MM209 Assignment Report

Objective : Write a program that gives a predominance diagram for the Zn-S-O system by giving temperature as input.

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Introduction: Predominance Diagrams

A ***predominance diagram*** is a graphical representation of a multi-equilibria system which shows the concentration conditions where a chemical species is stable. They are generally two dimensional graphs with the axes representing the logarithms of the concentrations of two species. The boundaries indicate conditions in which adjacent species are in equilibrium. Predominance diagrams are useful for predicting the conditions required for obtaining a particular phase and predict possible processing routes. In the metallurgical context, predominance diagrams help determine stable products formed in a process at different partial pressures of the various gases over the mixture. This information is used to decide composition of the gaseous mixture used during the process

Methodology

Roasting of ZnS in extraction of zinc from sphalerite has been considered. Presence of impurities such as iron has been neglected in this project. Formation of SO_3 will also be negligible as oxidation of SO_2 requires a catalyst which isn't present since we are considering no impurities. The gaseous mixture present is an SO_2- O_2 system with an $S_2 + 2O_2 \rightleftharpoons 2SO_2$ gaseous equilibrium present which can be described by two components since ΔG^o of the reaction is known. Hence the predominance diagram will be a two-dimensional one as the system needs two control parameters. The natural logarithms of the partial pressures of S_2 and O_2 have been used as the axes.

As a preliminary for drawing a predominance diagram, phase rule must first be considered. Since pressure is kept constant, phase rule is modified to

F = C - P + 1

The process gives rise to 5 phases: Zn, ZnO, ZnS, $ZnSO_4$ and the gaseous equilibrium mixture. The system effectively has 3 components: Zn, O_2 and S_2.

Implementing this information into the phase rule:

F = 4 - P

Therefore it can be seen that when three phases are in equilibrium, there is one degree of freedom and when four phases are in equilibrium it gives rise to an invariant point. Since the gaseous exists over the entire working range, one of the phases is always the gaseous one. Hence the boundaries with one degree of freedom correspond to equilibria between two condensed state phases. These possible 6 ($^4C_2$) pairs are represented in the table below. Note that the activities of solids are approximated as unity

The boundaries with one degree of freedom are linear with respect to $\ln(p(O_2))$ and $\ln(p(S_2))$ as can be seen below.

	Condensed State Phases	Chemical Equation	Equilibrium constant	Equation of phase boundary
1	ZnS & Zn	$2ZnS \rightleftharpoons 2Zn + S_2$	$p(S_2)$	$In(p(S_2)) = -\Delta G^o{}_1/RT$
2	ZnO & Zn	$2ZnO \rightleftharpoons 2Zn + O_2$	$p(O_2)$	$In(p(O_2)) = -\Delta G^o{}_2/RT$
3	$ZnSO_4$ & ZnS	$ZnSO_4 \rightleftharpoons ZnS + 2O_2$	$p(O_2)^2$	$2In(p(O_2)) = -\Delta G^o{}_3/RT$
4	$ZnSO_4$ & ZnO	$2ZnSO_4 \rightleftharpoons 2ZnO + S_2 + 3O_2$	$p(S_2) \cdot p(O_2)^3$	$In(p(S_2)) + 3In(p(O_2)) = -\Delta G^o{}_4/RT$
5	ZnS & ZnO	$2ZnS + O_2 \rightleftharpoons 2ZnO + S_2$	$p(S_2) / p(O_2)$	$In(p(O_2)) - 3In(p(S_2)) = -\Delta G^o{}_5/RT$
6	Zn & $ZnSO_4$	$2Zn + 4O_2 + S_2 \rightleftharpoons 2ZnSO_4$	$p(S_2) \cdot p(O_2)^4$	$In(p(S_2)) + 4In(p(O_2)) = -\Delta G^o{}_6/RT$

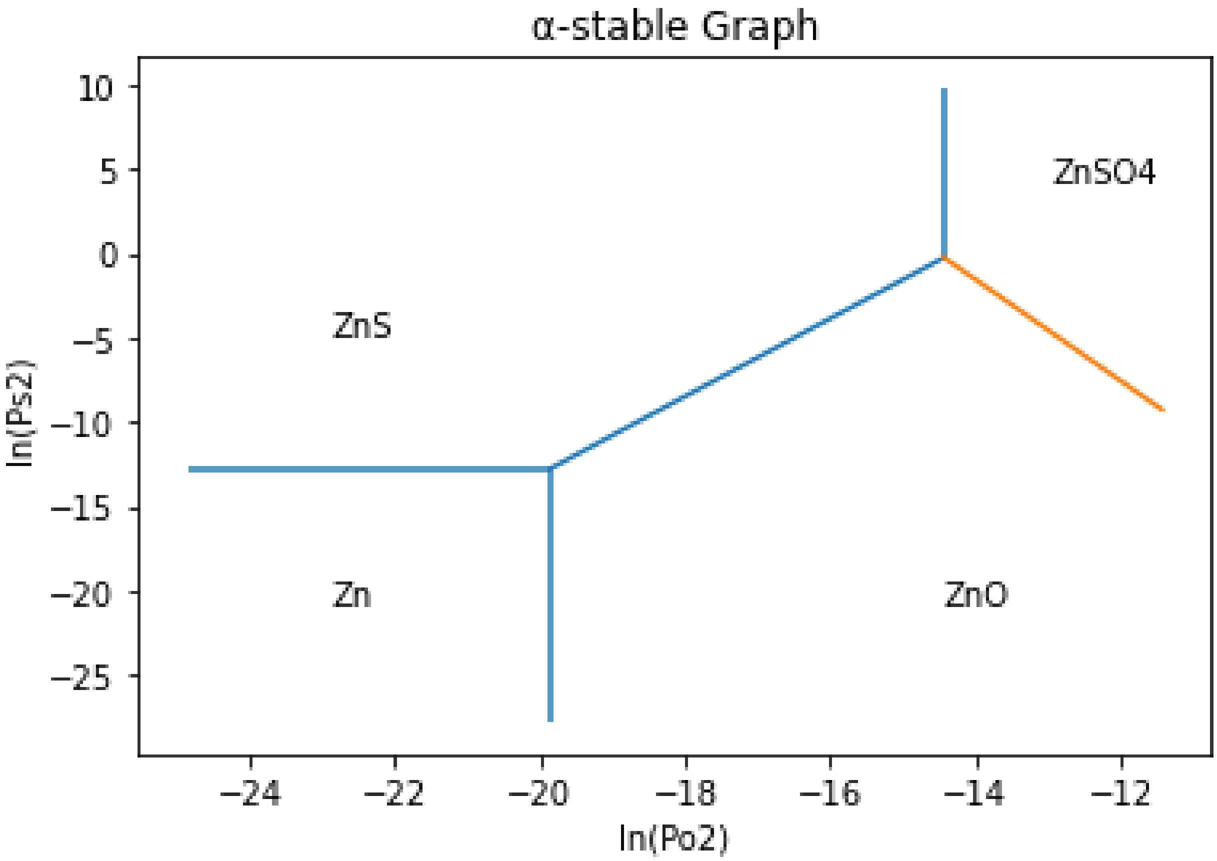
Hence if x axis is taken as $\ln(p(O_2))$ and y axis as $\ln(p(S_2))$, eqns 2 & 3 represent vertical lines and equation represents a horizontal line. Since 3 phases at most can be in contact, that too only at invariant points, it can be shown that there can be only 5 boundary lines. This implies that, at every temperature, only 5 of the above equations are valid which are selected based upon other constraints on the system.

Ultimately, such a diagram can be plotted at any given temperature T if ΔG^o_f values of ZnS, ZnO and $ZnSO_4$ since all other data can be derived from there.

Data Used :

1) $\Delta G^o = (960 - (348*0.001*T))*1000$; $ZnSO_4 \rightleftharpoons Zn + 0.5S_2 + 2O_2$
2) $\Delta G^o = (268.709 - (100.5*0.001*T))*1000$; $ZnS \rightleftharpoons Zn + 0.5S_2$
3) $\Delta G^o = (352.602 - (106.1*0.001*T))*1000$; $ZnO \rightleftharpoons Zn + 0.5O_2$

Result generated by code at T = 1300 K :



Conclusions :

1) A predominance diagram of the Zn-S-O system was constructed by implementing the phase rule and using the ΔG^{o}_{f} values of ZnS, ZnO and $ZnSO_4$.
2) A python script was written based on these constraints and values to generate such a diagram at any given value of temperature. The Matplotlib library was used to generate the images.
3) Functions such as text(), title() were used for labelling. Plot() and subplots() were used for plotting.

References :

https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781119078326.ch2

https://en.wikipedia.org/wiki/Predominance_diagram

https://janaf.nist.gov/tables/O-071.html

Contribution :

We had equally contributed to this project. We firstly researched and understood the problem statement individually and worked together to arrive at code and report.