

# THERMODYNAMIC PROPERTIES OF DESOLVATION PROCESS OF TETRAHYDROFURANATE OF LANTHANIDES BOROHYDRIDES

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Under existing methods of synthesis the lanthanides borohydrides form in solvated kind at tetrahydrofuranate (THF) medium. Discovered opportunities of desolvation conditions and obtaining of non-solvated lanthanides borohydrides are of scientifically-applied interest.

In the present work investigation results of desolvation tristetrahydrofuranate of lanthanides borohydrides process–  $\text{Ln}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ , where Ln–La, Nd, Sm, Er, Gd, Yb and Lu are presented. The investigation is carried out by tensimetry method with membranous zero pressure-gauge. The process runs slowly in time. The time for achieving equilibrium value of pressure in isothermal condition is 150-160 hours.

The curve of gas pressure dependence from temperature (barogram), presented as

$\lg p = f\left(\frac{1}{T}\right)$  consist of two crossing straight lines, proper to separate stages of desolvation process.

Equation of barograms and temperature interval of process stage processing are presented at table 1.

According to the results of quantitative tensimetric measuring it is determined that on first stage one mole of THF is desolvated, and other two moles during the second stage.

On the basis of barogram equation, the thermodynamic properties of both stages of desolvation process  $\text{Ln}(\text{BH}_4)_3 \cdot 3 \text{ THF}$  (table.2) are calculated. These data permitted by semi-empirical method [1,2], considering the influence of f-electrons number, contribution of spin (S) and orbital (L) moments of lanthanides ion motion to calculate thermodynamic properties of desolvation process stages of whole solvated lanthanide borohydrides range. (table 2).

Table 1.

Coefficients of equation of desolvation process  
 $\text{Ln}(\text{BH}_4)_3 \cdot 3 \text{ THF}$

| Compound                                       | $\lg P_{\text{THF}} = B - \frac{A}{T} \cdot 10^3$ |          |             |              |           |             |
|------------------------------------------------|---------------------------------------------------|----------|-------------|--------------|-----------|-------------|
|                                                | First stage                                       |          |             | Second stage |           |             |
|                                                | A                                                 | B        | $\Delta T$  | A            | B         | $\Delta T$  |
| $\text{La}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ | 0.8<br>1                                          | 4.4<br>3 | 300-<br>380 | 3.30         | 10.<br>66 | 380-<br>395 |
| $\text{Nd}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ | 0.9<br>8                                          | 4.2<br>8 | 300-<br>370 | 4.58         | 14.<br>03 | 370-<br>390 |
| $\text{Sm}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ | 0.7<br>4                                          | 4.3<br>1 | 300-<br>373 | 2.66         | 9.4<br>3  | 373-<br>390 |
| $\text{Gd}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ | 0.8<br>1                                          | 4.5<br>7 | 300-<br>369 | 2.13         | 8.1<br>2  | 369-<br>385 |
| $\text{Er}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ | 0.9<br>4                                          | 4.5<br>2 | 300-<br>360 | 3.37         | 11.<br>30 | 360-<br>380 |
| $\text{Yb}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ | 1.1<br>9                                          | 5.6<br>1 | 300-<br>363 | 3.49         | 11.<br>64 | 363-<br>380 |
| $\text{Lu}(\text{BH}_4)_3 \cdot 3 \text{ THF}$ | 1.3<br>7                                          | 5.8<br>3 | 300-<br>340 | 1.88         | 7.3<br>3  | 340-<br>375 |

## References

1. Poluektov N.S., Meshkova S.B., Korovin Y.V., Oksinenko I.I. //Dokl. AN SSSR, 1982, v.266, №5, p.1157.
2. Meshkova S.B., Poluektov N.S., Topilova Z.M., Donilkovich M.M. //Coord. khimiya, 1986, v.12, №4, p.481.

Table 2

Thermodynamic properties of stages of desolvation process  $\text{Ln}(\text{BH}_4)_3\text{TTHF}$

| Compound                               | First stage                                             |             |                                                                   |             | Second stage                                       |             |                                                                   |             |
|----------------------------------------|---------------------------------------------------------|-------------|-------------------------------------------------------------------|-------------|----------------------------------------------------|-------------|-------------------------------------------------------------------|-------------|
|                                        | $\Delta H^0_{T, \kappa\text{J} \cdot \text{mole}^{-1}}$ |             | $\Delta S^0_{T, \text{J} \cdot \text{mole}^{-1} - \text{K}^{-1}}$ |             | $\Delta H^0_{T, \text{kJ} \cdot \text{mole}^{-1}}$ |             | $\Delta S^0_{T, \text{J} \cdot \text{моль}^{-1} - \text{K}^{-1}}$ |             |
|                                        | Experiment                                              | Calculation | Experiment                                                        | Calculation | Experiment                                         | Calculation | Experiment                                                        | Calculation |
| $\text{La}(\text{BH}_4)_3 \text{ THF}$ | 15.1                                                    | 15.1        | 28.9                                                              | 28.9        | 124.3                                              | 124.3       | 293.3                                                             | 293.3       |
| $\text{Ce}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 17.1        | -                                                                 | 31.5        | -                                                  | 117.8       | -                                                                 | 285.7       |
| $\text{Pr}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 18.1        | -                                                                 | 32.3        | -                                                  | 113.0       | -                                                                 | 277.8       |
| $\text{Nd}(\text{BH}_4)_3 \text{ THF}$ | 18.8                                                    | 18.5        | 26.8                                                              | 32.8        | 108.4                                              | 108.4       | 267.4                                                             | 267.4       |
| $\text{Pm}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 18.5        | -                                                                 | 33.1        | -                                                  | 103.9       | -                                                                 | 254.6       |
| $\text{Sm}(\text{BH}_4)_3 \text{ THF}$ | 17.6                                                    | 17.8        | 38.1                                                              | 33.2        | 75.7                                               | 99.6        | 185.8                                                             | 239.4       |
| $\text{Eu}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 15.6        | -                                                                 | 30.8        | -                                                  | 88.9        | -                                                                 | 206.6       |
| $\text{Gd}(\text{BH}_4)_3 \text{ THF}$ | 14.6                                                    | 14.6        | 31.0                                                              | -           | 92.9                                               | 92.9        | 203.8                                                             | 203.8       |
| $\text{Tb}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 15.6        | -                                                                 | 30.8        | -                                                  | 102.2       | -                                                                 | 235.9       |
| $\text{Dy}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 16.3        | -                                                                 | 30.5        | -                                                  | 109.9       | -                                                                 | 261.7       |
| $\text{Ho}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 17.1        | -                                                                 | 31.7        | -                                                  | 114.5       | -                                                                 | 278.6       |
| $\text{Er}(\text{BH}_4)_3 \text{ THF}$ | 1.0                                                     | 18.0        | 31.4                                                              | 34.5        | 129.3                                              | 116.0       | 32.2                                                              | 286.9       |
| $\text{Tm}(\text{BH}_4)_3 \text{ THF}$ | -                                                       | 19.0        | -                                                                 | 38.7        | -                                                  | 114.5       | -                                                                 | 286.6       |
| $\text{Yb}(\text{BH}_4)_3 \text{ THF}$ | 20.5                                                    | 19.5        | 46.0                                                              | 43.2        | 103.3                                              | 106.8       | 259.8                                                             | 269.7       |
| $\text{Lu}(\text{BH}_4)_3 \text{ THF}$ | 20.9                                                    | 20.9        | 50.2                                                              | 50.2        | 103.7                                              | 103.7       | 261.9                                                             | 261.9       |