THE HEATS OF VAPORIZATION OF THE LIQUID HALOGEN HYDRIDES AND OF SULPHURETTED HYDROGEN

BY P. H. ELLIOTT AND D. MCINTOSH

Steele and McIntosh have calculated the value of the heats of vaporization of the hydrides of the halogens, of sulphur and of phosphorus from the slope of the vapor pressure curve, by means of the well-known Clausius equation

\[ \frac{dp}{dT} = \frac{PW}{RT^2} \]

where \( \frac{dp}{dT} \) represents the change of pressure with temperature, \( P \) the vapor pressure, \( R \) the gas constant, \( T \) the temperature on the absolute scale, and \( W \) the latent heat of vaporization. Being unaware of any direct measurements of the values of \( W \) we have attempted to determine these in a simple way. This was undertaken, not merely to ascertain whether the calculated values were correct, but on account of another research for which a fairly accurate knowledge of these numbers was of importance.

**Method and Apparatus**

The apparatus used was a modification of that described originally by Marshall and Ramsay, and since used by many investigators. It is shown in the accompanying figure, and consists of a small Dewar tube (A) used to contain the liquid under examination. This vacuum vessel is closed by a double bored rubber stopper through which pass the leads of the heating coil enclosed in glass, and an arm fitted with a three-way tap (B), the tubes of which are bent and terminate in two small cups, one of which (C) is indicated in the figure. The electrical energy used to heat the coil was measured by Weston.

---

instruments calibrated by means of a copper voltameter and a Weston cell.

![Diagram of experimental setup]

**Hydrogen Chloride**

A few moistened beads\(^1\) were placed in the bottom of the vacuum tube, and the apparatus was filled with the acid (boiling-point \(-83^\circ\)) to about two inches above the heating coil. A little mercury was put in the cups, and these were immersed in funnel-shaped tubes (D) filled with water. The vacuum tube was placed in a bath of carbon dioxide and ether (boiling-point \(-78^\circ\)) and a very small current\(^2\) passed through the heating coil to prevent superheating. The acid boiled away and was absorbed by the water. When a steady rate of evaporation was reached, the tap was turned and the gas was absorbed for a five-minute period. (This vaporization we shall refer to as "natural evaporation."\(^3\)) The tap was again turned, a current of from 0.5 to 1 ampere passed through the coil for one minute, and the quantity of acid evaporated in five minutes was absorbed as before. In this way the "natural evaporation" was determined immediately before and after each experiment. Any great variation in this evaporation


\(^2\) The energy supplied was about two percent of that actually used in the experiment.
pointed to some source of error, and the determination was discarded. The acid was titrated with standard ammonia.

The results for hydrochloric acid were: 14.7, 14.8, 15.3; mean $14.9 \times 10^{10}$ ergs for each gram molecule evaporated.

**Hydrobromic Acid**

The temperature of the carbonic acid bath being below the boiling-point of the hydrogen bromide; the vacuum vessel was covered with asbestos wound with fine platinum wire, through which a current sufficient to maintain slow evaporation was sent. In other respects the apparatus was the same as that previously described. The values found were 17.6, 17.3, 16.9; mean $17.3 \times 10^{10}$ ergs per gram molecule.

**Hydriodic Acid**

The calorimeter was placed inside a large silver vacuum vessel and covered with natural wool. The values given by these experiments were: 18.8, 18.9, 18.7; mean $18.8 \times 10^{10}$ ergs for the vaporization of 128 grams of acid.

**Hydrogen Sulphide**

The apparatus employed was that used in the hydrobromic acid experiments. The gas was absorbed by a strong potassium hydrate solution in Geissler bulbs. The results were: 19.4, 19.4, 19.2, 20.3; mean $19.6 \times 10^{10}$ ergs.

In all cases evaporation took place at pressures a little higher than that of the atmosphere, usually at 77 cm of mercury. The following table gives the values of $W$, calculated for 76 cm, and those found by experiment.

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid</td>
<td>$14.8 \times 10^{10}$ ergs</td>
<td>$14.9 \times 10^{10}$ ergs</td>
</tr>
<tr>
<td>Hydrobromic</td>
<td>$17.4 \times 10^{10}$</td>
<td>$17.3 \times 10^{10}$</td>
</tr>
<tr>
<td>Hydriodic</td>
<td>$20.7 \times 10^{10}$</td>
<td>$18.8 \times 10^{10}$</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>$19.3 \times 10^{10}$</td>
<td>$19.6 \times 10^{10}$</td>
</tr>
</tbody>
</table>

The calculated values are in fair agreement with those determined experimentally except in the case of hydriodic...
acid. Whether this variation is due to an error in the determination of the vapour pressure curve, which seems unlikely, or to a defect in the method of measuring \( W \), such as too large natural evaporation, we shall attempt to discover by new experiments.

The impossibility of determining \( W \) from the van't Hoff equation,

\[
\frac{0.02 T^2}{K} = W,
\]
on account of the association or dissociation of the solutes has been pointed out in a previous paper.

*McGill University, Montreal,*

*December, 1907.*