National Exams December 2012

04-Chem-B7, Extractive Metallurgy

3 hours duration

NOTES:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.
2. This is a Closed Book exam. Approved models of Casio or Sharp calculators may be used.
3. Any FIVE (5) questions constitute a complete exam paper. The first five questions as they appear in the answer book will be marked.
4. If question 8 is answered, detach the last page of this exam book and use it for your answer. Insert this page in your answer book.
5. All questions are of equal value; the approximate breakdown for each question is as follows.

Question	1	2	3	4	5	6	7	8
(a)	8	12	8	12	6	14	20	12
(b)	6	8	6	8	7	6	–	4
(c)	6	–	6	–	7	–	–	4
Total	20	20	20	20	20	20	20	20

Data: $R = 8.314\ J.mol^{-1}.K^{-1}$

$F = 96500\ C.mol^{-1}$

[1] Imperial Smelting Furnace allows simultaneous reduction of PbO–ZnO mixture by coke. Reduction of ZnO to metallic zinc takes place through the following reaction

$ZnO(s) + C(s) = Zn(g) + CO(g) \quad \Delta G^\circ = 338.9 - 0.28\ T\ (kJ.mol^{-1})$

a) What temperature is required for this reaction to proceed, if the total pressure is 1 atm?

b) As the gases rise in the furnace, CO is partially consumed by other reduction reactions to generate CO_2. Excessive amounts of CO_2 can result in re–oxidation of Zn(g) according to:

$Zn(g) + CO_2(g) = ZnO(s) + CO(g) \quad \Delta G^\circ = -178.3+0.111T\ (kJ.mol^{-1})$

Calculate the ratio of CO_2/CO at which re–oxidation occurs at 1000 °C, when the partial pressure of Zn is 0.06 atm.

c) What provisions are made in order to avoid oxidation of Zn to ZnO at the top of the furnace?

[2] Chromium plating is applied for various metals to create a corrosion resistance coating on the surface. Density of chromium is 7.2 $g.cm^{-3}$ and its atomic weight is 52 $g.mol^{-1}$.

a) Calculate the thickness of chromium coating deposited in 30 minutes at a current density of 2150 A/m^2 and current efficiency of 16%. Cr has valence of 6 in the plating solution.

b) The standard free energy change in the oxidation of Cr is given below. Suppose that a Cr–coated steel is heated to 600 °C in air (21% O_2). Is Cr oxidized under these conditions? Support your answer by calculations and discuss how Cr can protect steel against oxidation.

$2Cr(s) + 3/2\ O_2(g) = Cr_2O_3(s) \qquad \Delta G^\circ = -1120.3 + 0.26T\ (kJ.mol^{-1})$

[3] Desulphurization of steel is achieved by proper control of operating conditions such as slag chemistry and temperature.

a) Indicate a typical desulphurization reaction, and discuss briefly, what are the favorable conditions (high or low) in terms of slag basicity, and oxygen potential. Is addition of aluminum to the steel bath beneficial or detrimental to the extent of desulphurization?

b) For a refining practice, the rate of sulphur transfer from metal to slag is presented as following. Calculate the time required to reduce S from 0.05% to 0.02% in a ladle of steel.

$Rate = 1.5\times10^{-4}[S] \quad (\%.s^{-1})$

c) Briefly discuss how the rate of sulphur removal can be increased in order to reduce the refining time?

[4] A typical composition of dried blast furnace off–gas is provided below (mol%).

CO	24%
CO_2	26%
H_2	4%
N_2	46%

a) Calculate the energy loss per m^3 of this gas (under S.T.P. conditions), if its energy value is not used. Under the following operating conditions, calculate the energy loss as percentage of the chemical energy contained in coke.

Coke consumption :	400 kg per ton of hot metal
Coke composition:	90% carbon, balance ash.
Blast furnace off–gas rate:	1500 Nm^3 per ton of hot metal (under S.T.P.)

Given data (enthalpy of formation for the following compounds):

$H_2O(g)$	-242 kJ/mol
$CO_2(g)$	-393 kJ/mol
CO(g)	–110 kJ/mol

b) Describe how in the industry this energy is used to improve the efficiency of the process.

[5] a) While carbothermal reduction of SiO_2 is the dominant method to extract silicon metal, a similar process for production of Mg has not been commercialized. Explain why this is the case (hint: in the temperature of reduction, Si is liquid while Mg is vapor)

b) Currently, one method to produce Mg involves silicothermic reduction of magnesium oxide at 1200 °C according to the following reaction. Determine whether this reaction as written is thermodynamically feasible, and discuss how it is manipulated in industry for production of magnesium.

$2MgO\ (s) + Si = 2Mg(g) + SiO_2$ $\qquad \Delta G^\circ = 557.1 - 0.235\ T\ (kJ.mol^{-1})$

c). In another method, Mg is electrodeposited from a $MgCl_2$–NaCl–$CaCl_2$ molten salt at 750 °C, according to the following reaction

$MgCl_2(l) = Mg(l) + Cl_2(g)$ $\qquad \Delta G^\circ_{750°C} = 473\ kJ$

The concentration of MgCl2 in the salt is 15 mol%. Supposing that for this electrolyte, $MgCl_2$ follows an ideal behavior (i.e. Raoultian), calculate the theoretical voltage required for electrowinning of Mg. Cl_2 gas is released at 1 atm.

[6] a) List the major steps in production of nickel from sulphide ores, and briefly describe each step.

b) Explain what property of sulphide minerals makes their upgrading by physical concentration methods feasible. What is the most significant concentration method applied to sulphide minerals of nickel?

[7] A lead sinter to be smelted in a blast furnace analyses 8% CaO, 25% SiO_2, and 15% Fe. In smelting this sinter, a slag is desired with CaO, FeO and SiO_2 in the proportions: CaO:FeO:SiO_2 = 4:6:7.

To obtain the slag, iron ore and limestone of the following analyses are added to the charge:

	Wt% Fe	Wt% CaO	Wt% SiO_2
Iron ore	45.0	0.5	15.0
Limestone	2.0	46.0	8.0

In addition, coke is to be added to the charge as a fuel in an amount equal to 12% of the weight of (sinter + iron ore + limestone). The coke contains 2.5% Fe_2O_3 and 12% SiO_2.

Assuming that all the lime, iron and silica enter the slag as CaO, FeO, and SiO_2, calculate the weights of iron ore, limestone and coke to be used per metric tonne of lead sinter.

[8] a) The figures in the following page are the predominance diagrams for two metals, Ni and Fe at 700 °C. On these diagrams, identify various phases stable in each region. The phases to be identified for each system are:

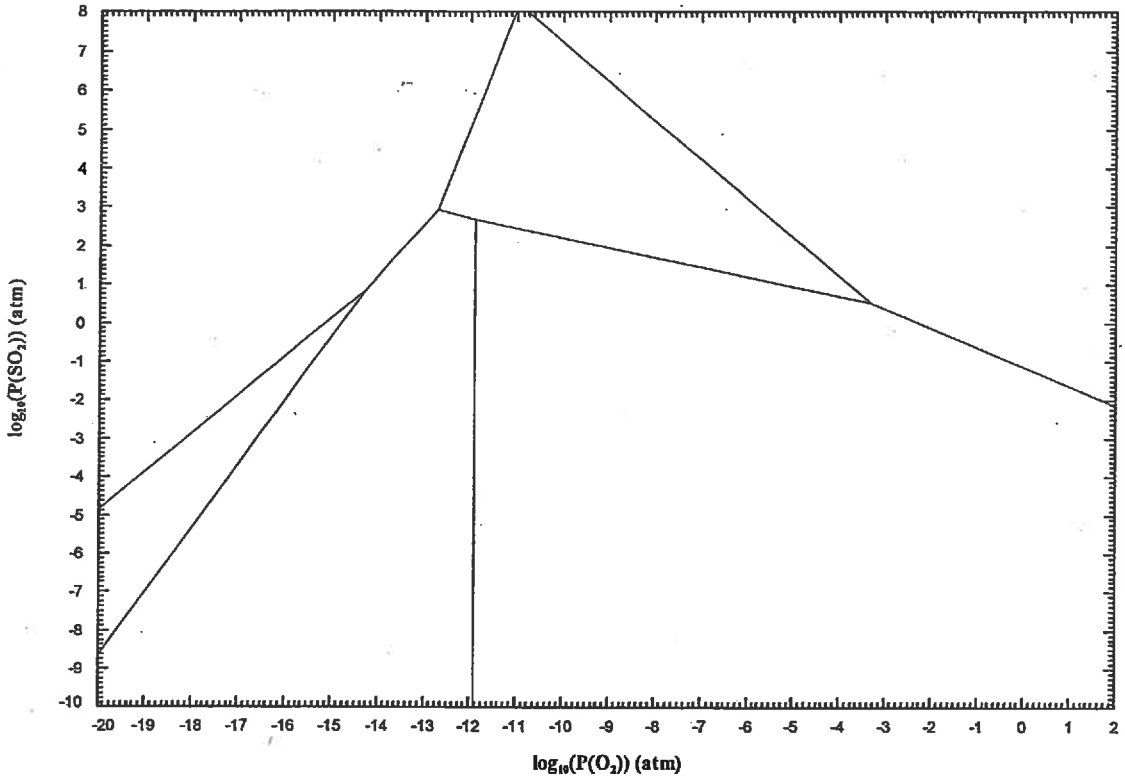
Ni diagram: Ni, $NiSO_4$, NiO, NiS_2, Ni_3S_2, NiS

Fe diagram: FeS_2, FeS, Fe_3O_4, $FeSO_4$, $Fe_2(SO_4)_3$, Fe_2O_3.

(Detach the sheet and include it with your answer book)

b) The flue gas from a roaster fed with a Ni concentrate, also containing iron, is 10% SO_2, 11% O_2, and 79% N_2 at 1 atm. What are the thermodynamically stable phases under these conditions?

c) List the steps involved in a typical treatment that is done for the roaster flue–gas to prevent emission of SO_2 to atmosphere.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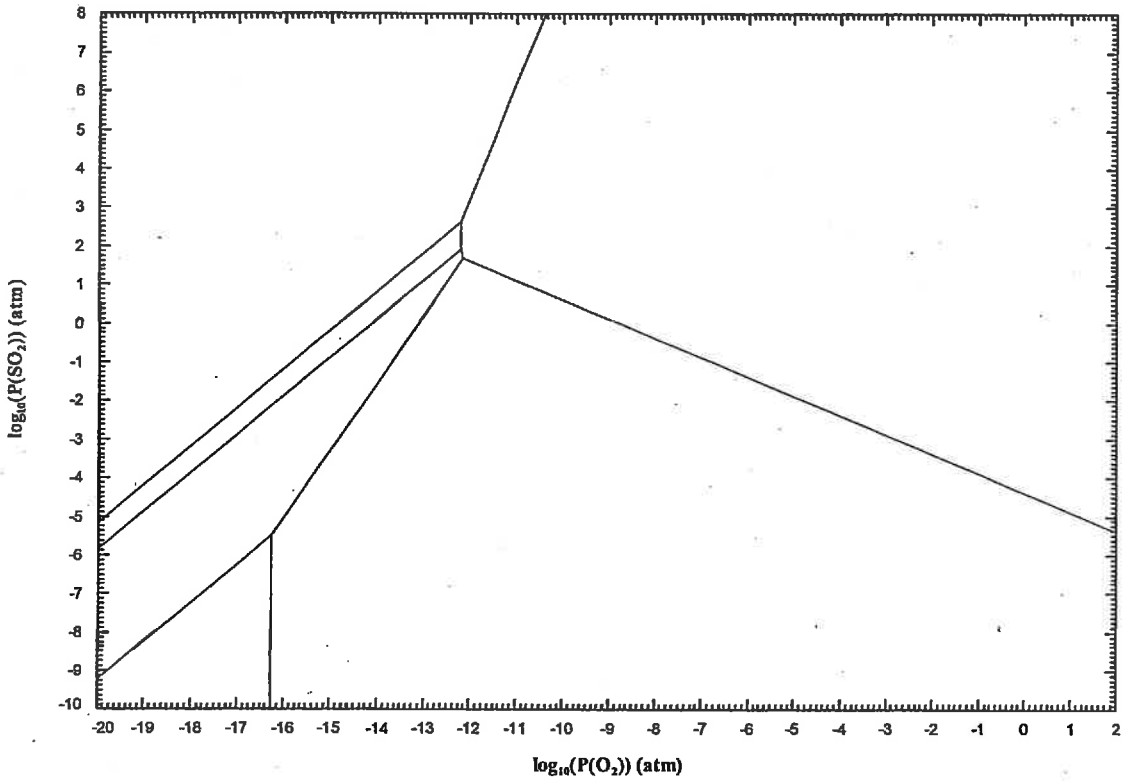
log10(P(SO2)) (atm)
-20 -19 -18 -17 -16 -15 -14 -13 -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2
log10(P(O2)) (atm)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log10(P(SO2)) (atm)
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log10(P(O2)) (atm)