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The Heat Capacity and Entropy of Beta-Lactose

BY EDWARD F. FURTSCH[1] WITH GEBHARD STEGEMAN

In this investigation the heat capacity of beta-lactose was measured over the temperature range from 83 to 298°K., and from these values and certain extrapolation data the entropy of the compound was calculated. The free energy of formation of the compound was also calculated by the use of the best combustion data available.

The apparatus employed was the same as that used by Haas and Stegeman.[2] The values of the molar heat capacity are shown in Table I. For the lower temperature range these values show an average deviation of 0.2 of one per cent. from the best curve drawn through them. The maximum deviation is 1.10%, which occurred in one measurement. At higher temperatures the average deviation rises somewhat, but in few cases is it more than 0.4 of one per cent.

The beta-lactose was of the best grade obtainable from the Eastman Kodak Company. It showed an initial $(\alpha)^{20}\text{D}$ 35.2 and final $(\alpha)^{20}\text{D}$ 55.0. Hudson's[3] test for the presence of the hydrate showed the sample to be perfectly anhydrous. Other tests show the absence of starch and sucrose. The sample was dried in an oven at 100° for twenty-four hours before being placed in the calorimeter. The weight of the sample was 92.96 g., not reduced to a vacuum basis.

Entropy Calculation

The entropy of beta-lactose was evaluated graphically between the temperatures of 90 and 298°K. and amounted to 70.4 entropy units. The extrapolation method of Kelly, Parks and Huffman[4] was used in estimating the entropy from 0 to 90°K., and gave a value of 26.00 entropy units. The sum of these two values amounts to 96.4 entropy units. If the generally accepted values for the entropies of the constituent elements ($C = 1.36$,[5] $^1/_2H_2 = 15.615$,[6] $^1/_2O_2 = 24.52$[7]), are employed $\Delta S_{298} = -533.17$ entropy units. The error in this value is difficult to estimate with assurance, but will depend largely on the accuracy of the measurements on the compound. If the extrapolation method of Parks is as reliable as it apparently is for other compounds of a similar type, then the error should not exceed one entropy unit.

The free energy of beta-lactose was then calculated by means of the fundamental equation $\Delta F = \Delta H - T\Delta S$. The value of ΔH_{298} for the compound was obtained from combustion data. The best available value for the heat of combustion of anhydrous beta-lactose appears to be that reported by Stohmann and Langbein,[8] and this value is 1,350,800 cal. at 18°. In making the calculation for the heat of formation, Rossini's[9] values, 94,240 and 68,313, respectively, for carbon dioxide and water, were used. The value for ΔH_{298} then appears as $-532,400$ cal. Using these values in the fundamental equation gives $\Delta F_{298} = -373,400$ cal. The uncertainty in this value is largely dependent upon the accuracy of the

TABLE I

HEAT CAPACITY OF BETA-LACTOSE PER MOLE

C_p in calories per mole

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
82.58	31.04	161.05	54.51	233.58	78.22
86.51	31.75	164.48	55.59	237.94	79.32
90.59	32.77	165.85	56.05	242.31	80.19
94.24	33.77	168.48	57.28	245.46	81.86
98.00	34.71	171.08	57.75	247.84	81.59
101.38	35.70	173.80	58.86	250.67	83.14
103.89	36.27	176.55	59.71	253.50	84.04
107.58	37.60	180.39	61.35	255.46	84.22
113.56	39.17	184.16	62.12	257.90	85.12
118.06	40.64	186.59	62.77	260.09	86.23
121.89	41.97	188.63	63.43	262.18	86.61
124.93	42.36	191.29	64.23	264.42	87.47
127.65	43.66	194.02	65.33	267.82	88.21
130.49	44.57	196.68	66.30	270.16	89.04
134.08	45.63	199.48	67.20	272.22	89.94
138.66	47.10	202.04	68.06	274.16	90.91
141.47	48.10	205.40	69.13	276.65	91.28
144.73	49.38	209.04	70.16	278.63	92.06
147.29	50.05	212.23	71.42	282.33	93.27
149.84	50.52	214.65	72.17	284.05	93.96
152.36	51.64	220.50	73.83	285.80	94.81
155.34	52.95	222.90	74.71	291.06	95.81
158.21	53.74	225.07	75.39	292.70	96.81
		227.88	76.47	295.87	98.00
		230.93	76.92	298.44	97.58

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(1) From a part of the thesis submitted by Edward F. Furtsch to the Graduate School of the University of Pittsburgh in partial fulfilment of the degree of Doctor of Philosophy.

(2) Haas and Stegeman, THIS JOURNAL, **58**, 879 (1936).

(3) Hudson and Brown, *ibid.*, **30**, 964 (1908).

(4) Kelly, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

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

(6) Giauque, *ibid.*, **52**, 4825 (1930).

(7) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

(8) Stohmann and Langbein, *J. prakt. Chem.*, [2] **45**, 305 (1892).

(9) Rossini, *Bur. Stds. J. Research*, **6**, 34 (1931); **13**, 28 (1934).

combustion data, which may be in error by as much as 5 kcal. per mole.

Table I presents the measured values of the specific heat of the compound expressed in calories per mole with the corresponding temperatures. The factor used for converting electrical energy to calories was 0.23895.

Summary

1. The heat capacity of beta-lactose was measured over the temperature range from 83 to 298°K.

2. The value of the entropy of the compound has been estimated from these measurements and certain other data.

3. The free energy of formation of the compound has also been calculated by the use of the entropy and the combustion data which appeared to be the most reliable.

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Reactivity and Influence of Fluorine in Aliphatic Compounds

BY ALBERT L. HENNE AND THOMAS MIDGLEY, JR.

Organic compounds containing fluorine, quite often fail to follow empirical generalizations derived from the behavior of similar organic combinations containing some other halogen in place of fluorine. Many such contradictions are particularly emphasized by a study of the stability and the reactivity of the simple aliphatic fluorides. The preparation and physical properties of all the compounds used as a basis for the present study have been reported by Swarts (see Beilstein) and by workers of this Laboratory.[1] All of Swarts' data used herein have been verified.

The discovery of the inertness of CCl_2F_2 was a distinct surprise to organic chemists. The fluorine in this molecule is not only quite inert but its presence seemingly strengthens the C–Cl bonds so that the chlorine is much less reactive than in any other similar chlorine compound such as CH_2Cl_2 or CBr_2Cl_2. This, naturally, suggests that the C–F bond is unusually strong; it is therefore again surprising to find that great stability and inertness is not an invariable function of the C–F bond.

The first four members of the normal alkyl monofluoride series are stable and distil without decomposition. Members of the series higher than amyl fluoride show a tendency to decompose spontaneously to hydrogen fluoride and ethylenic hydrocarbons. This tendency increases with the structural complexity and becomes so marked in secondary and tertiary fluorides that it is impossible to prepare them free from olefins. Similarly cyclohexyl fluoride[2] decomposes spontaneously to cyclohexylene.

Monofluorides of saturated hydrocarbons hydrolyze quite easily. It is to be noted that they are more sensitive to hydrolysis by concentrated acids than by concentrated bases. Acids act simultaneously in two ways, both saponifying and removing hydrogen fluoride. The experimental conditions determine which effect predominates.

The physiological effect of the alkyl fluorides is a further demonstration of their tendency to lose hydrogen fluoride. Inhalation of a 30% concentration of ethyl fluoride in air (by volume) is needed to produce anesthesia, and is invariably fatal; death is caused by a severe oedema of the lungs and upper respiratory tract; this oedema is characteristic of hydrogen fluoride burns.

The recurrence of a monofluoride group increases the instability of the molecule very markedly: ethylene fluoride decomposes spontaneously to hydrogen fluoride and butadiene at 0°, and merely passing it through water gives ethylene glycol. Similarly 1,2-difluorocyclohexane yields cyclohexadiene at room temperature, and its reaction with water yields 1,2-dihydroxycyclohexane; 1,2-difluorodioxane is likewise unstable.

The stability of a CH_2F group may be affected by the presence of another group in the molecule: for instance, monofluoroethanol and monofluoroacetic acid are quite stable.

A striking improvement in the stability of a molecule containing fluorine and decrease in the reactivity of the halogens is observed when the

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[1] THIS JOURNAL, 56, 1726 (1934); 58, 402, 404 (1936).

[2] Confirming a verbal communication from Dr. Swarts.