

On the applicability and predictive power of additive equations in the evaluation of standard enthalpies of formation of crystalhydrate salts of rare earths and actinoides

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The validity of equations for the additive evaluation of the standard enthalpies of formation (ΔH_f°) of crystalhydrates of rare-earth elements and actinoides is established on the basis of experimental data. Rozenfeld's equation, *i.e.*

$$\Delta H_f^\circ(\text{crystalhydrate}) = \Delta H_f^\circ(\text{anhydrous salt}) + b_1 \cdot N$$

where N is the hydration value and b_1 is the increment for one water molecule, shows the best approximation to the experimental data and offers the best predictive possibilities. For $N = 1$ b_1 is $-307.5 \text{ kJ mol}^{-1}$, for each from the second to the sixth water molecule b_1 is $-300.4 \text{ kJ mol}^{-1}$, while for any water molecule belonging to the second coordination sphere b_1 is $-292.9 \text{ kJ mol}^{-1}$. The present considerations corroborate the previously published conclusion that the experimentally obtained ΔH_f° values for crystalline phosphate dihydrates of 12 rare-earth elements should be reconsidered. The use of a general increment of low value ($-297.1 \text{ kJ mol}^{-1}$) is shown to be one of the causes for considering in the literature some ΔH_f° of crystalhydrates as subject to nonlinear changes and lack of additivity. Rozenfeld's equation is also shown to be useful in the rapid check of crystalhydrate ΔH_f° values in the cases where they do not agree with experimental data for other crystalhydrates of the same salt.

На основе экспериментальных данных доказана применимость уравнений для аддитивного определения стандартных энтальпий образования (ΔH_f°) кристаллогидратов редкоземельных элементов и актиноидов. Уравнение Розенфельда

$$\Delta H_f^\circ(\text{кристаллогидрата}) = \Delta H_f^\circ(\text{безводной соли}) + b_1 \cdot N$$

где N — гидратационное число, а b_1 — инкремент одной молекулы воды, предоставляет наилучшее приближение к экспериментальным данным и наилучшие возможности предсказания. Для $N = 1$ b_1 равняется $-307,5 \text{ кДж моль}^{-1}$, для каждой от второй до шестой молекулы воды b_1 равно $-300,4 \text{ кДж моль}^{-1}$, в то время, как для молекул воды из второй координационной сферы b_1 составляет $-292,9 \text{ кДж моль}^{-1}$. Данные результаты подтверждают ранее опубликованный вывод о не-

обходимости пересмотра экспериментально полученных значений ΔH_f° для кристаллических дигидратов фосфатов 12 редкоземельных элементов. Показано, что использование общего инкремента с низким значением ($-297,1$ кДж моль $^{-1}$) было одной из причин того, что в литературе некоторые ΔH_f° кристаллогидратов считались подверженными нелинейным изменениям и неаддитивными. Показано также, что уравнение Розенфельда полезно для быстрой проверки правильности значений ΔH_f° в тех случаях, когда они не согласуются с экспериментальными данными для иных кристаллогидратов той же соли.

The formation of crystallohydrates of salts is accompanied by reported differences in the values of the standard enthalpies of formation $\Delta H_f^\circ(298\text{ K}, 0.1\text{ MPa})$ of the initial anhydrous salts and of the crystallohydrates as well as of the energies of the bonds between the complexing ion and the coordinated water molecules. In spite of that a close similarity in the changes in the ΔH_f° of crystallohydrates depending on the content of water molecules (hydration value) is observed.

Karapetyants [1] has suggested the use of the following equation in the approximate determination of the ΔH_f° values of crystallohydrate (crh.) halides

$$\Delta(\Delta H_f^\circ) = \Delta H_f^\circ(\text{crh.}) - \Delta H_f^\circ(\text{anh. s.}) \approx -301.2\text{ kJ mol}^{-1} N \quad (1)$$

where N is the numerical value of amount of water in the corresponding crystallohydrate and $-301.2\text{ kJ mol}^{-1}$ is the increment of one water molecule.

Rozenfeld [2] has proposed the relationship

$$\Delta H_f^\circ(\text{crh.}) = \Delta H_f^\circ(\text{anh. s.}) + b_1 N \quad (2)$$

where $b_1 = -307.5\text{ kJ mol}^{-1}$ for $N = 1$,

$b_1 = -300.4\text{ kJ mol}^{-1}$ for $N = 2-12$.

It has been suggested [3] that a better agreement between the calculated and experimental data will be observed if the increment for the water molecules of the second coordination sphere is taken as $-292.9\text{ kJ mol}^{-1}$. The same study also showed the validity of eqn (2) for higher crystallohydrates, *i.e.* such with 13 to 32 molecules of water. We have indicated earlier the possibility of conductive additive evaluations of ΔH_f° for crystallohydrates of binary and ternary salts [4]. Other equations describing the additivity of ΔH_f° have also been put forward. An equation analogous to eqn (1) but using a constant of $-297.1\text{ kJ mol}^{-1}$ has been used [5]. Other researchers [6, 7] report the lack of agreement between the experimentally found and calculated values while using the lower increment ascribing it to the absence of additivity in ΔH_f° of crystallohydrates during changes of their hydration values. Agreement between the calculated and experimental values has been achieved [6, 7] by introducing individual correction terms valid solely for the crystallohydrates of a given salt. The following

equation has been offered for evaluating the ΔH_f° of crystallohydrates of lanthanoid nitrates containing 1–6 water molecules [8]

$$\frac{\Delta H_f^\circ(\text{Ln}(\text{NO}_3)_3 \cdot N\text{H}_2\text{O})}{\text{kJ mol}^{-1}} = \frac{\Delta H_f^\circ(\text{Ln}(\text{NO}_3)_3)}{\text{kJ mol}^{-1}} - 313.8 \cdot N + 3.5^{(N/2)-1} \quad (3)$$

It can be seen that the higher numerical value of the increment per water molecule, *i.e.* -313.8 is compensated by the term $3.5^{(N/2)-1}$.

The evaluation of ΔH_f° of sulfate crystallohydrates of magnesium and 3d elements is carried out by means of two equations [9], *i.e.*

$$\Delta H_f^\circ = a_1 - 296.240 \text{ kJ mol}^{-1} \quad (N = 1-7) \quad (4)$$

$$\Delta H_f^\circ = a_2 - 316.101 \text{ kJ mol}^{-1} \quad (N = 0-1) \quad (5)$$

where the coefficients a_1 and a_2 are dependent on the type of cation.

In recent years a series of data on crystallohydrate salts of rare-earth elements have been listed [10–13]. It is worth mentioning that hitherto the thermochemical constants have been determined experimentally only for a small number of these crystallohydrates. Moreover, only limited data regarding ΔH_f° of crystallohydrates of rare-earth elements and actinoides were available at the time of formulating the additive equations. The application based solely on analogy of these empirically derived equations to new systems without a preliminary verification also with respect to these crystallohydrates appears to be scientifically unsound. A partial check indicated that the experimental data regarding crystalline phosphate dihydrates of 12 different rare-earth elements published in [14] and [15] and those from [16] differ by 80–120 kJ mol^{-1} from the values obtained theoretically *via* the additive equations. However, in the literature are present also experimental data corroborating the validity of the additive equations regarding ΔH_f° of crystallohydrate salts [17–19]. It is especially worth noting that the reliability of the already mentioned series of 12 experimental data for ΔH_f° for phosphate double crystallohydrates of rare-earth elements requires further verification [18].

The aim of the present paper is to elucidate the scope and limitations of the additive equations with respect to the rare-earth and actinoides crystallohydrate salts. The paper also aims at evaluating the predictive power of the additive equations with respect to ΔH_f° of crystallohydrates of rare-earths and actinoides as well as of other elements. The presently used experimental values for ΔH_f° are taken from [15].

Discussion

In Table 1 are compared the increments from the experimentally obtained values for various numbers of water molecules and the increments obtained by

Table 1

 ΔH_f° Increments for water molecules in crystallohydrate salts of rare earths and actinoides

Hydrate value <i>N</i>	Coordination sphere I, I + II, II	Increments from experimental data - <i>b</i> /(kJ mol ⁻¹)	Number of crystallohydrate	Increments — additive evaluation [2, 3] - <i>b</i> /(kJ mol ⁻¹)
0.5	+	146.0 ± 12.1	3	153.8
1	+	305.0 ± 8.0	14	307.5
1.3	+	402.1	1	397.4
1.6	+	478.7	1	487.9
2	+	599.6 ± 14.2	16	607.9
2	+	697.4 ± 17.0	12	607.9
2.3	+	687.8	1	697.9
2.5	+	758.6	1	758.1
3	+	909.2 ± 8.4	18	908.4
3.5	+	1052.3 ± 27.1	2	1058.6
4	+	1222.2 ± 26.4	10	1208.8
5	+	1506.2 ± 111.7	2	1509.2
6	+	1836.4 ± 14.7	20	1809.6
7	+	2106.2 ± 12.6	6	2102.5
8	+	2401.6 ± 122.2	2	2394.4
9	+	2708.3	1	2688.2
1(2—1)	+	295.8 ± 5.4	10	300.4
2(6—4)	+	594.5 ± 5.9	7	600.8
2(8—6)	+	599.1	1	585.8
1(10—9)	+	288.7	1	292.9
3(6—3)	+	905.8 ± 18.4	2	901.2
3(8—5)	+	874.9	1	886.2
4(6—2)	+	1191.2 ± 57.5	2	1201.6
5.5(6—0.5)	+	1649.3	1	1656.0
7.5(8—0.5)	+	2248.5	1	2241.8

using eqn (2). The errors of the arithmetic means were calculated employing the Student coefficient for 95 % confidence. In the general case when the ΔH_f° for the anhydrous salts were known, the increments amounted to the difference in ΔH_f° between the given crystallohydrate and the corresponding anhydrous salt. ΔH_f° values for crystallohydrates were used even in cases where this thermodynamic function for the anhydrous salts was unknown. In these cases the increments amounted to the differences in ΔH_f° of crystallohydrates of the same salt with different hydration values.

The data listed in Table 1 indicate a satisfactory agreement between the additively obtained and experimentally obtained increments. It has also to be pointed out that the derivation of equations and increments in this case from

experimental results falls within the group of reverse problems the solution of which is hindered by the intrinsic ambiguity [20]. It has also to be borne in mind that the experimental values for ΔH_f° of the anhydrous salts and their crystallohydrates have been determined with certain errors and the differences between these values (the water molecules increments) sum these errors.

In Table 1 are given two considerably differing increment values for two water molecules calculated from experimental data, *i.e.* $-599.6 \text{ kJ mol}^{-1}$ and $-697.4 \text{ kJ mol}^{-1}$. The second value is obtained on the basis of the already mentioned 12 values of ΔH_f° of phosphate double hydrates of rare-earth elements which are subject to reevaluation [18], while the first increment value is obtained on the grounds of ΔH_f° for anhydrous salts and dihydrates of rare-earth elements and actinoides available from [15]. The fact that only the first value agrees well with the increments for all other hydrate values given in the table supports the view that the validity of the series of experimental data has to be re-examined [18]. In this case we had in mind that the approximate evaluation methods can be used in the most favourable cases even for checking some experimental data [21].

Unfortunately, the causes for some of the significant observed differences obtained at the turn of the century regarding ΔH_f° for some crystallohydrate salts based on the theory and the use of eqn (2) remain unclear. It is perhaps worth recalling the opinion voiced in [20] that universal and generally useful prediction theories are also prone to seemingly absurd conclusions.

In the examination of the validity of the remaining additive equations regarding the crystallohydrate salts of rare-earth elements and actinoides we found that eqn (3) has a wider scope than that shown in [8], *i.e.* it is valid for crystallohydrates of various salts containing up to 7 water molecules. The presence of the term $3.5^{(N/2)-1}$ in this equation indicates the existence of an upper limit at $N = 7$. Indeed, the experimental data [15] for four salts — 24 crystallohydrates are within the interval of minus 10666 to 12269 kJ mol^{-1} approximately, while the powered term amounts to about $4.2 \times 10^6 \text{ kJ mol}^{-1}$ being drastically different from the experimental values data, which is an indication of the inappropriate use of the equation. It can be also added that combining two values which minimize the differences between the increments obtained by calculation and from experimental data does not offer any advantage over the use of eqn (2), or eqns (4) and (5) for that purpose.

It can be concluded that the high predictive power of eqn (2) is based on the relationship between the increment and the order of the water molecules within the first coordinative sphere of the complexing agent, that these increment values are practically generally valid and are also based on the absence of jumps in the values.

Table 2

Comparison of numerical values regarding $-\Delta H_f^\circ$ of $\text{LaCl}_3 \cdot \text{NH}_2\text{O}$ ($N = 0-7$)

<i>N</i>					
0	1	3	5	6	7
1071.1 ^a	1296.2 ^a	1979.0 ^a	2586.1 ^a	2876.5 ^a	3178.4 ^a
1071.1 ^b	1378.6	1979.4	2580.2	2880.6	3173.5
988.7	1296.2 ^b	1897.0	2497.8	2798.2	3091.1
1070.7	1378.2	1979.0 ^b	2579.8	2880.2	3173.1
1077.0	1384.5	1985.3	2586.1 ^b	2886.5	3179.4
1067.0	1374.5	1975.3	2576.1	2876.5 ^b	3169.4
1076.0	1383.5	1984.3	2585.1	2885.5	3178.4 ^b

a) Data obtained from [15]; b) experimental value used in eqn (2) for calculating the ΔH_f° values for all other hydrate values; 1 cal = 4.1840 J.

The use of eqn (2) for differentiating the ΔH_f° values for crystallohydrates which do not agree well with the experimental data is worth noting.

In Table 2 are compared the experimental data for ΔH_f° for the anhydrous lanthanum chloride and its crystallohydrates with 1 to 7 molecules of water with the values for ΔH_f° obtained using eqn (2). It can be seen that only in the case of the lanthanum chloride — monohydrate are observed significant discrepancies between the calculated and experimental values, all remaining cases showing good agreement between the two groups of data. This allows the conclusion to be drawn that the ΔH_f° values for $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ require additional verification. It is obvious that this approach for differentiating ΔH_f° values for various crystallohydrates of the same salt cannot bring about a correlation between a considerable series of data, which can be achieved using the approach given in [22]. The use of this approach for checking the correlation between small series of data of ΔH_f° of crystallohydrates of a given salt is worth mentioning. It allows a rapid result to be obtained regarding the correlation prior to resorting to calculations.

Eqn (2) permits information to be obtained regarding the reliability of data which for various reasons have not been reproduced. Thus, in [15] are given 39 values for ΔH_f° for anhydrous rare-earth carbonates and their crystallohydrates from a total of 48 values listed in [23]. In Table 3 are given the ΔH_f° values for 9 crystal phases listed in [23] and those obtained additively with eqn (2) on the grounds of data given [15]. A very good agreement is observed between the calculated and experimentally found values which allows to conclude that the 9 values for ΔH_f° are reliable.

Table 3

 ΔH_f° of rare-earth carbonates (anhydrous and hydrates), not included in [15]

Crystal phases	$-\Delta H_f^\circ(\text{found})$	$-\Delta H_f^\circ(\text{calc.})$
	kJ mol^{-1}	kJ mol^{-1}
	[23]	Evaluated data from other hydrate values included in [15]
$\text{La}_2(\text{CO}_3)_3$	3287.8	3285.7
$\text{La}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	4187.4	4194.0
$\text{Ce}_2(\text{CO}_3)_3$	3270.6	3284.0
$\text{Ce}_2(\text{CO}_3)_3 \cdot 0.5\text{H}_2\text{O}$	3422.9	3437.6
$\text{Ce}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	4169.8	4192.4
$\text{Nd}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	4183.6	4190.3
$\text{Ho}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	4174.4	4202.4
$\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	4161.4	4163.1
$\text{Yb}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	4108.2	4109.9

The existence of a limited number of data regarding ΔH_f° of amorphous anhydrous salts and crystallohydrates also in anhydrous state for rare-earth elements and actinoides as well as for other elements prevented the determination of increments due to water molecules in amorphous phases.

On the basis of ΔH_f° for 18 anhydrous salts, in amorphous or crystalline state, we obtained the changes in ΔH_f° as a result of crystallization of the amorphous salts amounting to $(31.3 \pm 8.8) \text{ kJ mol}^{-1}$. This is an indication that the use of eqn (2) for determining ΔH_f° of crystallohydrates on the basis of ΔH_f° of amorphous anhydrous salts should not be reliable since it does not take into account the changes in ΔH_f° during crystallization of the amorphous anhydrous salts and crystallohydrates.

References

1. Karapetyants, M. Kh., *Zh. Fiz. Khim.* 30, 593 (1956).
2. Rozenfeld, M. G., *Zh. Fiz. Khim.* 43, 1410 (1969).
3. Yanakiev, N. I., *Comm. Departm. Chem. Bulg. Acad. Sci.* 11, 223 (1978).
4. Yanakiev, N. I., *Comm. Departm. Chem. Bulg. Acad. Sci.* 18, 44 (1985).
5. Le Van, M., *C. R. Acad. Sci. C272*, 125 (1971).
6. Burilev, B. P., *Zh. Fiz. Khim.* 50, 2689 (1976).
7. Burilev, B. P. and Kostenko, Yu. V., *Zh. Fiz. Khim.* 51, 2775 (1977).

8. Del'Pino, Kh., Chukurov, P. M., and Drakin, S. I., in *Termodinamika i stroenie rastvorov*, p. 54. Ivanovo, 1980.
9. Petrusenko, L. G. and Yaglov, V. N., *Deposited Doc. 1981, SPSTL 759 — khp — D81; Ref. Zh., Khim. 1981, 24B 888; Chem. Abstr. 98, 133145.*
10. *Soedineniya redkozemelnykh elementov. Gidridy, boridy, karbidy, fosfidy, pniktidy, khalkogenidy, psevdogalogenidy.* (Kost, M. E., Editor.) Nauka, Moscow, 1983.
11. *Soedineniya redkozemelnykh elementov. Silikaty, germanaty, fosfaty, arsenaty, vanadaty.* (Bondar, I. A., Editor.) Nauka, Moscow, 1983.
12. Bandurkin, G. A., Dzhurinskii, B. F., and Tananaev, I. V., *Osobennosti kristalloghimmii soedinenii redkozemelnykh elementov.* Nauka, Moscow, 1984.
13. *Soedineniya redkozemelnykh elementov. Karbonaty, oksalaty, nitraty, titanaty.* (Arsen'ev, P. A., Editor.) Nauka, Moscow, 1984.
14. Usubaliev, D., Batkibekova, M., Yusupov, V., and Kudunov, M., *IV Conf. Int. Thermodyn. Chim.*, 1975, *I Thermochimique*, p. 217. Montpellier, France, 1975.
15. *Termicheskie konstanty veshchestv, Vol. VIII.* (Glushko, V. P., Editor.) Izd. Akad. Nauk SSSR, Moscow, 1978.
16. Storozhenko, T. P., Khanaev, E. I., and Afanas'ev, Yu. A., *Deposited Doc. 1981, SPSTL 614 — khp — D81; Ref. Zh., Khim. 1981, 24B 887.*
17. Safina, R. A., Morozova, M. P., and Markovskii, L. Ya., in *Khimiya i tekhnologiya lyuminoforov*, p. 93. Leningrad, 1974; *Ref. Zh., Khim. 1974, 23B 760.*
18. Adamkovičová, K., Bondar, I. A., Mezentseva, L. P., Kosa, L., and Proks, I., *Chem. Zvesti 38, 41* (1984).
19. Yaglov, V. M., Rud'ko, P. K., Bondar, L. A., and Gerasimenok, S. V., in *Khimiya i khim. tekhnologiya*, p. 13, Vol. 11. Visheishaya shkola, Minsk, 1976.
20. Rosenblit, A. B. and Golender, V. E., *Logiko-kombinatornye metody v konstruirovani lekarstv*, p. 36. Zinatne, Riga, 1983.
21. Kubaschewski, O. and Alcock, C. B., *Metallurgical Thermochemistry*, 5th Edition, p. 204. (Russian translation.) Metallurgiya, Moscow, 1982.
22. Gol'dstein, A. D., Gurvich, L. V., and Medvedev, V. A., *Zh. Fiz. Khim.* 58, 2641 (1984).
23. Karapetyants, M. Kh., Maier, A. I., and Vas'kova, N. A., *Izv. Akad. Nauk SSSR, Neorg. Mater.* 13, 1279 (1977).