

nounced at very low pressures and rapidly reaches saturation capacity independent of further pressure increase.

5. The experiments indicate that the heat of adsorption is considerably greater than the heat of liquefaction and attains values characteristic of heats of adsorption on metal catalysts.

6. The mixed oxide catalyst shows greater adsorptive capacity than the zinc oxide in harmony with its higher order of catalytic activity.

7. The experimental results generally are shown to be in agreement with the known facts concerning methanol synthesis on these catalysts.

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## THE STANDARDIZATION OF PROFESSOR T. W. RICHARDS'S THERMOCHEMICAL DATA

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Professor T. W. Richards has authorized one of us to recalculate the values of the heats of combustion of organic compounds as examined by him, in order to standardize them and make them comparable with the standard unit now accepted in thermochemistry. As benzoic acid is established as this unit, the base for that comparison is the heat of combustion of 1 g. of benzoic acid weighed in a vacuum, 6319 cal. <sub>15°</sub>, or 1 g. of this acid weighed in air, 6324 cal. <sub>15°</sub>.

Discussing this question personally with Professor Richards, we accepted that, in the first column of each table containing the standardized thermochemical data, there must be cited the unchanged values, as given by the author in his original publication. Naturally, these values must be expressed in the same units used by the author. Therefore, we give in our two tables the values expressed in 18° calories or in kilojoules, respectively.

According to the different dates of publication, the measurements of Professor Richards are divided into two groups. The first series contains the determinations made with R. H. Jesse in 1910; the second one contains the rest, carried out after 1915, that is to say, after the appearance of Dickinson's investigations which established with great accuracy the heats of combustion of benzoic acid, cane sugar and naphthalene. This division is connected with the manner of determination of the heat capacity of the calorimetric system. In 1910, Professor Richards and R. H. Jesse carried out this determination using cane sugar as a standard substance. They accepted for the heat of combustion of this compound the value 16,545 kilojoules, proposed in 1909 by E. Fischer and Wrede. In the other papers, published after 1915, Professor Richards accepted the figures given by Dickinson.

The standardization of the data published after 1915 did not present any difficulty. In fact, Dickinson's values for the heats of combustion of benzoic acid, cane sugar and naphthalene had been accepted by the International Committee on Thermochemical Standards as the base for the establishment of the heat of combustion of benzoic acid. Therefore, the standardization in this case is a matter of expressing Professor Richards's data in terms of 15° calories instead of 18° calories or kilojoules, as was done in the original papers.

The coefficient rendering this recalculation possible is equal to 0.99942. It is calculated by using the following values of the mechanical equivalent of heat, determined by transforming electrical energy into heat at different temperatures.

Temp., °C.	Mech. equiv. of heat	Temp., °C.	Mech. equiv. of heat
15	4.1843	18	4.1819
16	4.1835	19	4.1812
17	4.1827	20	4.1805

The corresponding coefficient enabling us to standardize the data published in Professor Richards's first paper (1910) has been determined by comparing the values given by Fischer and Wrede for the heats of combustion of cane sugar and naphthalene with the figures established lately with great precision by several authors (Dickinson, Verkade, Swietoslowski and Starczewska and Schläpfer).

It has been shown by Swietoslowski,<sup>1</sup> in several papers concerning the establishment of a thermochemical standard unit, that the above-mentioned data of Fischer and Wrede are too high by +0.3%. The following comparison gives directly the value of the coefficient which ought to be accepted for the recalculation of the Richards data published in 1910.

Compound	Formula	Fischer and Wrede [Kj]	Standardized data [Kj]	Stand. data
				Fischer and Wrede
Naphthalene	C <sub>10</sub> H <sub>8</sub>	40,314 <sup>a</sup>	40,179	0.9967
Cane sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	16,545 <sup>b</sup>	16,501	0.9973
				Average value 0.9970

<sup>a</sup> Wrede

<sup>b</sup> Fischer and Wrede (2).

When the above-mentioned values have been expressed in kilojoules, the coefficient 0.9970 must be multiplied by 1000 and divided by 4,1843;  $\alpha = (0.9970 \times 1000)/4.1843 = 238.27$ .

In the two tables the first column contains the name of the substance with reference to original publication; the second, the formula; the third, the molecular weight *M*; the fourth, the heat of combustion of 1 g.

<sup>1</sup> Swietoslowski, *J. chim. phys.*, **22**, 391, 396, 399, 583 (1925); *Bull. soc. chim.*, (4) **37**, 84 (1925); *Bull. Acad. Polonaise Sc.*, (A) **1927**, 42, 43, 54.

(vac.) of substance ( $v = \text{const.}$ ) expressed in kilojoules  $A(Kj)$ ; the fifth, the same values expressed in calories  $A_{\text{cal. 18}^\circ}$ ; the sixth, the corresponding standardized values  $A$ ; the seventh and the eighth, the molecular heat of combustion of the substance at constant volume  $A_v$  and at constant pressure  $A_p$ .

TABLE I  
THE COEFFICIENT OF STANDARDIZATION 238.27

Substance <sup>a</sup>	Formula	M	A (Kj)	A (cal. <sub>18</sub> <sup>o</sup> )	A	A <sub>v</sub>	A <sub>p</sub>
<i>n</i> -Octane.....	C <sub>8</sub> H <sub>18</sub>	114.14	47.73	....	11,372.6	1298.1	1300.7
2,5-Dimethylhexane.	C <sub>8</sub> H <sub>18</sub>	114.14	47.68	....	11,360.7	1296.7	1299.3
2-Methylheptane....	C <sub>8</sub> H <sub>18</sub>	114.14	47.78	....	11,384.5	1299.4	1302.0
3,4-Dimethylhexane.	C <sub>8</sub> H <sub>18</sub>	114.14	47.70	....	11,365.5	1297.3	1299.9
3-Ethylhexane.....	C <sub>8</sub> H <sub>18</sub>	114.14	47.65	....	11,353.6	1295.9	1298.5
Benzene.....	C <sub>6</sub> H <sub>6</sub>	78.05	41.99	10,048	10,005.0	780.9	781.8
<i>o</i> -Xylene.....	C <sub>8</sub> H <sub>10</sub>	106.08	43.10	....	10,269.4	1089.4	1090.8
<i>m</i> -Xylene.....	C <sub>8</sub> H <sub>10</sub>	106.08	43.10	....	10,269.4	1089.4	1090.8
<i>p</i> -Xylene.....	C <sub>8</sub> H <sub>10</sub>	106.08	42.95	....	10,233.7	1085.6	1087.0
Methyl <i>isobutyrate</i> ..	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	102.08	28.419	....	6,771.4	691.2	692.1

<sup>a</sup> Richards and Jesse, THIS JOURNAL, 32, 268 (1910).

TABLE II  
THE COEFFICIENT OF STANDARDIZATION, 0.99942

Substance	Formula	M	A (Kj)	A (cal. <sub>18</sub> <sup>o</sup> )	A	A <sub>v</sub>	A <sub>p</sub>
Di- <i>iso</i> -amyl <sup>a</sup> .....	C <sub>10</sub> H <sub>22</sub>	142.18	...	11,339	11,332.4	1611.2	1614.4
Benzene <sup>a</sup> .....	C <sub>6</sub> H <sub>6</sub>	78.05	...	10,014	10,008.2	781.1	782.0
Benzene <sup>b</sup> .....	C <sub>6</sub> H <sub>6</sub>	78.05	41.79	9,993	9,987.2	779.5	780.4
Toluene <sup>b</sup> .....	C <sub>7</sub> H <sub>8</sub>	92.06	42.51	10,166	10,160.1	935.3	936.5
Toluene <sup>a</sup> .....	C <sub>7</sub> H <sub>8</sub>	92.06	...	10,155	10,149.1	934.3	935.5
<i>o</i> -Xylene <sup>b</sup> .....	C <sub>8</sub> H <sub>10</sub>	106.08	42.98	10,277	10,271.0	1089.5	1090.9
<i>m</i> -Xylene <sup>b</sup> .....	C <sub>8</sub> H <sub>10</sub>	106.08	42.98	10,277	10,271.0	1089.5	1090.9
<i>p</i> -Xylene <sup>b</sup> .....	C <sub>8</sub> H <sub>10</sub>	106.08	42.83	10,241	10,235.1	1085.7	1087.1
Ethylbenzene <sup>b</sup> .....	C <sub>8</sub> H <sub>10</sub>	106.08	42.96	10,273	10,267.0	1089.1	1090.5
Mesitylene <sup>b</sup> .....	C <sub>9</sub> H <sub>12</sub>	120.10	43.24	10,340	10,334.0	1241.1	1242.8
<i>n</i> -Propylbenzene <sup>b</sup> ...	C <sub>9</sub> H <sub>12</sub>	120.10	43.34	10,364	10,358.0	1244.0	1245.7
<i>Isopropylbenzene</i> <sup>b</sup> ...	C <sub>9</sub> H <sub>12</sub>	120.10	43.37	10,371	10,365.0	1244.8	1246.5
Pseudocumene <sup>b</sup> .....	C <sub>9</sub> H <sub>12</sub>	120.10	43.14	10,316	10,310.0	1238.2	1239.9
<i>Tert.</i> -butylbenzene <sup>a</sup> ...	C <sub>10</sub> H <sub>14</sub>	134.11	...	10,434	10,427.9	1398.5	1400.5
<i>Tert.</i> -butylbenzene <sup>b</sup> ...	C <sub>10</sub> H <sub>14</sub>	134.11	43.60	10,427	10,421.0	1397.6	1399.6
Cyclohexane <sup>b</sup> .....	C <sub>6</sub> H <sub>12</sub>	84.10	46.69	11,164	11,157.5	938.3	940.0
Methyl alcohol <sup>a</sup> .....	CH <sub>4</sub> O	32.03	...	5326	5322.9	170.5	170.8
Ethyl alcohol <sup>a</sup> .....	C <sub>2</sub> H <sub>6</sub> O	46.05	...	7101	7096.9	326.8	327.4
Propyl alcohol <sup>a</sup> .....	C <sub>3</sub> H <sub>8</sub> O	60.06	...	8033	8028.3	482.2	483.1
Butyl alcohol <sup>a</sup> .....	C <sub>4</sub> H <sub>10</sub> O	74.08	...	8615	8610.0	637.8	639.0
<i>Isobutyl alcohol</i> <sup>a</sup> ....	C <sub>4</sub> H <sub>10</sub> O	74.08	...	8599	8594.0	636.6	637.8
Cyclohexanol <sup>a</sup> .....	C <sub>6</sub> H <sub>12</sub> O	100.10	...	8882	8876.8	888.6	890.0

<sup>a</sup> Richards and Davis, THIS JOURNAL, 42, 1599 (1920).

<sup>b</sup> Richards and Barry, *ibid.*, 37, 993 (1915).