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# Estimation and revision of some thermodynamic data in the YBaCuO system. Part 2. Standard entropies of formation

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**Abstract**

From a review of the literature data, we have estimated the basic standard entropies of formation from the elements $\bar{S}^{\ominus}_{298}$ of $YBa_2Cu_3O_7$ (123-$O_7$), $YBa_2Cu_3O_6$ (123-$O_6$), $YBa_2Cu_4O_8$ (124-$O_8$), $YBa_2Cu_{3.5}O_{7.5}$ (123.5-$O_{7.5}$), $YCuO_2$ (101) and $Y_2Cu_2O_5$ (202). It is shown that for the $S^{\ominus}_{298}$(i) estimation, it is better to use the method of increments of the ions constituting the compound, rather than the method of addition of standard entropies of the simple oxides forming the compound. In addition, $S^{\ominus}_{298}$ values were calculated for $YBa_2Cu_5O_9$ (125-$O_9$), $YBa_4Cu_3O_{8.5}$ (143-$O_{8.5}$), $BaCuO_2$ (011), $BaCu_2O_2$ (012), $Ba_2CuO_3$ (021), $Ba_3CuO_4$ (031), $Y_2BaCuO_5$ (211), $Y_2BaO_4$ (210), $Y_2Ba_4O_7$ (240) and $Y_2Ba_2O_5$ (220).

## INTRODUCTION

Standard entropies of formation from the elements for 34 compounds of the YBaCuO system were calculated earlier [1, 2] using the method of ion increments [3, 4]: $S^{k}_{i}(Y) = 51.4386$; $S^{K}_{i}(Ba) = 63.1482$; $S^{k}_{i}(Cu) = 40.9836$; and $S^{A}_{i}(O^{2-}) = 3.722\ J\ K^{-1}$. For a definite compound, e.g. 123-$O_6$, calculation was made according to the scheme

$$S^{\ominus}_{298} \approx S^{k}_{i}(Y) + 2S^{k}_{i}(Ba) + 3S^{k}_{i}(Cu) + 6S^{A}_{i}(O^{2-}) \quad (1)$$

In refs. 5–7, was shown that it is possible to use the method of addition of standard entropies of the oxides for the estimation of $S^{\ominus}_{298}$(i). For 123-$O_6$, for example, the calculation was made according to the scheme

$$S^{\ominus}_{298} \approx 0.5S^{\ominus}_{298}(Y_2O_3) + 2S^{\ominus}_{298}(BaO) + 2S^{\ominus}_{298}(CuO) + 0.5S^{\ominus}_{298}(Cu_2O) \quad (2)$$

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TABLE 1

Standard entropies of formation of some compounds in the YBaCuO system

| $S^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ | | Ref. | Remarks |
|---|---|---|---|
| 123-$O_x$, $x = 6$–7 | | | |
| 321.7 | $x = 7$ | 8 | Experiment |
| 326.6 | $x = 7$ | 9 | Experiment |
| 321.7 | $x = 7$ | 5 | Experiment |
| 321.4 | | | Calculation by the additive scheme |
| 322.85 | $x = 6$ | 4 | Calculation by the method of ion increments |
| 327 | $x = 7$ | 10 | Calculation |
| 321.85 | $x = 6.9$ | 11 | Experiment |
| 322.4 | $x = 7$ | 12 | Experiment |
| 366.5 | $x = 6.5$ | 13 | Rough estimation |
| 323.5 | $x \cong 7$ | 14 | Experiment |
| 321.7 | | | Review data |
| 322.7 | $x = 6.98$ | 15 | Experiment |
| 310.14 | $x = 6.3$ | | |
| 325.16 | $x = 7$ | 16 | Experiment |
| 317.33 | $x = 6$ | | |
| 323.7 | $x = 6.7$ | 6 | Data review |
| 323.5 | $x = 6.85$ | | |
| 319.9 | $x = 6.9$ | | Calculation by the additive scheme |
| 321.7 | $x = 7$ | | |
| $322 \pm 3$ | $x = 7$ | 7 | Average value, calculated from the data, given in ref. 6 |
| 322.0 | $x = 7$ | | |
| 322.4 | $x = 7$ | 12 | Experiment |
| 124-$O_8$ | | | |
| 364.5 | | 12 | Experiment |
| 371.8 | | 1, 2 | Calculation by the method of ion increments |
| 362.5 | | 7 | Calculation by additive scheme |
| 123.5-$O_{7.5}$ | | | |
| 341.32 | | 17 | Experiment |
| 349.1 | | 1, 2 | Calculation by the method of ion increments |
| 342.25 | | 7 | Calculation by the additive scheme |
| 125-$O_9$ | | | |
| 405.1 | | 7 | Calculation by the additive scheme |
| 416.1 | | – | Calculated by the method described in ref. 4 |
| 143-$O_{8.5}$ | | | |
| 458.56 | | 1, 2 | Calculation by the method of ion increments |
| 211 | | | |
| 225.4 | | 1, 2 | Calculation by the method of ions increments |
| 243.0 | | 13 | Rough estimation |
| 101 | | | |
| 91.0 | | 18 | Experiment |
| 99.95 | | 1, 2 | Calculation by the method of ion increments |

TABLE 1 (continued)

| $S^{\circ}_{298}$ in J K$^{-1}$ mol$^{-1}$ | Ref. | Remarks |
|---|---|---|
| 202 | | |
| 171.0 | 18 | Experiment |
| 210 | 13 | Rough estimation |
| 203.7 | 1, 2 | Calculation by the method of ion increments |
| 197.5 ± 0.4 | 19 | Experiment |
| 210 | | |
| 196 | 13 | Rough estimation; |
| 181.1 | 1, 2 | Calculation by the method of ion increments |
| 220 | | |
| 248 | 1, 2 | Calculation by the method of ion increments |
| 240 | | |
| 381.8 | 1, 2 | Calculation by the method of ion increments |
| 011 | | |
| 85.7 | 20 | Evaluation calculation |
| 111.7 | 1, 2, 4 | Calculation by the method of ion increments |
| 138.0 | 13 | Rough estimation |
| 012 | | |
| 152.6 | – | Calculation by the method described in ref. 4 |
| 021 | | |
| 178.6 | 1, 2 | Calculation by the method of ion increments |
| 031 | | |
| 245.5 | 1, 2 | Calculation by the method of ion increments |

The results of experimental studies, together with the calculated data for selected phases, are given in Table 1.

The aim of the present paper is to attempt to correct the values of $S^{\circ}_{298}$ for some compounds in the YBaCuO system, to find ways of calculating standard entropies of formation from the elements and to revise our earlier data [1, 2, 4]. Data for the main phases of the YBaCuO system are described.

## ANALYSIS OF THE KNOWN VALUES OF THE STANDARD ENTROPIES OF FORMATION

From Table 1 and using selection principles described in ref. 21, we chose the most reliable values of $S^{\circ}_{298}$ for each compound. Then we determined the basic values of $\bar{S}^{\circ}_{298}$ as arithmetic means. The selected results and values of $\bar{S}^{\circ}_{298}$ are given in Table 2 together with average quadratic deviations from the arithmetic mean values. We consider the $\bar{S}^{\circ}_{298}(123\text{-}O_7)$ value of $323.06 \pm 0.77$ J K$^{-1}$ mol$^{-1}$ to be the most valid and $\bar{S}^{298}(101) = 95.48 \pm 4.48$ J K$^{-1}$ mol$^{-1}$ the least valid.

TABLE 2

Basic values of the standard entropies of formation from elements of some compounds in the system YBaCuO

| Compound | $S^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ | Ref. | Basic value of $\bar{S}^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| 123-$O_7$ | 321.7 | 8 | 323.06 ± 0.77 |
| | 326.7 | 9 | |
| | 321.4 | 5 | |
| | 321.85 | 11 | |
| | 322.7 | 15 | |
| | 325.16 | 16 | |
| | 323.5 | 6 | |
| 123-$O_6$ | 322.85 | 4 | 316.77 ± 3.66 |
| | 310.14 | 15 | |
| | 317.33 | 16 | |
| 124-$O_8$ | 364.5 | 12 | 366.27 ± 2.83 |
| | 371.8 | 1, 2 | |
| | 362.5 | 7 | |
| 123.5-$O_{7.5}$ | 341.32 | 17 | 344.22 ± 2.45 |
| | 349.1 | 1, 2 | |
| | 343.25 | 7 | |
| 101 | 91.0 | 18 | 95.48 ± 4.48 |
| | 99.9 | 1, 2 | |
| 202 | 203.7 | 1, 2 | 200.6 ± 3.10 |
| | 197.5 | 19 | |

TABLE 3

Comparison of $S^{\ominus}_{298}$(i) values, calculated by the method of the sum of ion increments and of the addition of $S^{\ominus}_{298}$(ox), with the basic values of $\bar{S}^{\ominus}_{298}$

| Composition | $\bar{S}^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ basic value | $\Sigma S^{\ominus}_{298}$(ox) [a] | | Σ of ion increments | |
|---|---|---|---|---|---|
| | | $S^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ | δ/% of the basic | $S^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ | δ/% of the basic |
| 123-$O_7$ | 323.06 ± 0.77 | 329.62 | +2.03 | 326.70 | +1.13 |
| 123-$O_6$ | 316.77 ± 3.66 | 322.16 | +1.70 | 322.85 | +1.92 |
| 124-$O_8$ | 366.27 ± 2.83 | 372.28 | +1.64 | 371.78 | +1.50 |
| 123.5-$O_{7.5}$ | 344.22 ± 2.45 | 350.95 | +1.96 | 349.10 | +1.42 |
| 101 | 95.48 ± 4.48 | 96.08 | +0.63 | 99.95 | +4.68 |
| 202 | 200.6 ± 3.1 | 184.42 | −8.06 | 203.70 | +1.54 |
| | | $\lvert\delta\rvert$ = 2.67% | | $\lvert\delta\rvert$ = 2.03% | |

[a] $S^{\ominus}_{298}$ of oxides are taken from ref. 22.

Table 3 gives the results of a comparison with the basic values of $S^{\circ}_{298}(i)$ calculated by the two methods in question. It can be concluded that both methods can be used to calculate the standard entropies of formation of compounds in the YBaCuO system. For the phase 202, however, calculation by the $\Sigma S^{\circ}_{298}(ox)$ method causes a considerable deviation of −8.06%. When the method of ion increments is used, a maximal deviation of +4.68% is found for the phase 101. The average absolute value of deviations from basic values for $\Sigma S^{\circ}_{298}(ox)$ is more than that for the increment method and thus we can consider the $S^{\circ}_{298}(i)$ values as more valid. However, it should be pointed out that the deviations in $S^{\circ}_{298}(i)$ from the basic value are positive, which allows the value of the increment $S^{A}_{i}(O^{2-})$ to be corrected.

In a previous paper [4], this value was estimated to be 3.722 J $K^{-1}$, using the basic value $S^{\circ}_{298}(123\text{-}O_7) = 326.7$ J $K^{-1}$ $mol^{-1}$ [9] and the equation

$$S^{A}_{i}(O^{2-}) = 1/7[S^{\circ}_{298}(123\text{-}O_7) - S^{k}_{i}(Y) - 2S^{k}_{i}(Ba) - 3S^{k}_{i}(Cu)] \quad (3)$$

where $S^{k}_{i}(i)$ is taken from ref. 3.

From the corrected basic values of $S^{\circ}_{298}(123\text{-}O_7)$, $323.06 \pm 0.77$ J $K^{-1}$ $mol^{-1}$ (Table 2), and eqn. (3), the corrected value of $S^{A}_{i}(O^{2-})$ is 3.1963 J $K^{-1}$. It is thus expedient to use the method of increments of the ions constituting the compound to obtain this value.

## DISCUSSION OF RESULTS

Table 4 gives the values of $S^{\circ}_{298}(i)$ for the main compounds of the YBaCuO system, calculated by eqns. (1) and (2). Equation (1) was employed to calculate the corrected value for the oxygen anion, and also for $S^{\circ}_{298}$ [1, 2]. However, there are not enough data in Table 4 to decide which method for calculation of $S^{\circ}_{298}(i)$ of the complex oxides gives more correct results. Comparing the basic values, it is preferable to use the method of increments with regard to the corrected value of $S^{A}_{i}(O^{2-})$. Moreover, until more detailed and valid data for $S^{\circ}_{298}(i)$ are available, the information given in column 4 of Table 4 may be used for any consequent thermodynamic studies.

The difference between these values and those for $S^{\circ}_{298}(i)$ calculated by eqn. (2), is not more than 2% for the majority of compounds. However, for phases 211, 202, 210, 031 and 012, the differences are larger, respectively, −4.87%, +8.17%, −5.21% and +7.87%. Comparison of the recommended $S^{\circ}_{298}(i)$ values with the data given in refs. 1, 2 and 4 does not show any considerable differences. As the average deviation is not more than 1.5%, the published values $S^{\circ}_{298}(i)$ [1, 2, 4] are considered satisfactory and can be employed for thermodynamic calculations.

TABLE 4

Standard entropies of formation of some phases in the system YBaCuO

| Compound | $S^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ calculated as $\Sigma S^{\ominus}_{298}$(Ox) | Method of ion increments [a] | | $S^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ by refs. 1 and 2 |
|---|---|---|---|---|
| | | $S^{\ominus}_{298}$ in J K$^{-1}$ mol$^{-1}$ | $\delta$/% from $\bar{S}^{\ominus}_{298}$ | |
| 123-$O_6$ | 322.16 | 319.86 | +0.98 | 322.85 |
| 123-$O_7$ | 329.62 | 323.06 | 0 | 326.70 |
| 123.5-$O_{7.5}$ | 350.95 | 345.15 | +0.27 | 349.10 |
| 124.$O_8$ | 372.28 | 367.24 | +0.26 | 371.78 |
| 125-$O_9$ | 414.94 | 411.42 | – | – |
| 143-$O_{8.5}$ | 459.06 | 454.15 | – | 458.56 |
| 211 | 212.15 | 223.00 | – | 225.41 |
| 202 | 184.42 | 200.83 | +0.11 | 203.66 |
| 101 | 96.08 | 98.81 | +3.5 | 99.95 |
| 210 | 169.50 | 178.81 | – | 181.08 |
| 220 | 239.88 | 245.16 | – | 248.00 |
| 240 | 380.64 | 377.84 | – | 381.82 |
| 011 | 113.04 | 110.52 | – | 111.66 |
| 021 | 183.42 | 176.87 | – | 178.57 |
| 031 | 253.80 | 243.21 | – | 245.48 |
| 012 | 163.43 | 151.51 | – | – |

[a] With regard to the corrected value of $S^{A}_{i}(O^{2-})$, 3.1963 J K$^{-1}$.

## CONCLUSIONS

From an analysis of the literature data, basic values of the standard entropies of formation from elements have been estimated for the 123-$O_7$, 123-$O_6$, 124-$O_8$, 123.5-$O_{7.5}$, 101 and 202 phases.

A comparison of the basic values of $\bar{S}^{\ominus}_{298}$(i) with those calculated by the method of the increments of the ions constituting the compound, and by the method of the sum of the standard entropies of formation of the simple oxides constituting the compound, showed that the increment method gives more correct results with regard to the correction of the increment of the oxygen anion.

Revision of $S^{\ominus}_{298}$ data obtained earlier [1, 2, 4] has shown that they are different from those recommended by not more than by 1.5%.

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