THE SOME PROBLEMS OF DECISION OF THERMODINANIC REVERSE TASKS

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We belong the determination of physic-chemical condition (T and P) of mineral forming for reverse tasks of thermodynamic (RTT). The main type of reverse tasks is determination of mineral forming mechanism, this is determination of type of chemical reaction, leading to excretion and sedimantion of minerals. This reserve tasks type doesn't use now. The decision of this task limit only by fabrication of chemical reaction equation; their truth doesn't based.

One of the methods of determination of RTT is the use of geochemical barothermometers (GBT). Two types of chemical equations are used for GBT tasks decision:

1. The main type: this are equations of elements geochemical exchange between two components (minerals, solutions and etc.) For example, be biotite (Bi)-garnet (Gr) RTT is based on reaction of Bi(Fe) + Gr(Mg)= Bi(Mg) + Gr(Fe) ([1];

2. More seldom is chemical reaction equation; for example, по В.А. Курепину (1987) O-An(oxyannite)= Sn (sanidine)+ Mt (nagnetite). В.И. Фонарев (1987) used likeness equations for fabrication of geochemical exchange equations. The equations with participation of volitites are necessary to recognize the most odious, because here it has full tyranny. Since Л. Л. Перчук classic works [1] many GBT types were created, but the works of comparison of GBT using results bring to light at their bad likeness. The absence of strict analyses of their reason gives birth to negative phenomenon of GBT using, for example, GBT dependence from element concentration (Л.Л. Перчук, 1981, 1984, 1990 and etc.), over- estimation of role of solid solution imperfect ([1], С. Саксена, 1975; В.А. Курепин, 1990; и т.д.). The GBT structure became complicated in result, creating difficulty of their use and demanding use of computer techniques and RTT decision at times. The analyze of GBT use brought to light impasse situation at decision of Y- P problems, and her appearance reasons (В.П. Макаров, 1999 г.).

We determined two groups of main mistakes:

1. **Methodical mistakes of GBT use.** They arise at GBT use in concrete investigations. These mistakes include:

  A. Investigation of isolated, most often individual probes with individual couples of minerals for analyses.
  B. The absence of evidence the some exchange equations.
  C. The absence of demonstration of thermodynamic equilibrium at elements distribution between minerals, and mechanism analyze of realization of these exchanges. It is important, because the ion exchange part of mineral forming, and distribution minerals forming are not great by experiments of В.И. Фонарев (1987), Л.Л. Перчук (1983) and other investigations.
  D. The scheme of minerals selection does not correspond to GBT theoretical scheme. The geochemical exchange between minerals is possible, either distance between minerals does not prevent from this exchange or at availability common border between minerals, across which exchange realizes. At practice minerals get out from gross probes, and third minerals are between investigated minerals.
  E. The bringing of corrections at imperfect of elements distribution. The point is that the thermodynamic parameters determination (TPD) is the result either on the basis of experimental investigation, or on the basis of TPD comparison with it, determinated at experimental investigations. Therefore, experimental TPD account nonideality influence at elements distribution in minerals.

2. **Theoretical mistakes of GBT use.** The geochemical processes thermodynamic is one from most strictly worked up scientific discipline; a many equations correspond to demand of dimension theory [4], postulating transparency of meaning of physic- mathematical equations (PME) elements and their parts. For example, equation is $A= RT\ln(V_2/V_1)$ [3, p. 49] or diffusion equation of $D= D_o\exp(-E/RT)$. But at RTT decision strict some TPD is doubtful. Lower the same examples and problems decision path are considered.

The method of concretization of notions is construction of multitude M, in which some arbitrary elements A, B, C, D and E take place, what A+ B= C; there are A, D and number N, for which have been executed operation of NA= D. In that multitude isn't multiplication operation in that sense, that absent element of E, equal multiplication of other elements multitude, for example, operation A·B = E

absent. There are absent the operations, connected with used operations (logarithmic operation and etc.). Therefore, expression of lnA, A^B, $\sqrt{C}$, D^N and etc. has not physical sense. Actually, for example, significances of ln2 or 2^3 are known, but sense of expression of ln (2 кг) or $(2кг)^{(3кг)}$ is not clear.

The elements of M are called **homogeneous** elements; they have common physical nature and dimension, that is [A]= [B]= [C]= [D]= [E]. Then sum of 2кг(Cu)+ 3кг(Cu) is understood, but the sun of 1кг(Cu)+ 3кг (meal) is not clearly physically. The example of M: the quantity of mineral from different minary of one and the same deposit; physical (magnetic and etc.) poles, the water streams from different springs and etc.; but Cu and meal are different multitudes.

Since N= D/A, so N is non-dimensional number (that is [N]= 0). Therefore (_determination_) non-dimensional number is the result of significance division of homogeneous elements on each other. If A and B belong to M (that is (A, B) ⊃M), so X= A/(A+ B) is non-dimension number, that is [X]= 0. Often it is used ratio of Y= A_{M1}/(A_{M1}+ B_{M2}), where A_{M1} ⊃ M_1 and B_{M2} ⊃ M_2 (the mole parts, the analyze results, expression in %, and etc.). These are **non-homogeneous** elements: they have common dimension, but different physical nature (Cu- meal, Cu- Fe and etc.). So as the sun of A_{M1}+ B_{M2} isn't determinated, so physical nature of Y and expression of type of lnY have not clearly; it is clearly only, that it isn't non-dimensional value, that is [lnY]≠ 0. Non-homogeneous elements use lead to infringement of dimension theory demands.

The examples of operations with psevdohomogeneous elements:

1. Absolute entropy, for example, S= (R/[(γ -1))lnY] + const; Y= $PV^γ$ [5, page.19]: since [V]≠ 0, then dimension of [$V^γ$] isn't determinate, and also [ln $PV^γ$]= ?. That is connected with expression of S= $C_v$lnT+ RlnV + const [6, page 128].

2. The Raul law of P_i = $X_i P_o$ [7, page 148], where P_o и P_i- are stream pressure for clear solvent and solution, containing X_i portions of dissolved matters. A corrected Raul law wording follows from Genry law.

3. The chemical potential of $μ_i$= $μ_o$ + RTlnY [7, pages 148 and 155] is fundamental notion of barothermogeochemistry. Y is parameter: X; C is concentration; «a» is component activity in solution.

4. The mixture parameters of $S_{смеш}$= -nR[$\Sigma(X_i lnX_i)$] and $\Delta G_{смеш}$ = RT[$\Sigma(X_i lnX_i)$] [7, page 147; 8, page 57]. Therefore mole portions significances of X are arguments in more cases, however they are belonged to non-dimention quantities mistakenly. The significances of types of X_i^n and X_i^{Xi} are used greatly too. In the capacity of arguments may be parameters, for example, P, V and C and etc., which dimension doesn't give rise to doubt.

5. «The activity» is other fundamental notion. By [7] this is more difficult notion for determination. However mechanism of it appearance can't restore. An acquaintance with other scientific notions (geochronology discordance and etc.) permit to assume, that activity notion is arisen account of methodical mistake: experimental determinations of some parameters didn't regard as indivisible system, in which these parameters are connected; they did regard parameters one from another.

6. The mathematical mistakes in some thermodynamic parameters; for example, non correct conduct of integration operation. So, it is had entropy expression of S= S_o + [(Cp/T)dT + (∂V/∂T)$_p$dP] in [7]. We copy it expression in the form of S- S_o = [(Cp/T)dT + (∂V/∂T)$_p$dP]; then left part of this expression determinate, but right part is undetermined integral. Transformation of chemical potential expression lead to expression of $μ$ - $μ_0$ = RTlnC, where left part is decision of determinate, but right part is indefinite integral of ∫dC/C. These situations are not permitted. Correct expression of chemical potential expression will have form $μ$ = $μ_0$ + RTln(C/C_o). Then it will satisfy dimension theory demands.

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