

# ROLE OF OXYGEN CHEMICAL POTENTIAL IN THERMODYNAMICS OF MINERALS OF APATITE GROUP

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Thermochemical investigation of minerals of apatite group was made at differential automatic microcalorimeter (DAK1-1A) for working in aggressive media Aqueous solution of hydrochloric acid of 20 wt% weight charge 1-3 mg (3.5 ml) was used. Minerals were dissolved at T=40°C (313.15 K). The obtained results were recalculated for the standard enthalpy of mineral formation.

Deficit of volatiles caused by the lack of minerals of CaF<sub>2</sub>, CaCl<sub>2</sub> and Ca(OH)<sub>2</sub>, which form solid solutions with phosphates, similar to vitlokite (Ca<sub>9</sub>P<sub>6</sub>O<sub>24</sub>) is typical for all natural apatites. A high mutual chemical similarity of these basic components of apatite is characterized by reactions 1-3 in tabl. 1.

The calculations with their participation of apatite equilibria (reactions 4-5 in tabl. 1) show complex thermodynamic relationships between the varieties of apatite, determined not only by T and P, but geochemical factors as well. Besides the basic factors - chemical potentials of fluoride, chloride and water, determining formation of F-Cl and hydroxyl apatites, respectively, the chemical potential of oxygen mainly determining equilibria of fluoride/chloride/apatites with hydroxylapatites (reactions 5, 6 in tabl. 1) also refers to their number.

$$\Delta G_T^o = \mu_{H_2O} + 0.5\mu_{O_2} - \mu_{F_2(Cl)_2}$$

Table 1

Thermochemical characteristics of reactions between minerals of apatite group and simple chemical compounds (enthalpy, kJ; T, K)

NN	Reactions	$\Delta H_{298}^o$	$\Delta G_{298}^o$	$\Delta G_{1000}^o$
1	Wh + CaF <sub>2</sub> = 2 Ap <sup>F</sup>	-152.78	-149.42	-151.09
2	Wh + CaCl <sub>2</sub> = 2 Ap <sup>Cl</sup>	-102.08	-107.95	-54.28
3	Wh + Ca(OH) <sub>2</sub> = 2 Ap <sup>OH</sup>	-94.90	-93.04	-94.99
4	2Ap <sup>F</sup> + Cl <sub>2</sub> = 2Ap <sup>Cl</sup> + F <sub>2</sub>	483.44	472.68	514.62
5	2Ap <sup>F</sup> + H <sub>2</sub> O + 0.5O <sub>2</sub> = 2Ap <sup>OH</sup> + F <sub>2</sub>	587.12	575.27	617.41
6	2Ap <sup>Cl</sup> + H <sub>2</sub> O + 0.5O <sub>2</sub> = 2Ap <sup>OH</sup> + Cl <sub>2</sub>	103.68	102.59	102.79
7	CaF <sub>2</sub> + Cl <sub>2</sub> = CaCl <sub>2</sub> + F <sub>2</sub>	433.44	428.83	418.35
8	CaF <sub>2</sub> + H <sub>2</sub> O = Ca(OH) <sub>2</sub> + F <sub>2</sub>	699.26	516.51	561.85
9	CaCl <sub>2</sub> + H <sub>2</sub> O + 0.5O <sub>2</sub> = Ca(OH) <sub>2</sub> + Cl <sub>2</sub>	96.50	87.68	143.50
10	CaF <sub>2</sub> = Ca + F <sub>2</sub>	1229.20	1176.86	1060.44
11	CaCl <sub>2</sub> = Ca + Cl <sub>2</sub>	795.76	748.03	642.09
12	2NiO = 2Ni + O <sub>2</sub>	479.48	423.16	298.44
13	2Mt + 3Q = 3Fay + O <sub>2</sub>	525.48	456.18	316.36

Note: Minerals symbols: Wh - vitlokite, Ap - apatite.

It is necessary to consider this factor while constructing phase diagrams of apatites, among which the diagram of chemical potentials of fluoride and chloride represented in Fig.1 is very important. It corresponds to the standard water pressure is equals 1 atm, and chemical potential of oxygen is equals  $\mu_{H_2O}=0$ , corresponding to the redox buffer 2NiO = 2Ni + O<sub>2</sub>,  $\Delta G_T^o = \mu_{O_2} = -423.16$  kJ (T= 298 K) and -298.44 kJ (T= 1000 K).

On the diagram the condition of standard water pressure determines a narrowed field of stability of hydroxylapatite, which must expand with the increase of fluid pressure and oxygen fugacity. However, also in this verse on it reflects rather fully thermodynamics of minerals of apatite group, where the main role belongs to fluorapatite, having a rather high chemical similarity to fluoride and occurring at rather low values of its chemical potential in the solu-

tions. It can be also seen on the diagram, that the field of stability of fluorapatite expands with the temperature rise due to the reduction of stability field of chlorapatite, whereas, with respect to hydroxylapatite reverse relationships can be seen: hydroxylapatite with T rise tends to remove fluorapatite and especially, chlorapatite. However, its spreading is mainly limited fluid (aqueous) pressure and redox conditions/oxygen chemical potential.

Regular thermodynamic relationships of the basic varieties of apatites shown on the diagram (fig.1) reflect the most general peculiarities of halogenide - oxide equilibria, embracing simple compounds of Ca, entering their composition, as minerals. The diagram of chemical potentials of fluoride, and chloride (fig.2) embrace oxides, hydroxides, fluorides and chlorides of calcium. These simplest compounds show the similar thermodynamic features

typical for hydroxyle-halohenid systems as difficult phosphate compounds represented by varieties of fluoride-chloride and hydroxylapatites.

Oxygen chemical potential in thermodynamic constructions is usually used when metals of variable valency are present in the systems, for example, of Fe and Ni in the above-considered buffer equilibria/reactions 12 and 13 in Tabl.1. However, in the apatite equilibria valence of all the elements is fixed and the effective influence of the chemical potential

of oxygen shows specifics of halohenid systems.

Petrographically the effect of the redox situation on apatite equilibria can be observed while comparing Earth's rocks with the moon ones and meteorites where due to low oxygen chemical potential hydroxylapatites are absent. Chloro- and fluorapatites there enter the assemblage with vitlokit, as well as with alkaline phosphates which are absent in Earth's rocks, having high solubility in the aqueous phase.

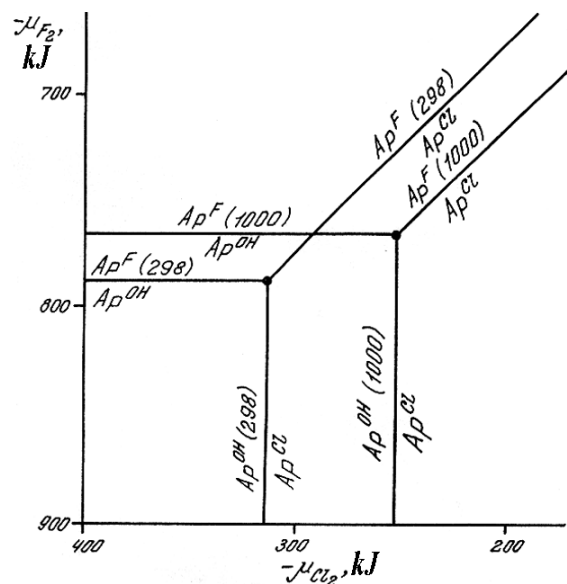


Fig.1. Isotherms of equilibria (298 K, 100K) of fluoride, chloride and hydroxylapatites on the diagram of chemical potentials of fluoride and chloride under standard water P (P=1 atm) in redox conditions, corresponding to buffer Ni-NiO

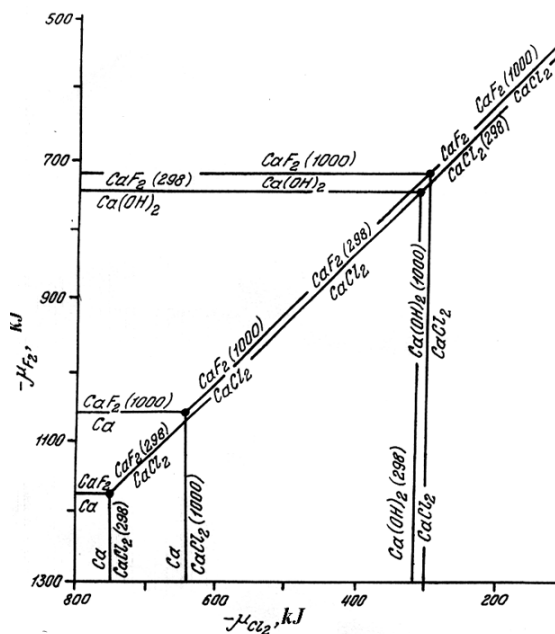


Fig.2. Diagram of chemical potentials fluoride, chloride and chloride calcium