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Pb-S-O Vapor System Re-evaluated Using Genetic Algorithms

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The efficacy of biologically inspired genetic algorithms for optimization is now well established. This article discusses the scope of using such an algorithm as an equation solver and presents detailed calculations on the Pb-S-O vapor system containing a total of 20 species as a paradigm case. This further increases the scope of applications of this evolutionary methodology in the domain of phase equilibria research, and this methodology is expected to be more advantageous than many other conventional techniques.

1. Introduction

Although a host of computational techniques are available for multicomponent equilibria studies[1,2] using a macroscopic description of Gibbs free energy, they can be broadly classified into two distinct categories: (1) the techniques based upon free energy minimization and (2) the techniques requiring solution of explicit equilibrium relationships, where the Gibbs phase rule determines the total number of equilibrium constants needed for a deterministic solution. Genetic algorithms,[3-7] a class of efficient optimizers, have already been successfully applied to multicomponent equilibria studies following the free energy minimization route.[8] However, to date, no published research exists in which the genetic algorithms have been exploited as nonlinear equation solvers pertinent to any phase equilibria problem that directly involves the equilibrium constants. In this article, the authors demonstrate how this can be done and present an analysis of the Pb-S-O vapor system to demonstrate the feasibility of this approach.

The genetic algorithms have been described in detail in many of the authors' previous publications.[9-15] Only a brief outline is presented here.

2. Genetic Algorithms in a Nutshell

In the natural world, populations of species evolve through well-defined biological processes such as selection, crossover, and mutation. One generation gives rise to the next, where, following a Darwinian scheme, the stronger individuals with a better fitness acquire a higher probability of survival. In genetic algorithms, this natural selection mechanism is mimicked in a figurative way. When it comes to problem solving using genetic algorithms, an individual is formed through an assembly of the probable variable values, denoting a tentative solution. A set of such tentative solutions constitutes the population. The mutation process adds small probabilistic perturbations to them. The crossover combines two individuals and forms newer members of the population. Normally, fitness of the individuals is attributed to the function values they denote and the selection procedure for the subsequent generations is related to the fitness. The procedure is repeated until convergence, as shown schematically in Fig. 1. The most common form of genetic algorithms employs a binary encoding and is popularly known as simple genetic algorithms (SGAs).

Further details of the genetic algorithms are available elsewhere.[3-7]

3. Pb-S-O Vapor System

This system has immense practical importance, particularly in connection with the analyses of emissions from lead

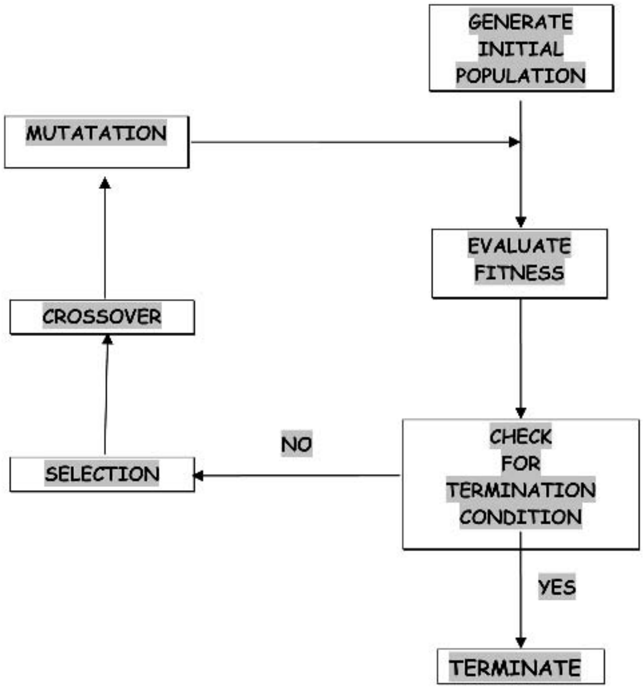

Fig. 1 Flow chart for genetic algorithms

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extraction and sintering units. Pyroprocessing of lead involves exothermic conversion of galena concentrates (PbS) to PbO, during which a significant amount of lead-bearing species can end up in the atmosphere due to their high vapor pressure. This problem is particularly significant in many developing countries where the lead production is bound to increase for economic reasons. For example, a recent news item[16] shows that a major Indian lead company is pumping in another $21 million to increase its annual production from 35,000 tons to 85,000 tons, simply to keep up with the domestic demands. In such a scenario, anyone with a minimum environmental concern would like to know how much of this lead would actually end up in the atmosphere, and in what form. A thermodynamic evaluation of the Pb-S-O vapor system would be absolutely essential to provide a quantitative answer.

The Pb-S-O vapor system contains a total of 20 constituents[17] identified as PbS, PbO, Pb_2O_2, Pb_3O_3, Pb_4O_4, Pb_5O_5, Pb_6O_6, Pb, S, S_2, S_3, S_4, S_5, S_6, S_7, S_8, SO, SO_2, SO_3, and O_2. Applying the phase rule for chemically reacting systems,[2] one can easily ascertain that a total of 17 independent reactions involving these constituents are required to sustain the equilibrium. Thus the system implicitly has a total of four degrees of freedom. For any given temperature and total pressure, an arbitrarily prepared gas mixture containing no stoichiometric restrictions would still be left with two degrees of freedom, and a unique solution can only be obtained by specifying two more external restrictions; fixed atomic ratios or chemical potentials, for example. The constrained chemical potential method (CCPM),[17-21] which is specifically devised for the equilibrium calculations of multicomponent systems obeying the phase rule, obtains a deterministic solution by specifying two chemical potentials. This technique employs an ingenious convergence condition and has been successfully applied earlier to compute the Pb-S-O vapor system.[17] (Further details of CCPM are provided in the Appendix.) In this study, the authors have recalculated the same system using genetic algorithms to establish the applicability of evolutionary methods in multicomponent equilibria calculations using explicit equilibrium constants. The required thermodynamic data were taken from the previous work.[17] The basic methodology is described below.

4. Genetic Formulation

A closed form solution for this system, as expected on the basis of the discussions in the previous section, would involve a simultaneous solution of the following equations:

(1) The 17 equilibrium relationships of the type:

$$f_i \equiv \frac{p_{\mathrm{Pb}}^{m} p_{\mathrm{O_2}}^{\mathrm{n}} p_{\mathrm{S_2}}^{\mathrm{p}}}{p_{\mathrm{Pb}_x\mathrm{S}_y\mathrm{O}_z}^{\mathrm{q}}} - K_i = 0$$

where $i = 1, 2, \ldots, 17$. The stoichiometric coefficients m, n, p, q, x, y, z are ≥ 0.

(2) The total pressure constraint is expressed as

$$f_{18} \equiv \sum_{j=1}^{N} p_j - P_{\mathrm{T}} = 0$$

where P_{T} denotes the total pressure, p_j is the partial pressure of the jth constituent, and N denotes the total number of species.

(3) The chemical potential constraints:

$$f_I \equiv \mu_l - k_l = 0$$

where $I = 19, 20$; $l = 1$ for $I = 19$ and is 2 otherwise; μ denotes chemical potential, and the k term denotes the constraint.

A total of 20 nonlinear algebraic equations, f_1 to f_{20}, containing 20 unknown partial pressures are thus formed, which the authors have attempted to solve using genetic algorithms. For this purpose they constructed a new objective function F and attempted to maximize it using the evolutionary approach. The explicit form of this objective function is given as

$$F = \frac{1}{1 + \sqrt{f_1^2 + f_2^2 + \ldots + f_{20}^2}}$$

The maximum value of this objective function would correspond to the minimum of the square root term in the denominator. This, in turn, would make all the f values zero, leading to a feasible solution of this set of 20 algebraic equations, which is thermodynamically known to exist.

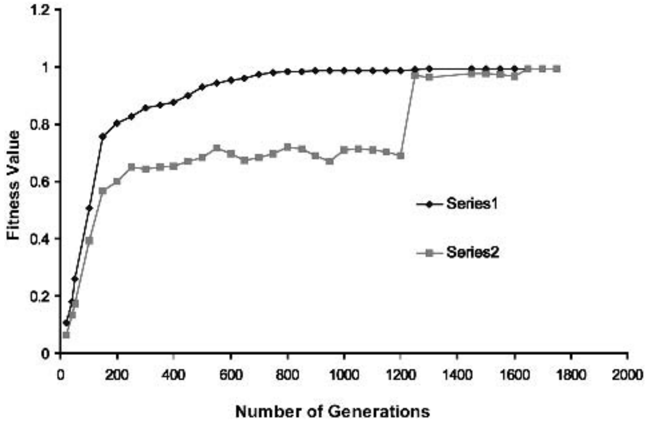

Fig. 2 Convergence demonstration for a typical simple genetic algorithm run; the points in Series 1 denote the maximum fitness values in the population, while the average fitness values are demonstrated by the points in Series 2.

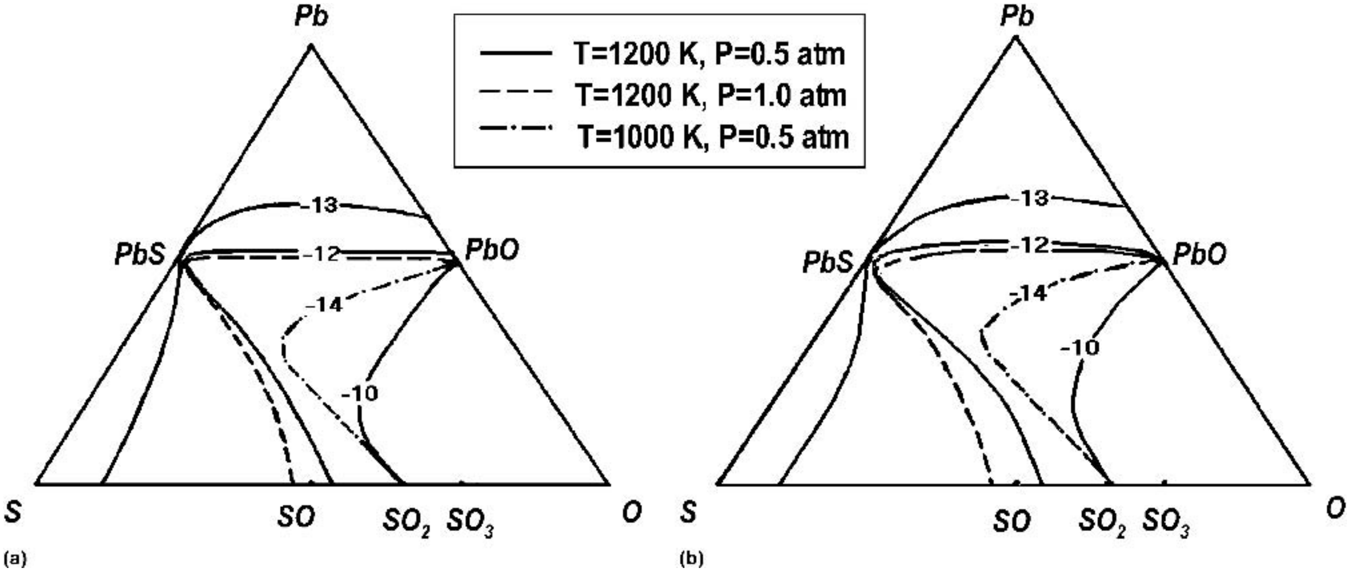

Fig. 3 Oxygen isobars at various temperatures and total pressure obtained by **(a)** CCPM and **(b)** genetic algorithm; all numbers are base 10 logarithms of P_{O_2} (atm) values.

All the calculations were performed in a UNIX workstation using a binary encoded genetic algorithm with an elitist option[3] that preferentially preserves the best solution of the previous generation. Upon convergence (i.e., $F \rightarrow 1$), the average and maximum fitness values of the population became quite close to each other, as shown in Fig. 2.

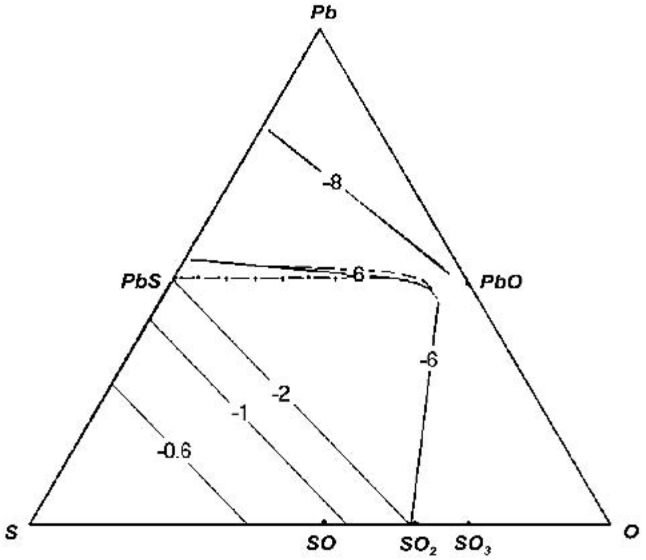

Fig. 4 S_2 isobars; all numbers are base 10 logarithms of P_{S_2} (atm) values. The rest are the same as in Fig. 3.

5. Results and Discussion

The atomic fractions of the respective elements were computed from the computed partial pressure data and the results were plotted as various isobar lines in a number of Gibbs triangles. The results obtained through the applications of genetic algorithms closely resemble the earlier calculations[17] where the CCPM was used. Figure 3 provides a typical comparison. The S_2, SO_2, Pb, and PbS isobars shown in Fig. 4-7, respectively, are also in good agreement with the previous calculations. The PbO isobars shown in Fig. 8, although in general agreement with the previous work, seem to form a closed loop, and the tendency is quite prominent in case of the $10^{-3.4}$ isobar lines, which could not be clearly resolved earlier through the CCPM.[17]

This tendency of forming closed loops becomes more prominent in case of $(PbO)_n$ polymers. The Pb_3O_3 and Pb_6O_6 isobars (Fig. 9 and 10), which were not calculated in the earlier work,[17] were studied during the present investigation and they show a tendency of clustering of such closed loops in various regions of the Gibbs triangles. The adjacent regions in these loops are often so closely placed that the genetic algorithm could not satisfactorily distinguish between them and due to this reason only the outer contours of various regimes are plotted in Fig. 9 and 10. The results, however, have a far-reaching environmental consequence, as the galena sintering machines essentially operate in the vicinity of the PbS-PbO pseudo binary line, while the lead blast furnaces operate close to the PbO-Pb region. In both cases, a comparison of Fig. 8-10 would indicate that the polymeric lead oxides are emitted at a much higher concentration than PbO. The lead-containing species with higher molecular weight have the tendency of settling in the lower layer of the atmosphere, thus posing a higher environmental threat due to their toxicity. This appears to be an important finding that could not be envisaged from the data of the previous investigation using CCPM.

Some of the isobars, the PbS isobars shown in Fig. 7 for

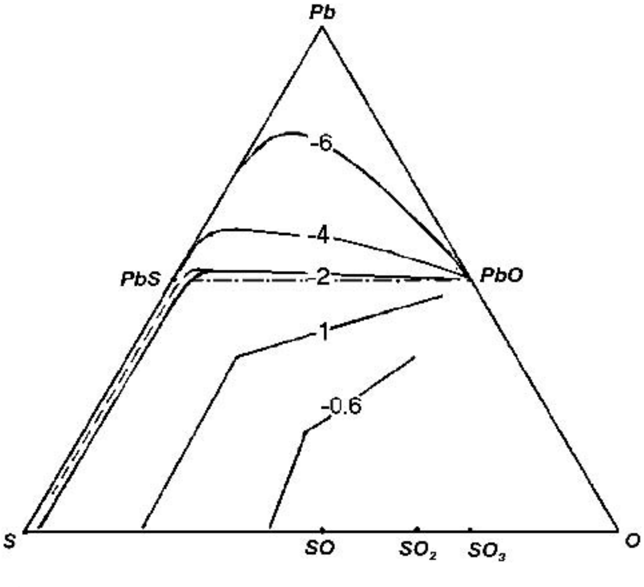

Fig. 5 SO_2 isobars; all numbers are base 10 logarithms of P_{SO_2} (atm) values. The rest are the same as in Fig. 3.

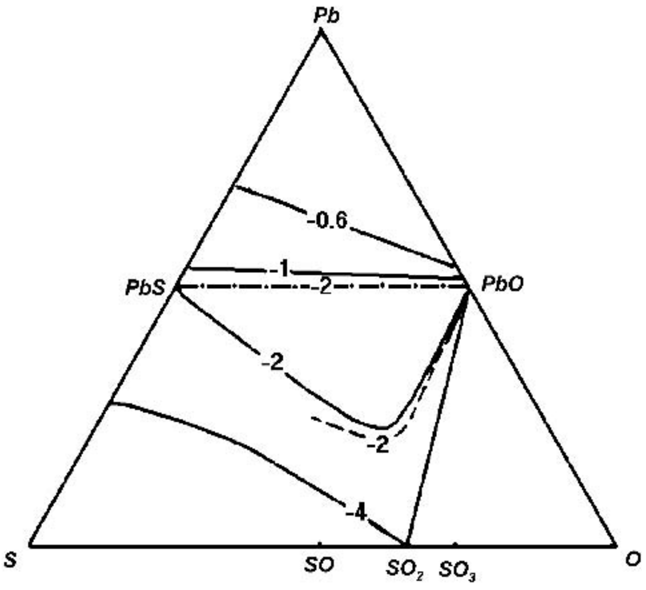

Fig. 6 Pb isobars; all numbers are base 10 logarithms of P_{Pb} (atm) values. The rest are the same as in Fig. 3.

example, show some predominantly linear regions. Since the same trends were observed in earlier calculations using CCPM,[17] the authors would like to take them for real. The nonlinearity in the isobar lines arises out of the nonlinear nature of the pertinent equilibrium relationships, and, presumably, for certain stoichiometry and species concentrations, it becomes rather weak. No two isobars at the same temperature can, however, touch or intersect each other, nor can a single component isobar terminate or continue along a binary axis devoid of its element, and those requirements are satisfied by all the computed isobar lines, linear and nonlinear alike.

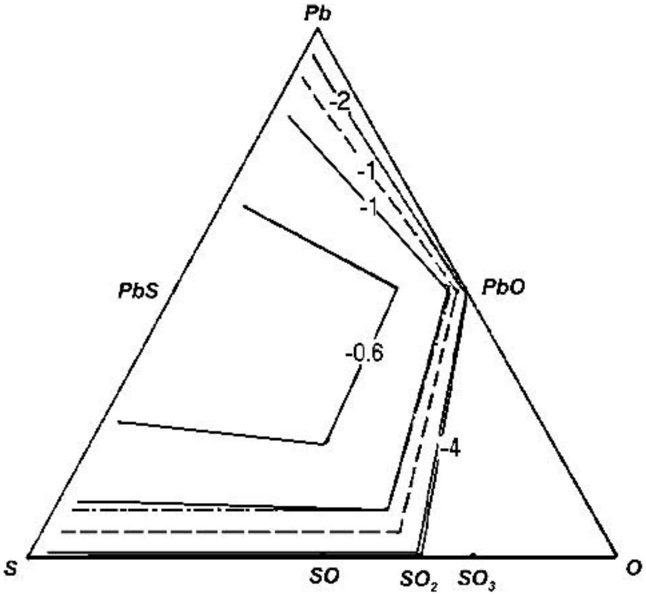

Fig. 7 PbS isobars; all numbers are base 10 logarithms of P_{PbS} (atm) values. The rest are the same as in Fig. 3.

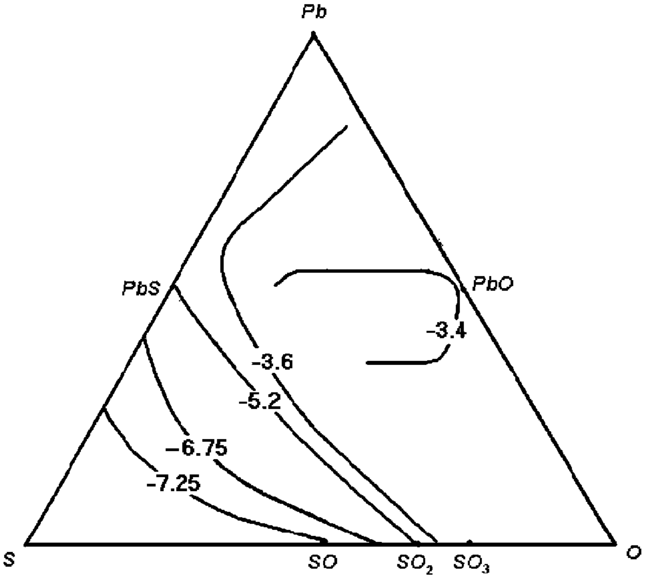

Fig. 8 PbO isobars; all numbers are base 10 logarithms of P_{PbO} (atm) values. The rest are the same as in Fig. 1.

6. Conclusions

This successful recalculation of the Pb-S-O vapor system opens up an alternate strategy of computing the multicomponent equilibria problems, which can now be extended to numerous phase equilibria studies that matter from a practical consideration. Genetic algorithms perform an exhaustive search, and for a highly nonlinear problem such as the one currently at hand, the nature of the solution appears to be more comprehensive than those obtained by the CCPM,[17] which sometimes proceeds very slowly and of-

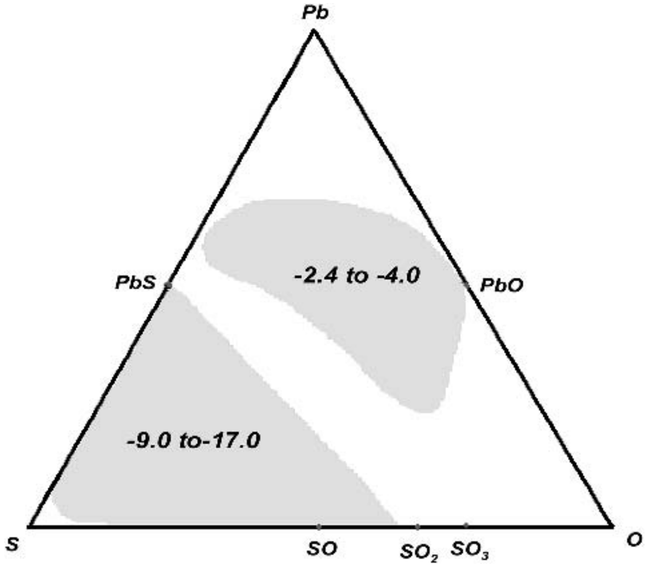

Fig. 9 Regions showing Pb_3O_3 concentrations; all numbers are base 10 logarithms of $P_{Pb_3O_3}$ (atm) values

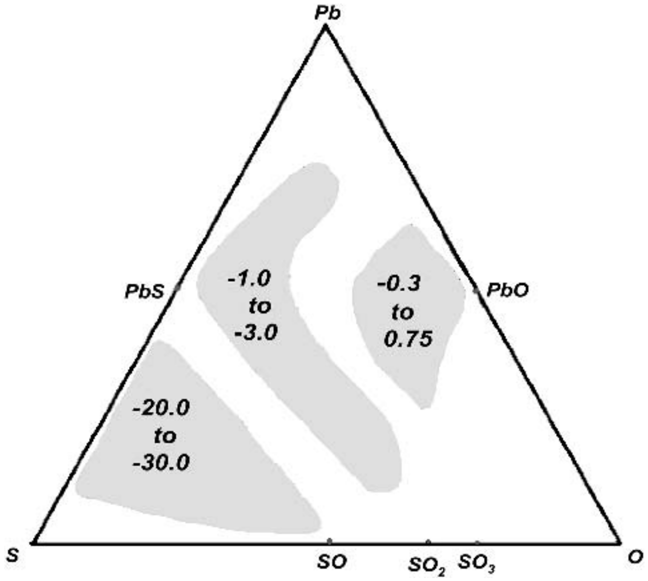

Fig. 10 Regions showing Pb_6O_6 concentrations; all numbers are base 10 logarithms of $P_{Pb_6O_6}$ (atm) values

ten does not resolve the entire range of the feasible solutions. What the authors have performed here is essentially a guided probabilistic search, which is more subtle and efficient than some of the earlier methods propagated by Bahn,[22] Kellogg,[23] and Rao[2] and, for that matter, does not require any cumbersome matrix inversions such as both the first and second order modified Newton-Raphson methods tried extensively for such problems.[24] In fact, most of the methods detailed in the classic text of Van Zeggeren and Storey[1] are highly sensitive to the initial guess values. Particularly on this count the genetic algorithms would score well above most of its competitors, as this method is built upon the evolution of a randomized initial set of solutions, where the accuracy of the initial guess values is neither a prerequisite nor of any particular advantage.

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Appendix

Constrained Chemical Potential Method

A brief description of the CCPM is provided here in terms of an O_2 isobar in the Pb-S-O vapor system. An analogous procedure can be adopted for calculating any other isobars. The essential steps are as follows.

As indicated in the main text, for this system, at a constant temperature T, and a total pressure P_T, fixing the values of two chemical potentials would satisfy the phase rule requirements of an invariant equilibrium. Since at a low total pressure the fugacity and partial pressure can be considered as synonymous, one can conveniently fix the values of p_{O_2} and p_{Pb} and initiate the calculation with an initial guess value of p_{S_2} say, p_{S_2I}. This would enable one to calculate the sum of the partial pressure of the constituents without oxygen as

$$\sum_{j=1}^{n} P_j = \sum_{j=1}^{n} f_j(K_j, P_{Pb}, P_{S_2I}) \tag{A-1}$$

where P_j is the partial pressure of the jth constituent, which does not contain any oxygen, and n denotes the total number of such constituents, K_j is the pertinent equilibrium constant, and the functions on the right-hand side are obtained from the equilibrium relationships.

Now one proceeds to determine the sum of partial pressures of all the m species that contain oxygen, using the relationship:

$$\sum_{k=1}^{m} P_k = P_T - \sum_{j=1}^{n} P_j \tag{A-2}$$

where P_k denotes the kth constituent containing at least one atom of oxygen. A check for the existence of a solution becomes necessary at this point, as no solution would exist while

$$P_T < \sum_{j=1}^{n} P_j \tag{A-3}$$

If this occurs then the initial guess values are altered until the inequality

$$P_T > \sum_{j=1}^{n} P_j \tag{A-4}$$

is satisfied.

The next step involves a redetermination of the sum of partial pressures of species with oxygen directly from the equilibrium relationships and is evaluated as

$$\sum_{k=1}^{m} P_k = \sum_{k=1}^{m} f_k(K_k, P_{O_2}, P_{Pb}, P_{S_2I}) \tag{A-5}$$

The functions on the right-hand side are once again determined from the equilibrium relationships. The K values, as before, denote the equilibrium constants.

Convergence requires that the values determined by Eq A-2 and A-5 should be equal, and the partial pressure of sulfur is now calculated as

$$P_{S_2IC} = [P_T - \sum_{j=1}^{n} P_j]/[(1.0/P_{S_2I}) \sum_{k=1}^{m} f_k(K_k, P_{O_2}, P_{Pb}, P_{S_2I})] \tag{A-6}$$

As a criterion of convergence, it is now checked whether the calculated value of the partial pressure of sulfur P_{S_2IC} matches with its current guess value P_{S_2I}. If not, then a repetitive half interval estimation for the new value of the sulfur partial pressure P_{S_2N} is obtained as

$$P_{S_2N} = 0.5\,(P_{S_2I} + P_{S_2IC}) \tag{A-7}$$

Calculations now resume from step A-1 by replacing P_{S_2IC} with P_{S_2N}. Upon convergence the respective atom fractions of Pb, S, and O are determined using the calculated partial pressure values. This essentially gives rise to one point in a particular isobar line. The calculations are now repeated for newer feasible values of P_{Pb}, keeping the value of oxygen partial pressure intact.