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The free energy of formation of pyridine may be calculated from the entropies and the heats of combustion of pyridine and the elements of which it is composed. To determine the entropy of pyridine at 298.1°K. it was necessary to measure its heat capacity over the temperature range, 90° to 298.1°K., its heat of fusion, and its melting point, the remaining data being available in the literature.

The calorimetric apparatus is similar to that of Latimer and Hoenshel (1). It consists of a cylindrical calorimeter, 12 cm. high and 6 cm. in diameter, a cylindrical brass shield, and a lead block. The calorimeter, containing the pyridine, is placed inside the shield and both suspended from the lead block. These three pieces hang inside a steel cylinder which is connected to a mercury diffusion pump. When the apparatus was in use the air pressure inside the steel cylinder was maintained at less than 10^{-5}mm. to insure adequate thermal insulation of the calorimeter. The steel cylinder is suspended in a Dewar flask containing the refrigerant.

The temperatures of the block, shield, and calorimeter were measured with copper-manganin thermels calibrated against a Bureau of Standards platinum resistance thermometer. The voltages of the thermels and the electrical energy for heating the calorimeter were measured with a Leeds and Northrup "Type Super K" potentiometer.

Table 1. The Molar Heat Capacity of Pyridine

°K.	C_p cals. per degree	°K.	C_p cals. per degree
90.0	18.40	203.1	22.62
93.1	18.41	213.1	23.76
103.1	18.42	223.1	24.98
113.1	18.44	233.1	26.35
123.1	18.51	243.1	27.75
133.1	18.61	253.1	29.01
143.1	18.77	263.1	30.06
153.1	19.02	273.1	30.82
163.1	19.43	283.1	31.35
173.1	20.01	293.1	31.72
183.1	20.72	298.1	31.86
193.1	21.61		

The pyridine was distilled three times over dry sodium hydroxide.

The heat of fusion of pyridine was found to be 741 calories per mol, and the melting point 230.38°K. The heat capacity of the pyridine was measured at temperature intervals of four to ten degrees. These results were plotted on a large scale, a smooth curve was drawn through the experimental data, and heat capacity values were read from this curve for various even temperatures. These values are recorded in Table I.

The entropy of pyridine at 298.1°K. may be calculated by means of the relation,

$$(1)\quad S_{298.1} = S_{90} + \int_{90}^{T_f} C_p \text{ (crystals) } dT/T + \int_{T_f}^{298.1} C_p \text{ (liquid) } dT/T + Q_f/T_f.$$

The entropy of the pyridine at 90°K., S_{90}, is determined by the method of Kelley, Parks and Huffman.[2] They found that the heat capacity-temperature curves from 0° to 120°K. for organic compounds may be divided into two classes, one for aliphatic, the other for cyclic compounds. From the data for these classes two curves were constructed which are called the curves for the standard aliphatic and the standard cyclic compound. The value of the heat capacity per mol, C_p°, of the standard compound and the heat capacity per mol, C_p, of any actual cyclic compound at the same temperature are related by the equation,

$$(2)\quad C_p = (A + BT)\, C_p^\circ,$$

where T is the absolute temperature and A and B are constants characteristic of the substance. A and B are determined by substituting the values of C_p and C_p° at two temperatures, such as 90° and 120°K., and solving the two equations simultaneously for A and B. A and B were found to be 1.900 and –0.006720, respectively. S_{90} may now be expressed in terms of A, B, and C_p° as follows

$$(3)\quad S_{90} = \int_{0}^{90} C_p dT/T$$

$$= A \int_0^{90} C_p^\circ dT/T + B \int_0^{90} C_p^\circ dT$$

$$= A\, S_{90}^\circ + B \int_0^{90} C_p^\circ dT.$$

By graphic integration Kelley, Parks, and Huffman[2] have found the value of S_{90}° to be 13.7 E. U. and that of the integral to be 697 cals. for the standard cyclic compound. Substituting these values in the above equation we obtain for the entropy of pyridine at 90°K. 21.35 E. U.

The two terms involving the integrals in (1) were evaluated graphically by means of a polar planimeter. The increase in entropy on heating pyridine from 90° to 298.1°K. is 25.72 E. U. The entropy of fusion, calculated by dividing the heat of fusion of one mol, 741 cals., by the absolute temperature of the melting point, 230.38°K., is 3.22 E. U. Thus, by equation (1) the entropy of pyridine at 298.1°K. is 50.29 E. U.

Taking the entropy of C as 1.36 E. U. per mol,[3] that of H_2 as 31.23 E. U.[4], and that of N_2 as 45.78 E. U. per mol,[4] we find the entropy of formation of pyridine at 298.1°K. to be –57.48 E. U.

The heat of combustion of pyridine is 659,900 cals. per mol, of C 94,380 cals. per mol, and of H_2 78,380 cals. per mol.[5]

Employing the fundamental thermodynamic equation, $\Delta F = \Delta H - T\,\Delta S$, we obtain the free energy of formation of pyridine at 298.1°K., $\Delta F = 34{,}100$ cals. per mol.

The thermal data for pyridine are listed in Table II.

Table II. Thermal Data for Pyridine

Entropy of crystals at 90°K.	+ 21.35 E. U.
Entropy of fusion	+ 3.22 E. U.
ΔS from 90° to 298.1°K.	+ 25.72 E. U.
Entropy at 298.1°K.	+ 50.29 E. U.
ΔS at 298.1°K.	— 57.48 E. U.
ΔH at 298.1°K.	+ 17,050 cal.
ΔF at 298.1°K.	+ 34,100 cal.
ΔH of fusion	741 cal.
Melting point	230.38°K.

Summary

The heat capacity of pyridine has been determined for temperatures between 90° and 298.1°K. Its heat of fusion and melting point have been measured. From this data the free energy and entropy of formation of pyridine have been calculated.

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