

THE PAPUA NEW GUINEA UNIVERSITY OF TECHNOLOGY

THIRD YEAR MINERAL PROCESSING ENGINEERING

MP343 - PYROMETALLURGY I

FIRST SEMESTER EXAMINATION

TUESDAY 23rd JUNE 2020 – 12:50 PM

TIME ALLOWED – 3 HOURS

INFORMATION FOR STUDENTS

1. You have 10 minutes to read the paper. You **MUST NOT** begin writing during that time.
2. **Attempt ALL questions.** Write all answers in the answer booklet provided.
3. Write your **NAME** and **STUDENT NUMBER** clearly on the **ANSWER BOOKLET**. Do this **NOW**.
4. **NO** mobile phones, tablets or laptops allowed in the examination room.

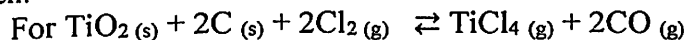
Marking Scheme:

All question carry equal marks. Total mark is 100.

Question 1

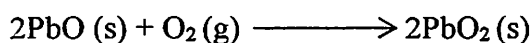
- (a) The following compounds are subject to complete combustion in a bomb calorimeter. Assuming the mean temperature to be 298 K, calculate ΔnRT and hence the difference between ΔH^θ and ΔU^θ for each reaction, given that $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$.
- (i) Oxalic acid: $(\text{COOH})_2 (\text{s}) + \frac{1}{2}\text{O}_2 (\text{g}) \longrightarrow 2\text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l})$
- (ii) Elementary calcium: $\text{Ca} (\text{s}) + \frac{1}{2}\text{O}_2 (\text{g}) \longrightarrow \text{CaO} (\text{s})$
- (b) Calculate the equilibrium constant for the reaction of graphite reacting with hydrogen gas to form methane gas at 25°C , given that $\Delta G^\circ_{298} = 74.9\text{kJ}$
- (c) Solid TiO_2 is being converted to TiCl_4 by treatment with Cl_2 in presence of carbon. Calculate the thermodynamic efficiency of utilizing Cl_2 gas at 1000K. Assume oxidation of carbon to CO and total pressure as 1atm.

Given:



$$\Delta G^\circ = -318\text{kJ/mol at } 1000^\circ\text{C}$$

- (d) The following table gives the equilibrium constant, K_p , at different temperatures for the oxidation of metal oxides, PbO, according to:



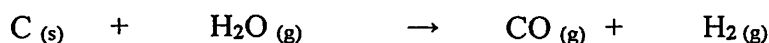
T (K)	600	700	800	900	1000
K_p (atm^{-1})	140	5.14	0.437	0.0625	0.0131

Plot $10^3/T$ against \ln (or \log_{10}) K_p on the graph provided and obtain a value for ΔH^θ from the slope of the graph. Explain your answer regarding the reactions within the process.

Question 2

- (a) Answer the following questions, using the Ellingham diagram in Figure 1.0:
- (i) Estimate ΔG° for the reduction of copper (I) oxide with carbon at 1200 K.
- (ii) Estimate ΔG° for the reduction of manganese oxide by cobalt at 1000°C .
- (iii) Determine the ΔS for nickel oxide formation at 1000°C .

- (iv) Determine the temperature at which the coke must be maintained for the reaction blow to be feasible.



- (v) Calculate the p CO/O₂ for the reaction
 $\text{NiO}_{(s)} + \text{CO}_{(g)} \rightarrow \text{Ni}_{(s)} + \text{CO}_2_{(g)}$ at 1000 °C

- (vi) Calculate the p H₂/H₂O for the reaction:
 $\text{SnO}_{(s)} + \text{H}_2_{(g)} \rightarrow \text{Sn}_{(s)} + \text{H}_2\text{O}_{(g)}$ at 1000 °C

- (b) Why is zinc sulfide concentrate partially roasted in the flow sheet of zinc production from zinc sulfide concentrate? Show the reactions of the process by chemical equations.
- (c) Study Figure 2.0 to answer the following questions:
- Which substance is independent of temperature?
 - Which substances are less stable at higher temperatures?
 - Give reasons why coke & coal are not viable on industrial scale.
 - Which product of carbon is more stable at a higher temperature?
 - Explain why most of the organic compounds are not reducible by carbon.

Question 3

- (a) With the aid of a diagram, discuss the behavior of the hydroxides and moist material with regards to increase in temperature in a drying process.
- (b) With the aid of a diagram, discuss the heat distribution and the calcination reactions within a shaft furnace.
- (c) Discuss the decomposition of Mg (OH)₂ and MgCO₃ with respect to their decomposition pressure and temperature in Figure 3.0.
- (d) A laboratory test on calcination of Mumeng lime stone (70 % CaCO₃) sample of particle size ±150 μm was performed in Kaindi laboratory. Data collected using the first order kinetic model [- ln (1 - f) = Kt] verses T was plotted in Figure 4.0.

Study the Plots in Figure 4.0 and answer the following questions:

- (i) Determine the reaction rates (k) for each temperature.
- (ii) Evaluate the variables used in this test to optimize the calcination temperature and time for oxidizing this material.
- (iii) Predict the direction of the process if calcination time was prolonged beyond 100 minutes

Question 4

- (a) A sulfide ore containing CuFeS_2 , Cu_2S and FeS_2 , has been roasted to 700°C at normal atmospheric conditions and SO_2 pressure of $\log 10^{-5}$ atm. With the help of the Kellogg diagram in Figure 5.0, discuss the types of products that would be formed and the relative ease of oxidation of the sulfide minerals.
- (b) Using the predominance area diagram for the Ni – S – O system given in Figure 6.0 to answer the following questions:
 - i. Why are the boundary lines between the phase straight lines?
 - ii. What does a triple point indicate?
 - iii. What are the reactions involved between two condensed phases, as indicated by each line?
 - iv. How do you define the conditions for roasting of NiS to NiO?
- (c) A zinc sulfide concentrate contains 50 % Zn, 13 % Fe, 32 % S, and 5 % SiO_2 . When 100 kg of this material is roasted with air, 85 kg of the product (calcine) is produced. Composition of the product shows 54.4 % Zn, 14.1 % Fe, 2.7 % S and 5.4 % SiO_2 . The remaining composition is assumed to be oxygen. The flue dust is assumed to have the same composition as the calcine. The roast gas contains 8 volume % SO_2 .

Calculate:

- (i) The weight of the flue dust and its content of the various components,
- (ii) The of the flue dust in Nm^3 ,
- (iii) The composition of the roast gas, and
- (iv) The volume of air used (air has 21 vol. % O_2 and 79 vol. % N_2).

END OF PAPER

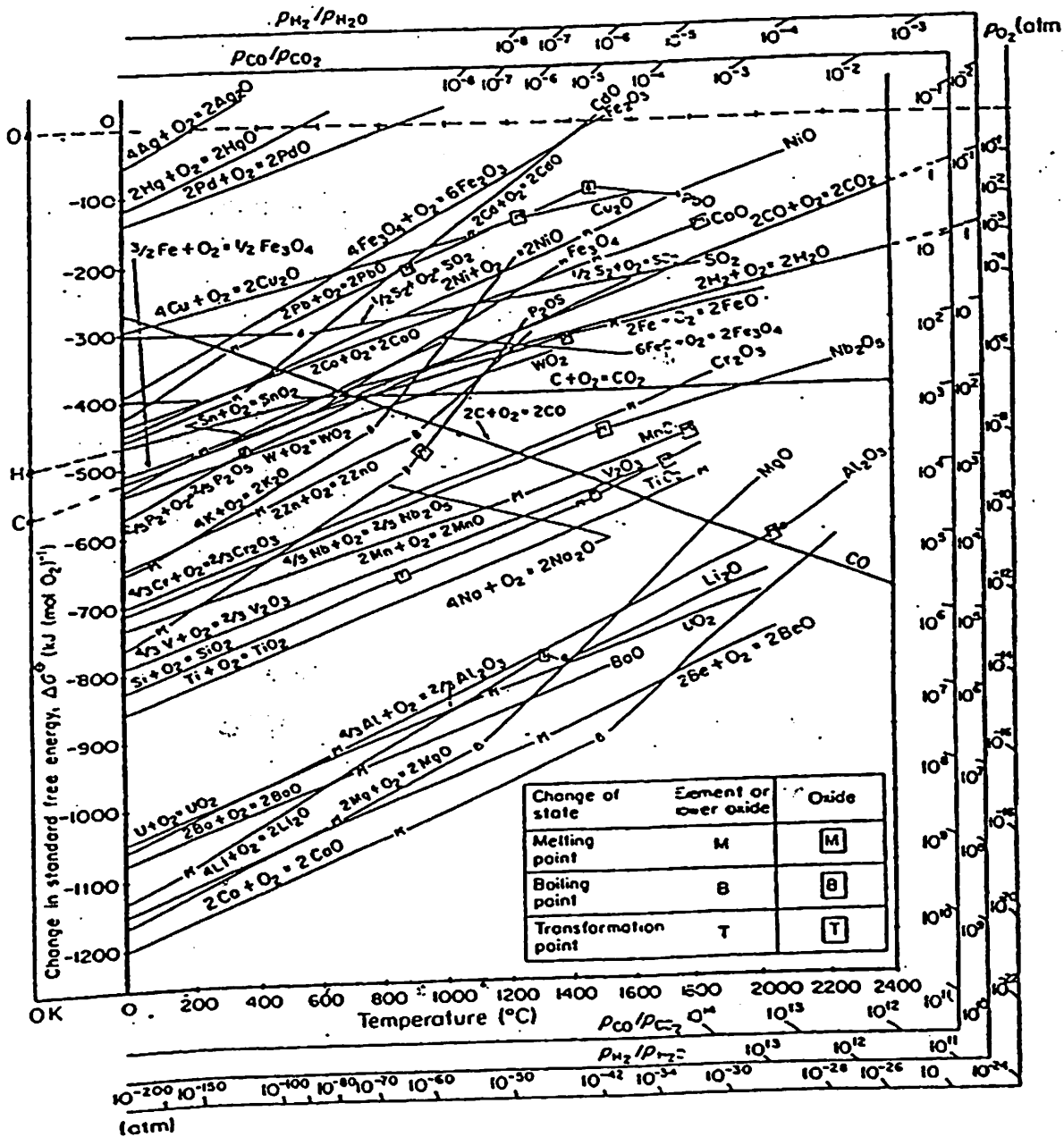


Figure 1.0 $\Delta G^\circ - T$ diagram for the formation of oxides. For equilibrium $p_{O_2}, p_{CO}/p_{CO_2}$ and p_{H_2}/p_{H_2O} values use points O, C and H respectively on the ΔG° axis at 0 K

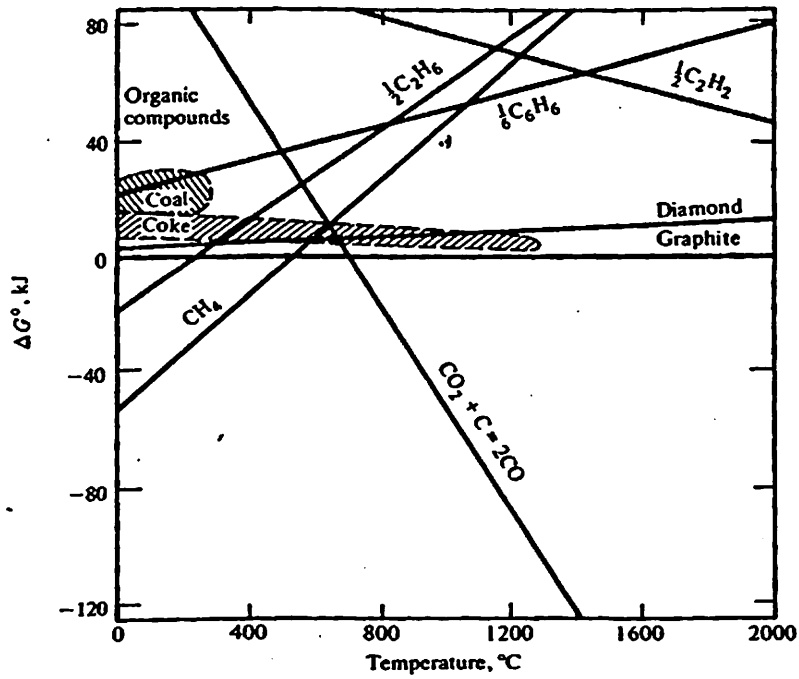


Figure 2.0 Standard Gibbs energy of formation, per mole of carbon of various compounds relative to graphite.

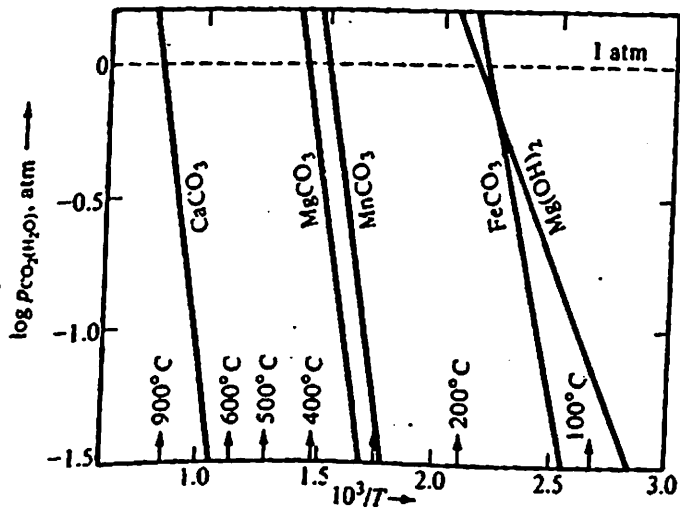


Figure 3.0 Decomposition pressure (logarithmic) of various carbonates and hydrates as function of temperature.

-Ln(1-f) Vs Time

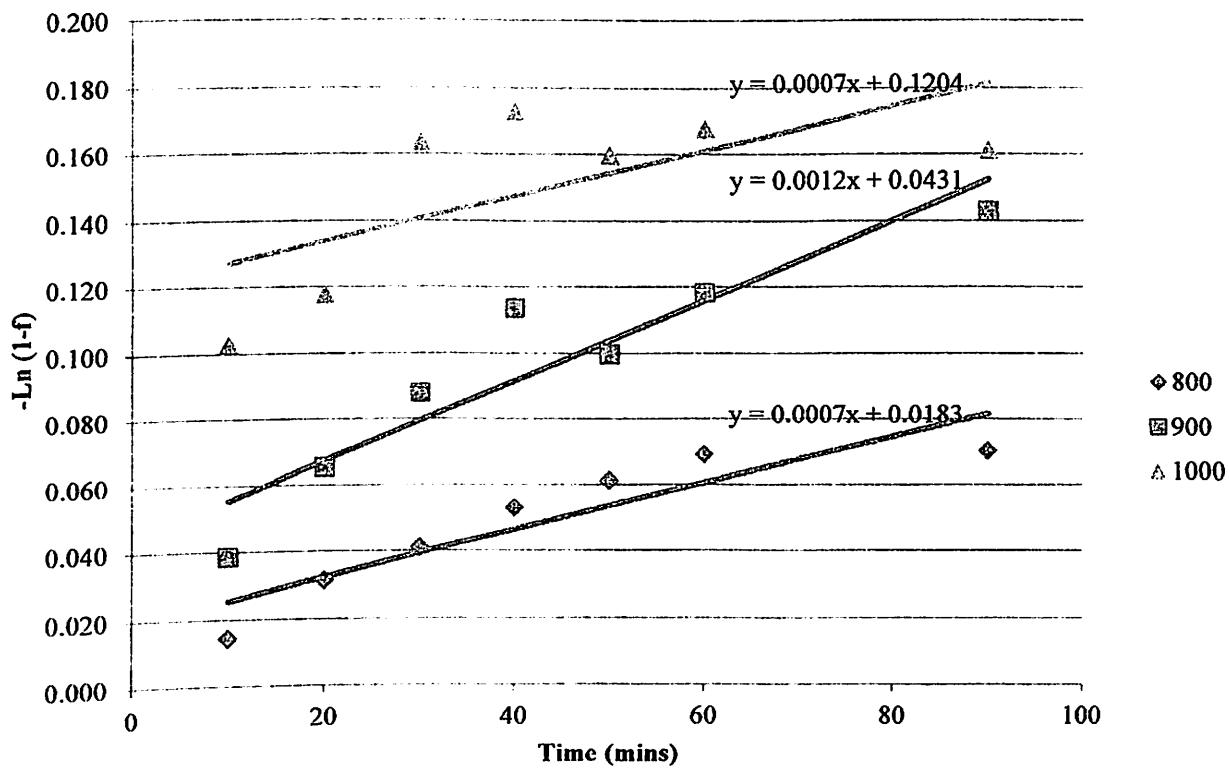


Figure 4.0 The first order kinetic model $[-\ln(1-f) = Kt]$ versus Temperature for Mumeng lime stone

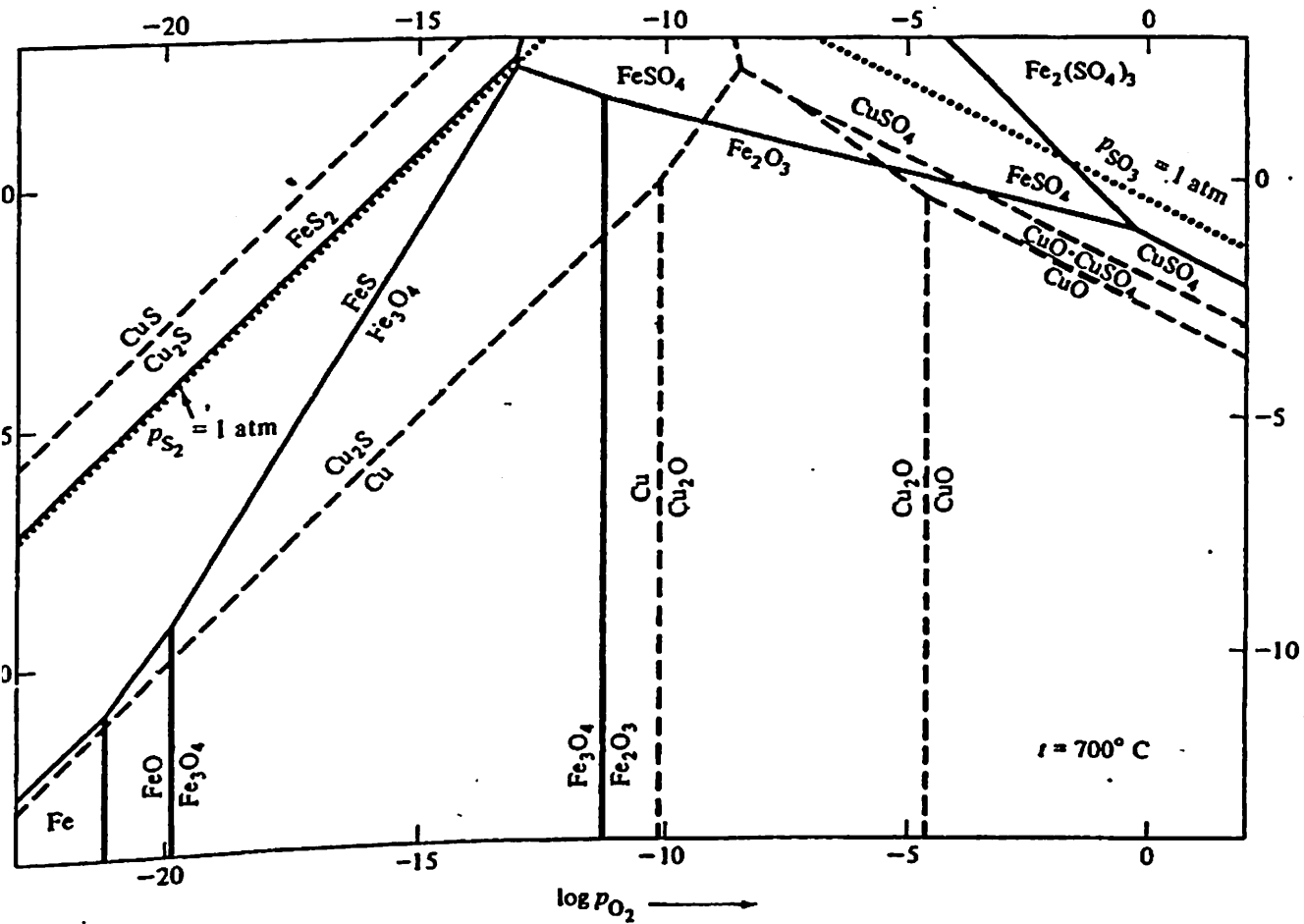


Figure 5.0 Kellogg diagram for the roasting of iron and copper sulfides at 700 °C. Solid lines = Fe compounds, dashed lines = Cu compounds, dotted lines = gases. Ternary compounds are disregarded.

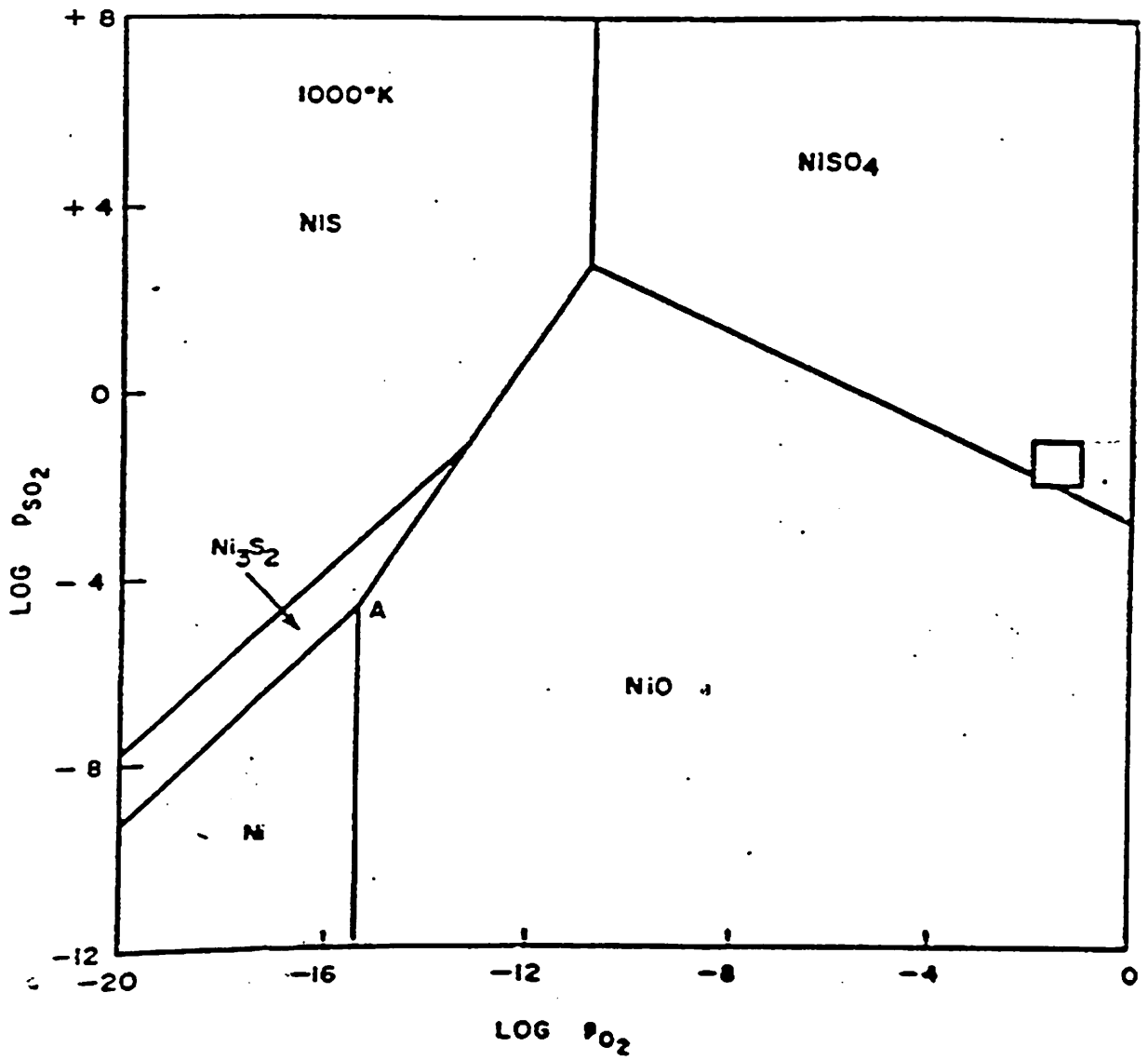


Figure 6.0 Predominance Area Diagram for Ni-S-O System at 1000 °K