.1 pK units in the extrapolated value, $pK_u^{\text{II}}$.

Using our values for $\Delta F^\circ$, the potential of the sulfide−sulfur couple is

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

### TABLE III

<table>
<thead>
<tr>
<th></th>
<th>$\text{HS}^-$</th>
<th>$\text{S}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta F^\circ$</td>
<td>3.00</td>
<td>20.6 ± 2</td>
</tr>
<tr>
<td>$\Delta H^\circ$</td>
<td>$-4.10 \pm .08$</td>
<td>7.8 ± .8</td>
</tr>
<tr>
<td>$S^\circ_{\text{eu}}$</td>
<td>15.0 ± 4</td>
<td>-4 ± 3</td>
</tr>
</tbody>
</table>

Acknowledgment. We would like to thank Dr. William L. Jolly for many helpful discussions in connection with this work.
REFERENCES


