

# MINIMIZATION OF THE THERMODYNAMIC POTENTIAL OF AN OPEN CHEMICAL SYSTEM\*

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Numerical minimization of the thermodynamic potential of a chemical system in order to obtain its equilibrium composition is widely used in geochemical investigations. Attention is often devoted to the Gibbs free energy ( $G$ ), the potential of a closed chemical system under isobaric-isothermal conditions. The problem of the calculation of the equilibrium composition of such a system is formulated as that of finding the minimum of the function  $G$  in the presence of linear constraints in the form of equations of the mass balance and the stipulation of a non-negative character of molar amounts of the phases of the system.

However, many natural systems cannot be regarded as closed, but correspond fairly accurately to the concept of an "open" system, according to D.S. Korzhinskiy. We will examine a particular but very important class of open systems, the equilibrium factors of which include the chemical potentials of completely mobile components [1]. In such systems we postulate exchange of certain (Completely mobile) components with the ambient medium, the chemical potentials of these components being constant and independent of the composition of the system.

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Since the ambient medium contains by definition unlimited amounts of completely mobile components, it is difficult to compare the equations of mass balance; however, there is no need for this. Bearing in mind that the completely mobile components are constant, we can represent an open system of this type as closed but possessing sufficient amounts of the completely mobile components to attain equilibrium. Certain calculation procedures may even not require explicit assignment of these amounts. Thus the formal constraint of the concept of an "ambient medium" permits the use of minimization of the Gibbs energy for open isobaric-isothermal systems.

Another approach to calculation of equilibria in open systems is based on a report by Korzhinskiy [2], in which he showed that we can examine the phases of a system consisting only of inert (i.e., not completely mobile) components, the overall mass of which in the system is constant and independent of the ambient medium. Clearly, such a system will be closed and the minimal value of the potential, obtained by subtracting from  $G$  the energy introduced into each phase by the completely mobile components, corresponds to its equilibrium state.

Table 1

Chemical Composition of Primary Rocks, mole ([4])

Element	Granite	Grano-diorite	Plateau-basalt	Element	Granite	Grano-diorite	Plateau-basalt
Si	1.1675	1.0825	0.812	Mg	0.02183	0.0474	0.166
Ti	0.00488	0.007	0.0274	Ca	0.0355	0.0788	0.1673
Al	0.283	0.313	0.274	Na	0.1122	0.12	0.0836
Fe	0.0444	0.0382	0.181	K	0.089	0.0584	0.0146

Table 2

## Thermodynamic Potentials and Stable Mineral Associations

Mineral	Potential of phases, cal/mole		Equilibril composition, mole		
	$-\frac{K}{gT}$	$-gT$	granite	granodiorite	plateau-basalt
Almandine	1 081 730	1 243 660	—	—	—
Ferrocordierite	1 742 110	1 985 000	—	—	—
Fayalite	299 485	353 460	—	—	—
Ilmenite	254 252	294 735	—	—	—
Magnetite	215 384	269 361	—	—	—
Hematite	153 040	193 525	0.0222	0.0153	0.0905
Annite	996 750	1 221 100	—	—	—
Hercynite	411 190	465 170	—	—	—
Ferrosilite	245 600	286 090	—	—	—
Quartz	184 960	211 950	0.4875	0.4012	0.1293
Periclase	127 840	141 340	—	—	—
Rutile	194 360	211 350	0.0049	0.0070	0.0274
Brucite	122 050	211 460	—	—	—
Mg cordierite	1 902 390	2 145 300	—	—	0.0107
Pyrope	1 316 034	1 477 970	—	—	—
Anorthite	882 127	990 100	0.0355	0.0673	0.0665
Forsterite	456 905	510 900	—	—	—
Spinel	484 270	538 250	—	—	—
Sphene	534 362	601 832	—	—	—
Phlogopite	1 296 080	1 520 431	0.0073	0.0158	0.0146
Diopside	669 410	750 370	—	—	0.1008
Enstatite	321 622	362 100	—	—	—
Wollastonite	343 390	383 870	—	—	—
Microcline	821 515	929 470	0.0817	0.0426	—
Albite	812 450	920 400	0.1122	0.1200	0.0836
Grossular	1 379 395	1 541 325	—	—	—
Anthophyllite	2 436 075	2 822 360	—	—	—
Muscovite	1 166 970	1 391 322	—	—	—
Calcite	158 950	285 430	—	—	—
Magnesite	131 810	258 289	—	—	—
Tremolite	2 490 500	2 876 780	—	—	—
Chlorite	1 567 255	2 059 840	—	—	—
Dolomite	292 978	545 940	—	—	—
Zoisite	1 395 498	1 602 130	—	—	—
Talc	1 149 325	1 373 677	—	—	—
Serpentine	763 588	1 009 879	—	—	—
Paragonite	1 155 468	1 379 820	—	—	—
Prehnite	1 214 135	1 438 470	—	—	—
Pyrophyllite	1 079 108	1 303 459	—	—	—
Analcime	617 960	774 841	—	—	—
Perovskite	352 422	392 905	—	—	—
Andalusite	532 895	600 366	0.0054	—	—
Nepheline	430 814	490 190	—	—	—
Siderite	51 267	177 750	—	—	—
Daphnite	1 283 750	1 776 330	—	—	—
Hedenbergite	587 435	668 400	—	—	—
Staurolite	2 423 760	2 778 830	—	—	—
Chloritoid	585 784	742 665	—	—	—
Ferrotremolite	2 080 070	2 466 350	—	—	—
Andradite	1 188 070	1 350 000	—	0.0038	—
Ferropargasite	2 258 370	2 644 650	—	—	—
	2 578 820	2 965 100	—	—	—

Note. The value of  $gT$  given by Karpov et al. [4] is -1,458,000 cal/mole.

In certain cases the result obtained by Korzhinskiy [2] permits simplification of analysis of the equilibria, but in no case does this signify the inapplicability of the Gibbs energy to open systems, as assumed by certain investigators. On the contrary, when calculation of the equilibrium compositions of open systems by minimization of the thermodynamic potentials is performed on a computer, it is precisely the first approach which is preferable. Its advantage is that we use as the initial data the tabulated thermodynamic values; furthermore, it is simpler to assign and change the chemical potentials of the completely mobile components than in the case of the second approach. Thus to calculate the Korzhinskiy potential of each phase we must express the composition of this phase in terms of the inert and completely mobile components; naturally, this presents certain difficulties if the components have a complex composition. For each phase, from the Gibbs energy  $G$  we must then deduct the energy of the completely mobile components, according to the result obtained. These calculations must be repeated afresh each time the chemical potentials of the completely mobile components change. However, the use of the potential  $G$  for open systems makes these calculations unnecessary. This simplification reduces not only the overall amount of work involved in preparing the initial data for calculation on the computer but also the number of errors incurred.

The equivalence of the two approaches to calculation of the equilibrium composition is most simply illustrated by the example of an open system consisting only of constant-composition phases. The potential of such a system is a linear function of molar amounts of the phases; therefore, the problem of finding its equilibrium composition is the standard problem of linear programming.

To calculate equilibria in such systems we compiled a specialized "Stable association" program for the Minsk-32 computer, realizing the simplex method of solving the problem of linear programming. The initial data for the program are the stoichiometric coefficients of the phases and the completely mobile components (if the system is open), the values of the chemical potentials of the phases and completely mobile components, and the empirical formulas of the system. The assigned set of phases is automatically supplemented by all the simple substances permitted in this system if they were not assigned in the initial set of phases.

The completely mobile components are regarded as individual phases and differ from the other phases only by the fact that the stipulation of a nonnegative character is not extended to them. From this it follows that the completely mobile phases are present in the basis in each iteration and cannot be excluded from it. Therefore, after inclusion of the completely mobile components in the basis, their corresponding lines and columns are removed from the calculation table. The table so obtained now corresponds to a closed system in which the transformed potential is then minimized. This transformation is the standard process of elimination of unknowns, unrestricted with respect to sign, in the problem of linear programming [3].

Examining the rule of transformation of the objective function, with inclusion of the completely mobile components in the basis, we see that the characteristic function obtained for the closed system coincides with the Korzhinskiy potential; this proves the equivalence of the two approaches to minimization of the potential of an open chemical system.

As a control we took the calculation of the equilibrium composition of the ground on Venus by Karpov et al., who used the Korzhinskiy potential for this purpose. In [4], Karpov et al. examined a system (Table 1) consisting of a certain amount of primary rock (granite, granodiorite, or plateau-basalt), open with respect to atmospheric water, carbon dioxide, and hydrogen; this enabled them to take the elements C, O, and H as completely mobile components. From the known composition of the atmosphere of Venus they calculated the chemical potentials of these elements at a given temperature and pressure, and then calculated the Korzhinskiy potentials of all the minerals included in the system. Note that the latest data on the parameters of the atmosphere of Venus (see, for example [5]) markedly differ from those used in [4]; this example must therefore be regarded solely as a control.

Table 2 gives the values of the chemical potentials, taken from [4], and the results of calculation of the equilibrium compositions. The calculation was performed by the "Stable association" program in two versions: with minimization of the Korzhinskiy potential (the  $g^K$  value) and of the Gibbs potential ( $g$ ). In the second case we took  $H_2O$ ,  $CO_2$ , and  $H_2$  as the completely mobile components;

their chemical potentials are  $-75.91$ ,  $-112.98$ , and  $-62.42$  cal/mole, respectively. Both calculations gave the same results, coinciding with the data obtained by Karpov et al. [4].

Thus minimization of the Gibbs free energy can be used to calculate the equilibrium compositions not only of closed systems but also of open isobaric-isothermal systems, including systems containing solutions and gaseous and liquid phases, because the properties of the completely mobile components — unlimitedness of the molar amounts and constancy of the chemical potentials — do not depend on the state of the system.

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