

[CONTRIBUTION NO. 378 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Combustion of Some Mono- and Disaccharides

BY THEODORE H. CLARKE^{1,2} AND GEBHARD STEGEMAN

A program has been instituted at this Laboratory for obtaining the thermal data on compounds of physiological interest. Studies are being carried out on carbohydrates and glycerides, and in this paper are presented the combustion data on six carbohydrates.

Method and Apparatus.—Since the proposed course of study will involve only liquids and solids, the "bomb calorimeter" method has been adopted. The determinations were made isothermally, that is, the rise in temperature of the calorimeter is observed while the temperature of the jacket is kept constant.

The calorimeter system was patterned after that of Dickinson.³ A hollow removable head was so arranged that the calorimeter could be surrounded completely by a well-stirred water-bath kept constant to within $\pm 0.002^\circ$. Two ball-bearing mounted stirrers driven by constant speed motors were employed to circulate the water in the jacket and to pump water through the head. The jacket also was provided with a cooling coil for use in warm weather. The calorimeter proper had a stirrer mounted in a side-tube and connected by means of a hard rubber connector to a shaft extending through the head. This stirrer was driven by a belt to the main stirrer shaft.

An "Emerson double-valved bomb" of 516-ml. capacity was used throughout the investigation. Gold-plated electrodes with threaded binding posts, gold-plated crucible support, and gold-plated inner linings for the bomb were employed to eliminate any corrosion. The material to be burned was placed in a platinum cup.

The temperature measuring system consisted of a Bureau of Standards calibrated platinum resistance thermometer, a White double potentiometer, and a type H. S. galvanometer, all supplied by Leeds and Northrup Co. A shunt of seventy ohms was placed across the galvanometer which then had a sensitivity of 0.000005 ohm (0.00005 C) per 0.1 mm. deflection and was quite stable. The galvanometer was used as a deflection instrument.

Burgess-Parr oxygen bomb fuse wire was used to ignite the sample. As the same length of wire and the same source of energy for its ignition were used throughout all the determinations, the heat evolved by the ignition of the wire was included in the heat equivalent of the calorimeter. As in general sugars tend to melt rather than to ignite, a small disk of filter paper was placed on top of the sample to start the combustion. Whatman's No. 42 ashless filter paper, kept in a constant humidity container, having a determined heat of combustion of 3999.2 cal./g. was used. The error for the size of filter paper disk was less than 0.1 cal.

The mass of the calorimeter and water was determined to ± 0.05 g. by means of a large capacity balance having a sensitivity of ± 0.01 g. The mass of the sample was determined to ± 0.00002 g. by means of a good analytical balance. Weighings were made on both arms of the balance to eliminate any differences in the arms of the balance.

The bomb was first evacuated and then filled with commercial oxygen to a pressure of 30 atm.; 3 g. of water was placed in the bomb for each determination.

Units.—The unit of energy used throughout this paper is the defined conventional calorie which has been derived from the international joule by the factor 1 cal. = 4.1833 int. j.^{4,5} The unit of mass is the "gram true mass" which is derived from the mass in air against gold-plated brass weights by the use of a suitable conversion factor.

Errors.—In the calculation of the precision of these determinations the procedure proposed by Rossini⁶ has been used. The errors are defined: "assigned error" on the standardizing substance, $\pm e\%$; error on the standardization or "calibration error" $\pm c\%$; error on the actual determination or "reaction error," $\pm b\%$; and the final precision error, \pm p. e. %. This procedure gives an error larger than the usual "probable error" but as Rossini states, "it seems better because it yields an 'error' which is conservative and reasonable."

Calibration of the Calorimeter

The energy equivalent of the calorimeter was determined by burning benzoic acid (sample No. 39e) supplied by the Bureau of Standards. Benzoic acid has been chosen as the primary standard for combustion calorimetry and the value for the isothermal heat of combustion of this sample is given as 26.419 international kilojoules per gram mass.⁶ In Table I are presented a series of values of the energy equivalent of the calorimeter as determined from the heat of combustion of benzoic acid.⁷ It was not always possible to obtain complete combustion of benzoic acid, but in the cases where carbon appeared it was present in such small quantities as to be impossible to weigh. Any uncertainty due to this effect appears to be within the experimental error.

From the results in Table I, the energy equivalent of the calorimeter has been assigned the value of 2769.1 ± 0.3 cal. per $^\circ\text{C}$. at 25° .

(4) Technical News Bull. Bur. of Standards, No. 156 (1930).

(5) Rossini, *Chem. Rev.*, **18**, 252 (1936).

(6) Jessup and Green, *Bur. Standards J. Research*, **13**, 491 (1934).

(7) It was felt desirable from the way that the measurements were made to carry one more figure than the exact number of completely significant figures and to express the final results to the correct number of significant figures.

(1) From a thesis submitted by T. H. Clarke in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939.

(2) This work was made possible by a grant from the Buhl Foundation, Pittsburgh, Penna.

(3) Dickinson, *Bull. Bur. Standards*, **11**, 243 (1915).

TABLE I
 CALIBRATION WITH BENZOIC ACID

ΔR , corr. rise, ohms	Δt , corr. rise, °C.	Total heat evolved, cal.	True mass	Fe	Corr. + HNO ₃	Energy equivalent, cal./°C.	Δ	(Δ) ²
0.355297	3.3305	9223.44	1.46048		1.59	2768.91	0.19	0.0361
.333560	3.3132	9176.08	1.45298		1.08	2769.23	-.13	.0169
.330492	3.2828	9092.33	1.43972		2.13	2769.04	.06	.0036
.329841	3.2763	9071.75	1.43646		1.13	2768.90	.20	.0400
.335990	3.3374	9243.64	1.46368		1.74	2769.19	-.09	.0081
.328920	3.2672	9049.64	1.43206		1.74	2769.31	-.21	.0441

$$M = 2769.10 \text{ cal. } ^\circ\text{C.}^{-1}$$

Errors: e = $\pm 0.007\%$, c = $\pm 0.005\%$, p. e. = $\pm 0.009\%$ (± 0.3 cal.)

 TABLE II
 TABLE ON PREPARATION

Sample	Source	Filtrations	Pptg. medium	Time in medium, days	Washing medium	Drying temp., °C.	Drying time, days over "Drierite"
α -Lactose monohydrate	B	1	40% alcohol	10	Cold abs. ether	50	10
α - <i>d</i> -Galactose	E	6	60% alcohol	4	Cold abs. ether	45	7
α - <i>d</i> -Galactose	P	3	60% alcohol	4	Cold abs. ether	45	8
β - <i>d</i> -Levulose	E	3	80% alcohol	5	Cold abs. alc.	45	8
β - <i>d</i> -Levulose	P	5	80% alcohol	5	Cold abs. alc.	45	8
β -Maltose monohydrate	E	3	60% alcohol	5	Cold abs. ether	50	8
β -Maltose monohydrate	P	4	60% alcohol	5	Cold abs. ether	50	8
<i>l</i> -Sorbitose	U. S. D. A.	1	H ₂ O	..	Cold water	47	8
<i>l</i> -Sorbitose	Pf	1	H ₂ O	..	Cold water	47	8
β -Lactose	E	1	H ₂ O	..	Cold water	100	7

B = Borden Research Laboratory.⁹ E = Eastman Kodak Co. P = Pfanstiehl Chemical Co. Pf = Pfizer Chemical Co.⁹ U. S. D. A. = United States Department of Agriculture.⁹

 TABLE III
 COMPARISON OF OPTICAL VALUES

Sample	Source	Values determined		Hudson's values	
		Initial	Final	Initial	Final
β -Lactose	E	35.0	55.0	35.2	55.3
β - <i>d</i> -Levulose	P	-132.6	-92.3	-133.0	-92.5
β - <i>d</i> -Levulose	E	-132.4	-92.3		
β -Maltose monohydrate	E	111.9	131.0	112.0	131.0
β -Maltose monohydrate	P	112.0	131.1		
α -Lactose monohydrate	B	89.0	55.0	90.0	55.3
α - <i>d</i> -Galactose	E	143.9	80.3	144.0	80.5
α - <i>d</i> -Galactose	P	144.0	80.0		
<i>l</i> -Sorbitose	Pf	...	-43.2	...	-43.1
<i>l</i> -Sorbitose	U. S. D. A.	...	-43.1	...	-43.1

Preparation of Samples

As the procedure developed was somewhat similar in the case of all the sugars investigated, only a general discussion of the method will be given and the specific conditions for each sample tabulated at the end of this discussion (Table II). The sugar under investigation was dissolved in sufficient water to make a fluid liquid and filtered through best grade filter paper to remove any carbon, silica, etc., carried through from the manufacturer's filters. The water was then evaporated under vacuum (in order to avoid heating the sample in excess of 35–40°) until the amount

of water remaining equaled the water necessary to form the aqueous fraction of the water-ethyl alcohol mixture used for recrystallization of a single isomeric form. The sample was allowed to stand for a given period of time in contact with this alcohol solution to ensure that only one isomer was present in the solid phase. This is the procedure developed by Hudson.⁸ The sam-

(8) Hudson and Yanovsky, THIS JOURNAL, 39, 1013 (1917).

(9) α -Lactose monohydrate was secured through the courtesy of Borden Research Laboratory, Bainbridge, N. Y.; *l*-sorbitose through the courtesy of Charles Pfizer Chemical Co., N. Y.; and *l*-sorbitose through the courtesy of J. J. Stubbs, Bureau of Chemistry and Soils, United States Department of Agriculture.

TABLE IV
 THE COMBUSTION DATA

		ΔR corr. rise, ohms	Δt corr. rise, °C.	Total heat evolved, cal.	Corr. filter paper, cal.	Corr. Fe + HNO ₃	True mass	$-\Delta U_B/M$ cal. g. ⁻¹	Δ
<i>l</i> -Sorbitose	Pf	0.320854	3.1870	8825.11	147.37	1.64	2.32944	3724.54	-0.10
<i>l</i> -Sorbitose	Pf	.324333	3.2216	8920.93	156.45	1.56	2.35222	3725.38	-.94
<i>l</i> -Sorbitose	Pf	.323577	3.2141	8900.16	147.37	1.49	2.34992	3724.08	.36
<i>l</i> -Sorbitose	U. S. D. A.	.308256	3.0619	8478.70	87.90	1.09	2.25247	3724.67	-.23
<i>l</i> -Sorbitose	U. S. D. A.	.308848	3.0678	8495.04	91.34	1.09	2.25647	3723.91	.53
<i>l</i> -Sorbitose	U. S. D. A.	.307795	3.0573	8465.97	88.06	1.17	2.24929	3724.17	.27
<i>l</i> -Sorbitose	U. S. D. A.	.308226	3.0616	8477.88	87.66	0.06	2.25278	3724.36	.08
Mean = 3724.4 ₄ cal. g. ⁻¹									
Errors: e = ±0.007%, c = ±0.005%, b = ±0.010%, p. e. = ±0.013% (±0.5 cal.)									
β - <i>d</i> -Levulose	P	0.317635	3.1551	8736.79	93.02	..	2.31598	3732.29	-0.03
β - <i>d</i> -Levulose	P	.308538	3.0646	8486.18	92.02	1.02	2.24877	3732.32	-.06
β - <i>d</i> -Levulose	P	.305090	3.0305	8391.76	79.82	0.87	2.22683	3732.24	.02
β - <i>d</i> -Levulose	E	.306549	3.0454	8433.02	78.62	1.12	2.23774	3732.91	-.65
β - <i>d</i> -Levulose	E	.308278	3.0621	8479.26	94.82	1.37	2.24645	3731.70	.56
β - <i>d</i> -Levulose	E	.317229	3.1510	8625.43	90.14	1.20	2.31346	3732.11	.15
Mean = 3732.2 ₈ cal. g. ⁻¹									
Errors: e = ±0.007%, c = ±0.005%, b = ±0.009%, p. e. = ±0.012% (±0.5 cal.)									
α - <i>d</i> -Galactose	E	0.316599	3.1448	8708.27	95.70	1.06	2.32459	3704.53	0.30
α - <i>d</i> -Galactose	E	.306756	3.0470	8437.45	89.58	1.20	2.25270	3705.18	-.35
α - <i>d</i> -Galactose	P	.307239	3.0518	8450.74	88.26	1.17	2.25659	3705.29	-.46
α - <i>d</i> -Galactose	P	.304659	3.0262	8379.85	91.98	1.26	2.23719	3704.03	.80
α - <i>d</i> -Galactose	E'	.305088	3.0304	8391.48	89.74	1.17	2.24032	3705.08	-.25
Mean = 3704.8 ₈ cal. g. ⁻¹									
Errors: e = ±0.007%, c = ±0.005%, b = ±0.013%, p. e. = ±0.015% (±0.6 cal.)									
β -Lactose	E	0.318287	3.1615	8754.51	...	1.39	2.22567	3932.80	0.08
β -Lactose	E	.315229	3.1312	8670.60	...	1.22	2.20458	3932.44	.28
β -Lactose	E'	.313892	3.1179	8633.78	...	1.36	2.19499	3932.78	-.06
β -Lactose	E'	.314856	3.1275	8660.36	...	1.29	2.20186	3932.62	.10
β -Lactose	E''	.289556	2.8762	7964.49	...	0.94	2.02429	3932.77	-.05
β -Lactose	E''	.290500	2.8855	7990.24	...	2.06	2.03112	3932.89	-.17
Mean = 3932.7 ₂ cal. g. ⁻¹									
Errors: e = ±0.007%, c = ±0.005%, b = ±0.004%, p. e. = ±0.009% (±0.4 cal.)									
β -Maltose monohydrate	E	0.314177	3.1207	8641.53	115.54	1.28	2.25660	3777.68	0.10
β -Maltose monohydrate	E	.312056	3.0996	8583.10	121.17	1.17	2.23927	3778.36	-.58
β -Maltose monohydrate	E	.311066	3.0898	8555.96	115.18	1.17	2.23410	3777.64	.14
β -Maltose monohydrate	P	.311426	3.0934	8565.93	119.38	1.36	2.23524	3778.20	-.42
β -Maltose monohydrate	P	.311772	3.0968	8575.34	117.78	1.34	2.23851	3777.61	.17
β -Maltose monohydrate	P	.307546	3.0548	8459.04	120.25	1.20	2.20703	3777.74	.04
β -Maltose monohydrate	P	.311504	3.0942	8568.15	120.37	1.28	2.23606	3777.40	.38
β -Maltose monohydrate	P	.311017	3.0893	8554.58	116.17	1.29	2.23346	3777.60	.18
Mean = 3777.7 ₈ cal. g. ⁻¹									
Errors: e = ±0.007%, c = ±0.005%, b = ±0.006%, p. e. = ±0.010% (±0.4 cal.)									
α -Lactose monohydrate	B	0.306716	3.0466	8436.34	104.54	14.97	2.21134	3760.99	0.59
α -Lactose monohydrate	B	.310056	3.0797	8527.99	120.41	1.44	2.23431	3762.30	-.72
α -Lactose monohydrate	B	.310256	3.0818	8533.87	112.78	3.21	2.23733	3762.47	-.89
α -Lactose monohydrate	B'	.311070	3.0900	8556.58	118.46	1.44	2.24353	3760.45	1.13
α -Lactose monohydrate	B'	.310333	3.0825	8535.75	116.26	1.31	2.23743	3762.43	-0.85
α -Lactose monohydrate	B'	.310236	3.0816	8533.32	119.98	1.42	2.23670	3760.86	.72
α -Lactose monohydrate	B''	.305216	3.0317	8395.08	84.42	1.21	2.20877	3762.02	-.44
α -Lactose monohydrate	B''	.296546	2.9456	8156.66	77.86	1.08	2.14768	3761.13	.45
Mean = 3761.5 ₈ cal. g. ⁻¹									
Errors: e = ±0.007%, c = ±0.005%, b = ±0.015%, p. e. = ±0.017% (±0.6 cal.)									

ple was then filtered, washed with a suitable medium, vacuum dried over "Drierite" and stored over calcium chloride for some time before usage. This procedure was used for α -lactose monohy-

TABLE V
 SUMMARY OF DERIVED DATA^a

	Mol. wt.	$-\Delta U_B$ kcal. mole ⁻¹	$-\Delta U_R$ kcal. mole ⁻¹	$-\Delta H_{298.16}^\circ$ kcal. mole ⁻¹	$-\Delta H_R$ kcal. mole ⁻¹
<i>l</i> -Sorbitose	180.157	670.98 ± 0.09	670.30 ± 0.09	303.80	309.13
β - <i>d</i> -Levulose	180.157	672.39 ± 0.08	671.70 ± 0.08	302.38	307.71
α - <i>d</i> -Galactose	180.157	667.45 ± 0.10	666.76 ± 0.10	307.33	312.66
β -Lactose	342.298	1346.16 ± 0.12	1345.47 ± 0.12	534.38	544.16
β -Maltose monohydrate	360.314	1361.19 ± 0.13	1360.50 ± 0.13	587.68	598.35
α -Lactose monohydrate	360.314	1355.35 ± 0.23	1354.66 ± 0.23	593.52	604.19
Sucrose ³	342.298	1349.68	1348.99	530.87	540.65
α - <i>d</i> -Glucose ¹³	180.154	670.17 ± 0.07	669.58 ± 0.13	305.73	311.06
α - <i>d</i> -Glucose hydrate ¹³	198.169	667.37 ± 0.12	666.73 ± 0.18	376.90	383.12

^a All thermal values are for 25°C. See text for explanation of symbols.

drate, α -*d*-galactose, β -*d*-levulose, β -maltose monohydrate. β -Lactose and *l*-sorbitose were treated similarly with the exception of the alcohol treatment.

The number of filtrations varied with the sample and are tabulated. The pressure varied between 1–3 mm. Samples were kept for ten to fourteen days over calcium chloride, were bottled and stored over calcium chloride while being used.

As standards of purity of the samples used, the following criteria were adopted: agreement in optical rotation values with those of Hudson and others and the checking of results on samples from different sources or in some cases the checking of results on samples from the same source secured from different batches. In this way it is believed that the possibility of error caused by poor samples has been practically eliminated.

Heats of Combustion.—In Table IV the experimental results of the combustions on these six compounds are listed with the errors stated as discussed earlier in this paper.

Calculated Values.—In addition to the results in Table IV we have calculated the value of $-\Delta U_B$, the heat evolved in the bomb process in kcal. per gram formula weight; $-\Delta U_R$, the decrease in energy for the chemical reaction at the standard state as defined by Washburn¹⁰; and $-\Delta H_{298.16}^\circ$, the heat of formation of the compound from the elements by the use of $-68,318.1^{11}$ and $-94,029.8$ cal.¹² for the heats of formation of water and carbon dioxide. A summary of the derived values is given in Table V.

(10) Washburn, *Bur. Standards J. Research*, **10**, 543 (1933), equations 2 and 81.

(11) Rossini, private communication.

(12) Rossini and Jessup, *J. Research Bur. Standards*, **21**, 1491 (1938).

(13) Huffman and Fox, *THIS JOURNAL*, **60**, 1403 (1938).

Discussion of Results

The values determined here along with those on sucrose³ and glucose¹³ complete the combustion data on the three physiologically most important disaccharides (maltose, lactose, sucrose) and their component monosaccharides (levulose, galactose, glucose). Investigations on the specific heats of these compounds are being carried on in this Laboratory and the values for the free energy of formation of these sugars will be reported at a future date.

The assignment of the precision errors to our measurements is a mathematical process without assumptions, but a statement of the limits of accuracy involves factors difficult to evaluate. Optical rotation as a criterion of purity is not extremely accurate; but by its use and the method of checking samples from different sources and batches, it is believed that the absolute errors due to purity of sample have been nearly eliminated. A conservative estimate might place the accuracy error as 0.025–0.035%.

No error is stated for the value of $-\Delta H_{292.16}^\circ$ as this would involve the errors on the determination of the heats of formation of water and carbon dioxide. Since in the comparison of values the influence of the errors on water and carbon dioxide would be constant, the uncertainties are probably those of the heats of combustion of the compounds.

Galactose was burned by Stohmann¹⁴ and anhydrous lactose by Stohmann,¹⁴ and by Karrer and Fioroni,¹⁵ whose results are higher by several tenths of one per cent. than the values here reported. The reported values for the hydrated form of lactose^{14,16,17} and maltose^{14,16} lie as much

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

(15) Karrer and Fioroni, *Ber.*, **55B**, 2854 (1922).

(16) Emery and Benedict, *Am. J. Physiol.*, **28**, 310 (1911).

(17) Van Rechenberg, *J. prakt. Chem.*, [2] **22**, 11 (1880).

as 1% lower than our values. The authors believe, however, that due to the higher precision attainable today, preparation of the samples by the method of Hudson,⁸ and carefully controlled drying conditions, the reported values are worthy of consideration.

Summary

1. A brief description of a precise calorimetric system for measuring heats of combustion and the standardization of the apparatus with a precision of 0.009% have been presented.

2. The heats of combustion, reduced to the standard state $-\Delta U_R$, are reported as: *l*-sorbitol, -670.30 ; β -*d*-levulose, -671.70 ; α -*d*-galactose, -666.76 ; β -lactose, -1345.47 ; β -maltose monohydrate, -1360.50 ; α -lactose monohydrate, -1354.66 kcal. per mole for the constant pressure process at 25° .

3. A comparison of these results with older values in the literature shows discrepancies of from 0.1–1%.

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Equilibria of Mercuric Oxide in Solutions of Dilute Nitric Acid. Evidence for Stepwise Dissociation of Bases

BY A. B. GARRETT AND W. W. HOWELL

Equilibrium data for mercuric oxide in alkali¹ showed no minimum in the mercuric oxide–alkali graph and showed only a very low degree of dissociation for mercuric hydroxide as an acid. This paper presents equilibrium data in *acid* solutions; such data make possible the determination of (1) the position of minimum solubility of mercuric hydroxide, (2) the equilibrium constants of mercuric hydroxide as a base, and (3) the direct evidence for stepwise dissociation of bases. In addition to this, these data, together with the equilibrium data of mercuric oxide in alkali, give the complete record of the behavior of mercuric oxide in dilute solutions of nitric acid and sodium hydroxide.

Procedure.—The general procedure in the determination of the solubility of mercuric oxide in acid was similar to that described by Garrett and Hirschler.¹ The red mercuric oxide used was prepared by the calcination of mercuric nitrate which had been prepared from especially purified mercury and nitric acid. The yellow mercuric oxide was Merck Reagent Quality Mercuric Oxide. The nitric acid was c. p. quality acid. Conductivity water was used for all solutions. All preparations were made in an atmosphere of nitrogen. The temperature was $25.00 \pm 0.02^\circ$.

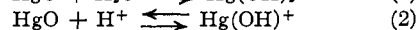
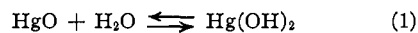
The equilibrium periods, sedimentation periods, method of filtration, and determination of the mercury content of the samples were the same as those described by Garrett and Hirschler.¹

(1) Garrett and Hirschler, *THIS JOURNAL*, **60**, 299 (1938).

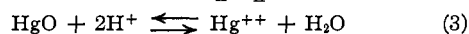
The concentration of acid was determined by preparing the samples with standard solutions of the acid used. The acidity was corrected for the amount of acid used to react with the oxide. The *pH* value of each of the solutions was determined (after equilibrium was established) by means of a glass electrode.

The Data.—The data are given in Tables I and II and in Figs. 1, 2, 3, and 4. All of the data are expressed in moles of mercuric oxide and moles of acid per 1000 g. of water. In most of these data is given the average value of a pair of samples one of which approached equilibrium from undersaturation (*u*) and the other from supersaturation (*s*). Several samples, for which the mate was lost, are marked (*u*) or (*s*) to indicate the approach to equilibrium.

The data were calculated on the assumption of the following reactions



$$K_2 = \frac{m_{\text{Hg(OH)}^+} \gamma_{\text{Hg(OH)}^+}}{m_{\text{H}^+} \gamma_{\text{H}^+}}$$



$$K_3 = \frac{m_{\text{Hg}^{++}} \gamma_{\text{Hg}^{++}}}{m_{\text{H}^+}^2 \gamma_{\text{H}^+}^2} a_{\text{H}_2\text{O}}$$

The acidity of the standard solutions of which the samples were made was corrected for the acid used in reactions indicated in equations (2) and (3). The curvature of the mercuric oxide–acid graph (Figs. 1, 3, and 4) indicates that reaction (3) is appreciable. While no direct method is