METHODS OF DESCRIPTIVE STATISTICS IN FORECAST OF THERMODYNAMIC PROPERTIES OF HYDRATES

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The thermodynamic properties of many hydrates are uncertain due to their instability near standard conditions.

For the statistical analysis the database of thermochemical properties for 198 class of hydrates ($A \cdot xH_2O$) has been created. Thermodynamic functions of hydrates were represented by interpolate lines:

$$\Delta_f F^0_i\,(x) = a_i x + b_i, \qquad (1)$$

where b_i – potentials of substances without water (basis A), x – quantity of crystal waters, a_i - line's slope. Let's put the following potentials for indeces i from (1): $i=1$, $\Delta_f G^0(x)$– Gibbs standard energy of formation; $i=2$, $\Delta_f H^0\,(x)$– standard enthalpy formations from elements; $i=3$, $S^0(x)$ - absolute entropy of hydrates. Then, factors a_i (1) can be identified with corresponding properties for hydrate classes: a_1– hydratability, a_2 - hydrophilicity [1], a_3 – disorder of structure.

In the table factors a_2 for some classes of hydrates are submitted. Hydrates hydrophilicity (sulfates, nitrates, chlorides, etc.) were analyzed with connection of cation radii. By methods of linear correlation it is revealed, that affinity to molecules of water increases with reduction of cation radius. Use of hierarchical agglomerative methods has shown that the basic groups of similarity salts and minerals are defined by size of structure components. For most hydrates the group of "big" cation is allocated: Na, Ca, Cd, Sr and, in general, clusters are formed by cations with similar cation size. The dendrogram for sulfatic hydrates has been shown on Figure.

Correlation of thermodynamic characteristics of crystal water in hydrates with the sizes of their structural components opens opportunities for estimation and the forecast of physical and chemical characteristics for substances with scattered water.

Table. Hydrophilicity (a_2, kJ/mole) and cation radii (Angstrem) for some classes of hydrates

	R	SO_4^{2-}	NO_3^-	Br^-	Cl^-
Mn^{2+}	0.75	295.6		294.2	301.1
Sr^{2+}	1.21		294.3	301.5	298.5
Ba^{2+}	1.68			300.0	294.3
Cd^{2+}	1.03	298.0	299.4	294.1	296.1
Ca^{2+}	1.20	295.1	298.9	302.7	300.5
Cu^{2+}	0.81	301.0	300.8		300.6
Zn^{2+}	0.83	298.2	302.4	304.3	
Ni^{2+}	0.64	300.9			299.4
Fe^{2+}	0.69	297.4	320.8		302.8
Co^{2+}	0.73	297.9		302.8	300.1
Mg^{2+}	0.80	301.5	302.9	314.4	309.4

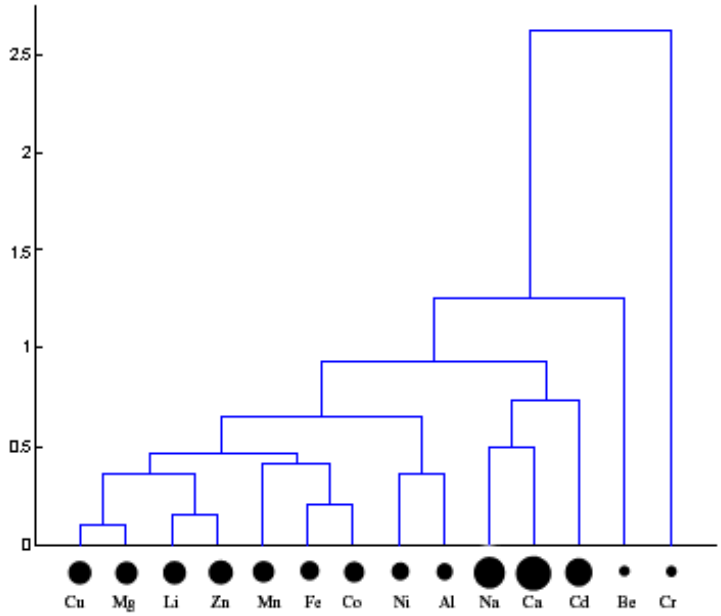

Fig. Cluster link of sulfate hydrates hydrophilicity with cation radii

Reference

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