# Calculating Equilibrium Phase Assemblages in Systems Subject to Generalized Chemical Potential Constraints

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The equilibrium state of a system is characterized by a minimum in the Gibbs free energy at specified temperature, pressure and bulk composition. Under these conditions the system evolves from a disequilibrium to a equilibrium state under the restriction that the system boundary is closed to mass transfer, but is open to heat exchange with its surroundings and to any volume change accompanying phase formation. Korzhinskii [1] generalized the concept of thermodynamic equilibrium to "open" systems subject to mass exchange with their surroundings for the specific case that the constancy of component mole number may be exchanged with constancy of the equivalent chemical potential, e.g. equilibrium in a system open to exchange of a fugitive component like $H_2O$ may be uniquely determined if the chemical potential of $H_2O$ is somehow externally imposed upon the system. The thermodynamic potential that is minimal under these "open" system conditions is the "Korzhinskii potential" [2], which may be defined by a suitable Legendre transformation of the Gibbs free energy.

While the usual application of the Korzhinskii potential is to the characterization of equilibrium in systems constrained by externally fixed chemical potentials, the theory equally applies to the case where a chemical potential, or some linear combination of chemical potentials, is constrained by the demand that a particular phase or collection of phases is present in the system. Computational thermodynamics algoruithms are developed to compute chemical equilibrium under generalized chemical potential constraints of this type. An example of magma constrained to be in equilibrium with multiple mineral phases is presented.

[1] Korzhinskii DS (1959) Physiochemical Basis of the Analysis of the Paragenesis of Minerals. Consultants Bureau, 142 pp.

[2] Ghiorso MS, Kelemen PB (1987) Special Publication, Geochemical Society, 1, 319-336