in explaining changes in stability and color of the amylose–iodine complex with changes in amylose chain length is pointed out, and some application of the proposal is made to other blue iodine complexes.

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[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

# Thermal Data. XVIII. The Heat Capacity, Heat of Fusion, Entropy and Free Energy of Ethylbenzene

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Some time ago this Laboratory began a research program involving the study of certain thermal properties of hydrocarbons. Because of the importance of ethylbenzene in hydrocarbon chemistry a study was made of its low temperature thermal properties. In this paper we present the results of this investigation. These data have been utilized to calculate the entropy and free energy of liquid ethylbenzene at 298.16°K.

**The Ethylbenzene.**—The material used in this investigation was supplied to us in the purified condition by the Shell Development Co. An estimate of the liquid soluble–solid insoluble impurity was made from data obtained by observing the equilibrium temperatures corresponding to known fractions of the material in the solid and liquid form. The impurity estimated from the above data was 0.070 mole per cent.

**Experimental.**—The experimental method has been described in a recent paper by Ruehrwein and Huffman[2] and only a brief description need be given here. An adiabatic calorimetric system was used in which the material under investigation was contained in a sealed copper calorimeter. A measured quantity of electrical energy was supplied to the calorimeter and at all times during the measurements the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for the determination of the energy and of the resistance of the thermometer were made on a White double potentiometer in conjunction with a high sensitivity galvanometer and accurately calibrated resistances. The precision of our measurements is in general better than 0.1% and we believe that above 30°K. the accuracy should be about the same as the precision. The energy measurements were made in terms of the international joule and were converted to the conventional calorie by dividing by 4.1833.

The ethylbenzene was distilled into the calorimeter in an air-free system. The gas space was filled with helium at one atmosphere pressure at room temperature and the calorimeter was then sealed by the application of a drop of soft solder.

The results of the heat capacity measurements are given in Table I. Most of the temperature range was covered at least twice and the results of the measurements in the different series were in excellent agreement. In Table II we have listed the values of the heat capacity at integral temperatures as selected from a smooth curve through all of the data.

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(2) Ruehrwein and Huffman, THIS JOURNAL, 65, 1620 (1943).

TABLE I

MOLAL HEAT CAPACITY OF ETHYLBENZENE

Molecular weight = 106.160; 0°C. = 273.16°K.

| $T_M$, °K. | $\Delta T$ | $C_p$ cal./degree | $T$, °K. | $\Delta T$ | $C_p$, cal./degree |
|---|---|---|---|---|---|
| | Crystals | | 109.43 | 6.235 | 17.960 |
| 13.34 | 1.351 | 1.013 | 115.01 | 16.868 | 18.604 |
| 15.01 | 1.973 | 1.380 | 116.53 | 7.950 | 18.749 |
| 16.91 | 1.831 | 1.846 | 126.79 | 12.578 | 19.859 |
| 19.72 | 4.067 | 2.585 | 133.33 | 19.762 | 20.629 |
| 19.84 | 4.030 | 2.638 | 138.98 | 11.814 | 21.222 |
| 23.90 | 4.098 | 3.809 | 150.47 | 11.167 | 22.482 |
| 24.09 | 4.676 | 3.859 | 154.21 | 22.013 | 22.952 |
| 27.99 | 4.080 | 4.965 | 160.62 | 9.130 | 23.677 |
| 28.40 | 3.946 | 5.086 | 166.84 | 3.244 | 24.622[a] |
| 32.28 | 4.493 | 6.150 | 170.04 | 3.158 | 25.464[a] |
| 32.97 | 5.186 | 6.333 | 173.13 | 3.022 | 26.926[a] |
| 37.07 | 5.085 | 7.374 | | Liquid | |
| 38.59 | 4.217 | 7.728 | 181.51 | 9.249 | 37.648 |
| 42.06 | 4.889 | 8.513 | 190.70 | 9.152 | 37.936 |
| 46.39 | 9.538 | 9.375 | 199.81 | 9.056 | 38.257 |
| 47.14 | 5.288 | 9.524 | 208.81 | 8.954 | 38.626 |
| 52.28 | 4.994 | 10.480 | 216.27 | 9.601 | 38.982 |
| 55.96 | 9.605 | 11.120 | 218.15 | 9.733 | 39.048 |
| 57.76 | 5.971 | 11.436 | 221.14 | 17.426 | 39.211 |
| 62.40 | 3.916 | 12.177 | 225.80 | 9.473 | 39.446 |
| 63.91 | 6.284 | 12.410 | 234.98 | 10.249 | 39.989 |
| 66.21 | 3.696 | 12.755 | 244.70 | 10.074 | 40.532 |
| 71.14 | 6.165 | 13.445 | 255.52 | 11.553 | 41.246 |
| 77.09 | 5.741 | 14.272 | 266.96 | 11.346 | 42.016 |
| 83.19 | 6.452 | 15.028 | 277.41 | 9.556 | 42.787 |
| 89.95 | 7.063 | 15.874 | 286.89 | 9.406 | 43.504 |
| 96.82 | 6.692 | 16.617 | 296.23 | 9.254 | 44.275 |
| 103.37 | 6.413 | 17.318 | 305.41 | 9.113 | 44.994 |
| 103.43 | 5.766 | 17.320 | | | |

[a] These values include premelting.

**The Melting Point.**—In Table III we have given the equilibrium temperatures corresponding to the known fraction of calorimeter contents in the liquid state.[3] Utilizing these data we have calculated the melting point of the mixture in the calorimeter and also for pure ethylbenzene. The values of the melting point given in the last column of Table III were calculated, by an approximate method, on basis of an impurity of 0.070 mole per cent. From these data we conclude that the melting point

(3) The value given as per cent. liquid is actually the per cent. of the calculated heat of fusion of the contents of the calorimeter but for practical purposes this may be taken as representing the per cent. of the ethylbenzene in the liquid form.

TABLE II

MOLAL HEAT CAPACITY OF ETHYLBENZENE AT INTEGRAL TEMPERATURES

| T, °K. | $C_p$, cal./degree | T, °K. | $C_p$, cal./degree |
|---|---|---|---|
| Crystals | | 130 | 20.23 |
| 13 | 0.94 | 140 | 21.34 |
| 15 | 1.39 | 150 | 22.47 |
| 20 | 2.68 | 160 | 23.61 |
| 25 | 4.12 | 170 | 24.75 |
| 30 | 5.53 | 175 | 25.32[a] |
| 35 | 6.85 | Liquid | |
| 40 | 8.06 | 180 | 37.61 |
| 45 | 9.11 | 190 | 37.91 |
| 50 | 10.06 | 200 | 38.26 |
| 55 | 10.96 | 210 | 38.68 |
| 60 | 11.80 | 220 | 39.16 |
| 65 | 12.57 | 230 | 39.68 |
| 70 | 13.30 | 240 | 40.25 |
| 75 | 13.99 | 250 | 40.88 |
| 80 | 14.64 | 260 | 41.54 |
| 85 | 15.26 | 270 | 42.24 |
| 90 | 15.86 | 280 | 42.98 |
| 100 | 16.96 | 290 | 43.76 |
| 110 | 18.04 | 300 | 44.56 |
| 120 | 19.14 | | |

[a] Extrapolated.

of pure ethylbenzene is 178.17 ± 0.03°K. We wish to point out that the observed value for the melting point when 5.7% of the ethylbenzene was liquid is not in agreement with the calculated value. This may be taken as indicating a deviation from the laws of the ideal dilute solution.

TABLE III

MELTING POINT SUMMARY

| % Melted | Obs. m. p., °K. | M. p., °C. (calcd.)[a] |
|---|---|---|
| 5.7 | 177.880 | 177.814 |
| 25.0 | 178.090 | 178.090 |
| 45.4 | 178.122 | 178.124 |
| 75.5 | 178.142 | 178.142 |
| 93.5 | 178.147 | 178.147 |
| 100.0 | (178.149) | 178.149 |
| Pure | 178.169 ± 0.03° | |

[a] These values calculated on the basis that the solid insoluble-liquid soluble impurity is 0.070 mole per cent.

We have also determined the heat of fusion of ethylbenzene and the results of two determinations of this quantity are given in Table IV. It is to be noted that this quantity is somewhat arbitrary since it is impossible to uniquely determine the true heat capacity curve in the region below the melting point. This uncertainty in the heat of fusion will have only a minor effect on the entropy calculated from these data.

TABLE IV

FUSION DATA SUMMARY

| Fusion | Cal./mole | Dev. |
|---|---|---|
| 1 | 2189.1 | −1.2 |
| 2 | 2191.5 | +1.2 |
| Mean | 2190.3 | |

We have also calculated the entropy of liquid ethylbenzene at 298.16°K. The results of these calculations are summarized in Table V. The entropy of ethylbenzene

TABLE V

THERMAL DATA FOR ETHYLBENZENE, SUMMARY ENTROPY

$S$ (0–14°) = 0.3984 (Debye 6° freedom, $\theta$ = 128)

$\Delta S$ (14.0–178.17) = 27.604 graphical

$\Delta S$ (fusion, 178.17) = 12.293

$\Delta S$ (178.17–298.16) = 20.654

$S$ (Liquid 298.16) = 60.95 ± 0.10 cal. degree$^{-1}$ mole$^{-1}$

was also calculated by Huffman, Parks and Daniels[4] from the results of their low temperature measurements which extended only down to 90°K. They obtained a value of 61.2 E. U./mole in excellent agreement with our more accurate value of 60.95 E. U./mole. Prosen and Rossini have recently determined the heat of combustion of ethylbenzene and give the value $\Delta H^0_R$ = −1091.03 kcal./mole.[5] This datum has been utilized in conjunction with the entropy reported in this paper and other data to calculate the free energy of formation of liquid ethyl benzene. The data are summarized in Table VI. In

TABLE VI

THE MOLAL FREE ENERGY OF FORMATION OF LIQUID ETHYLBENZENE AT 298.16°K.

| Heat of comb., $\Delta H°$, kcal. | $\Delta H^0_f$, kcal. | $\Delta S$, cal./degree | $\Delta F^0_f$, kcal. |
|---|---|---|---|
| −1091.03 | −2.98 | −106.08 | 28.65 |

making this calculation we have used the values 1.36[6] and 31.23[7] E. U. for the entropies of graphitic carbon and hydrogen gas, respectively, and the values 68318.1[8] and 94,052[9] calories for the molal heats of formation at 25° of liquid water and gaseous carbon dioxide, respectively.

In conclusion we wish to express our thanks to the Shell Development Co. for supplying the sample of ethylbenzene and also for financial assistance which made this investigation possible.

## Summary

The heat capacity, heat of fusion and melting point of ethylbenzene have been measured.

The molal entropy and free energy of formation of liquid ethylbenzene at 298.16°K. have been calculated, $S$ = 60.95 cal./degree and $\Delta F^0_f$ = 28.65 kcal.

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(4) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930).

(5) Prosen and Rossini, private communication, to be published in *J. Research Nat. Bur. Standards.*

(6) Jacobs and Parks, THIS JOURNAL, **56**, 1513 (1934).

(7) Giauque, *ibid.*, **52**, 4816 (1930).

(8) F. D. Rossini, *Bur. Standards J. Research*, **22**, 407 (1939).

(9) Prosen and Jessup and Rossini, private communication, to be published in *J. Research Natl. Bur. Standards.*