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THE HEAT OF DISSOCIATION OP Big

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THE HEAT OF DISSOCIATION OF Bi$_2$

Elizabeth Brackett and Leo Brewer

March 8, 1957

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ABSTRACT

Widely different values are reported for the heat of dissociation of Bi$_2$. However, if the data are recalculated by use of the third-law method, the values are found to agree, giving a dissociation energy for Bi$_2$ of 47 ± 1 kcal. The vapor-pressure data are then re-evaluated to give

$\Delta H_{298}^\circ$ for Bi = 49.5 ± 1 kcal,

and

$\Delta H_{298}^\circ$ for Bi$_2$ = 52.5 ± 2 kcal.
THE HEAT OF DISSOCIATION OF Bi₂
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It is difficult to evaluate the vapor-pressure data of bismuth to obtain the heat of vaporization, because the dissociation energy of Bi₂, and thus the proportion of Bi to Bi₂, is not well known. The spectroscopic value is the most generally accepted. The Birge-Sponer extrapolation for the first excited state yields 39.2 kcal, and a similar extrapolation for the ground state (which usually gives a value somewhat high) gives 42.7 kcal. Owing to the poor resolution of the spectroscopic work, band heads instead of band origins had to be used for the extrapolation. Therefore one should ascribe considerable uncertainty to the value of the dissociation energy. If the dissociation energy is 39.2 kcal, then Bi is much more important than Bi₂, its pressure being at least 20 times that of Bi₂ throughout the temperature region 700° to 1200° K. Other experiments, however, indicate that there is a higher proportion of Bi₂ than this.

With a modification of the Knudsen effusion cell using a torsion balance, Yoshiyama was able to measure the average molecular weight and the total vapor pressure of bismuth. He found that there were roughly equal amounts of Bi and Bi₂, and obtained a value of 69.9 kcal for the dissociation energy of Bi₂ in the range 900° to 1000° K. Ko determined the relative abundance of Bi and Bi₂ by analyzing the velocity distribution in a beam emerging from a Knudsen cell. This method yielded a value of 77.1 ± 1 kcal for the dissociation energy. 3

By subjecting a beam of bismuth vapor to a nonuniform magnetic field, Leu was able to obtain the relative amounts of Bi and Bi₂ in the beam. Leu calculated 60 ± 15 kcal for the dissociation energy, but failed to account for the fact that the gas effusing from a Knudsen cell is not of the same composition as the equilibrium vapor. Fraser recalculated Leu's data, and reported 26.5 ± 12 kcal. However, as Ko pointed out, 3 this last value is in error by a factor of 2.3, i.e., it should be 61 ± 27 kcal.

In all three of these experiments the heat of dissociation was obtained from the slope of a plot of -log K vs 1/T. This method can lead to results seriously in error owing to small temperature-dependent errors in the data. This is especially bad when the temperature region covered is fairly small (in these cases, about 100°). This effect can be avoided, or at least minimized, if the dissociation energy is calculated by the third-law method. The necessary data—a tabulation of (Fₜ - H₂⁰₈) / T for monatomic, diatomic, liquid, and solid bismuth—are given by Stull and Sinke. 6 The third-law calculations yield the following results for the dissociation energy of Bi₂:
In the recalculation of Leu's data, the vapor-pressure measurements by Yoshiyama and Ko were used, since Leu's were undoubtedly in error. The uncertainties listed cover, in each case, the entire spread of the values calculated. There is one other possible source of error, in the values of the \((F_\text{r} - H_{298})/T\) function for Bi\(_2\). The value for the rotational contribution to the entropy is based on an estimate of the internuclear distance. However, at most, this would lead to an error of only 1 kcal in \(\Delta H_{298}\).

Therefore it appears that 47 kcal is the best value for the dissociation energy. This means that both Bi and Bi\(_2\) are about equally important throughout the range 700\(^\circ\) to 1200\(^\circ\).

In re-examination of the vapor-pressure data, the \(\Delta H\) of sublimation for both Bi and Bi\(_2\) can be calculated directly from Yoshiyama's data, again using the third-law method. This gives 53.3 kcal for \(\Delta H_{298}\) of sublimation of Bi\(_2\), and 50.1 kcal for Bi. An extrapolation of Yoshiyama's values for the total vapor pressure gives figures that agree very well with Ko's data at a higher temperature. At lower temperatures (700\(^\circ\) to 800\(^\circ\) K) O'Donnell's values are higher by a factor of about 2 than those calculated using the \(\Delta H\)'s of sublimation determined from Yoshiyama's data. This factor of two corresponds to a difference of 1 kcal in the heat of sublimation. Considering all the data, the best values for the heats of sublimation are:

\[
\begin{align*}
\text{Bi} & \quad \Delta H_{298} = 49.5 \pm 1 \text{ kcal}, \\
\text{Bi}_2 & \quad \Delta H_{298} = 52.5 \pm 2 \text{ kcal}.
\end{align*}
\]

The temperatures (\(^\circ\)K) for various partial pressures between 10\(^{-6}\) atmos and 1 atmos of Bi and Bi\(_2\) were calculated from these heats of sublimation and are as follows:

<table>
<thead>
<tr>
<th>Vapor Species</th>
<th>Pressure (atmos)</th>
<th>(10^{-6})</th>
<th>(10^{-5})</th>
<th>(10^{-4})</th>
<th>(10^{-3})</th>
<th>(10^{-2})</th>
<th>(10^{-1})</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td></td>
<td>887(^\circ)</td>
<td>973(^\circ)</td>
<td>1080(^\circ)</td>
<td>1210(^\circ)</td>
<td>1380(^\circ)</td>
<td>1610(^\circ)</td>
<td>1950(^\circ)</td>
</tr>
<tr>
<td>Bi(_2)</td>
<td></td>
<td>874(^\circ)</td>
<td>960(^\circ)</td>
<td>1060(^\circ)</td>
<td>1210(^\circ)</td>
<td>1400(^\circ)</td>
<td>1660(^\circ)</td>
<td>2060(^\circ)</td>
</tr>
</tbody>
</table>

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References

   American Chemical Society, 1956 p. 55-57.