UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATION, APRIL 2001

SECOND YEAR – PROGRAM 08

MMS203S – Thermodynamics II

EXAM TYPE: A

EXAMINERS – A. MCLEAN AND R. R. ROY

ANSWER ANY FIVE (5) QUESTIONS

If you attempt questions 1 and/or 2, please write your answers in a separate examination book.

Wherever appropriate, make full use of balanced chemical reactions, thermodynamic equations and carefully drawn diagrams.

QUESTION 1

(a) A liquid B is placed on a solid A. Assuming that there is no mass transfer between the two phases, derive a criterion in terms of surface tensions γ_{AV} and γ_{BV} and the interfacial tension γ_{AB} for the liquid B to spread on solid A.
(Hint: A liquid is said to spread on a solid, when the contact angle between them becomes equal to zero.)

(5 marks)

(b) A drop of liquid 1 is resting on another denser liquid 2 forming a liquid lens as shown in Figure 1. Derive an equation relating the visible contact angle to surface tensions of liquids 1 and 2 and the interfacial tension between these two liquids. (7 marks)

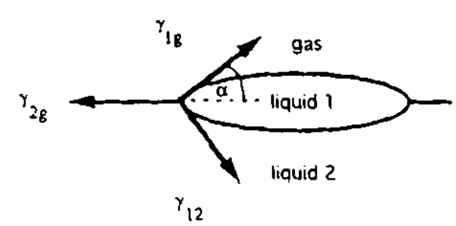


Figure 1

(c) The surface tension of liquid 1 is equal to 40.0 dyne/cm, that of liquid 2 is equal to 75.0 dyne/cm and the interfacial tension between liquid 1 and liquid 2 is equal to 50 dyne/cm. Initially there is little mass transfer between the two liquids and the surface tensions and interfacial tension have the values quoted above. With time, however, the interfacial tension between liquid 1 and liquid 2 decreases to a value of 45.0 dyne/cm. Calculate the change in the visible contact angle from the initial to the final stage. (8 marks)

QUESTION 2

(a) A surface active species, 2, adsorbs on 1 by building a close-packed monolayer. The atomic radius of species 2 is 1.5 Å. Assuming that the area per atom is equivalent to a hexagon with an inscribed circle of the atomic radius, what is the value of Γ_2 at saturation coverage (in mol/m^2)? (8 marks)

(b) Adsorption of a surface active species, 2, at saturation coverage is equal to 0.5×10^{-4} mol/m^2. What is the fraction of surface area occupied by species 2, when adsorption of species 2 is equal to 0.1×10^{-4} mol/m^2? (4 marks)

(c) Consider a two component system water (component 1) and nitrogen (component 2). The liquid phase consists of a saturated solution of nitrogen in water and the gaseous phase of nitrogen and water vapour. Relative adsorption of nitrogen on the water surface is governed by the following equation:

$$\Gamma_2^{(1)} = -(p_2/RT)*(d\sigma/dp_2)$$

The following results were obtained in an experiment measuring surface tension as a function of nitrogen partial pressure:

Nitrogen partial pressure (atm.)	Surface tension (dyne/cm)
1.0	72.80
1.5	72.75
2.0	72.70

Calculate the relative adsorption (in mol/cm^2) of nitrogen on the water surface, when the nitrogen partial pressure is equal to 1.5 atm. (8 marks)

QUESTION 3

(a) Describe an experimental approach you would follow to determine the interaction coefficient e_N^C in liquid iron. Indicate the type of data you would collect and how you would process this information. (10 marks)

(b) Derive the relationship between ε_N^C and e_N^C assuming the solvent is liquid iron. (4 marks)

(c) Calculate the Henrian activity on the weight percent scale of 0.002 wt%N in hot metal containing 3.5 wt% C, 1 wt% Mn and 0.5 wt% Si. (4 marks)

(d) Explain the significance of the value you have calculated. (2 marks)

QUESTION 4

At 1500C, the Raoultian activity of copper in an iron melt containing 0.4 mol fraction of copper is 0.8. The Henrian Coefficient for copper is 10.

(a) Draw a schematic diagram to illustrate the activity/mol fraction relationship for the iron-copper system. (2 marks)

(b) In the specified alloy, calculate the Raoultian activity coefficient of copper and also the Henrian activity coefficient on the mol fraction scale. (4 marks)

(c) Explain the significance of the magnitude of the values you have calculated for the activity coefficients. (4 marks)

(d) Derive an expression to convert activity on the Raoultian Standard state to activity on the Henrian 1wt% standard state. (4 marks)

(e) Calculate the Henrian activity of Cu on the wt% scale for the above alloy ($X_{Cu} = 0.4$) (2 marks)

(f) Stating any assumptions, calculate the change in standard free energy when liquid copper dissolves in liquid iron at 1600°C to form a hypothetical 1wt% solution.(4 marks)

QUESTION 5

(a) Using silicon as an example, describe the thermodynamic basis for the construction of a deoxidation diagram. (5 marks)

(b) Sketch a deoxidation diagram to illustrate the relative affinity for oxygen of the elements silicon, manganese and aluminum and explain the reason for the gradients of the lines you have drawn. (5 marks)

(c) Use the data provided to calculate the oxygen content of liquid iron containing 0.2 wt.pct. silicon at 1600°C assuming equilibrium is established with pure silica and that the solutes obey Henry's Law. (10 marks)

QUESTION 6

With the aid of diagrams, chemical reactions and thermodynamic equations where appropriate, use about one page, for a total of four pages, to discuss **Four** of the following topics:

(a) Lime dissolution in molten slags. (5 marks)

(b) Sievert's Law and the formation of porosity in metal castings. (5 marks)

(c) Water vapour dissolution in oxide melts. (5 marks)

(d) Derivation of a relationship between carbonate and sulphide capacities.(5 marks)

(e) Thermodynamic conditions for dephosphorization of iron alloys. (5 marks)

QUESTION 7

(a) Discuss fully the significance of Figures 2 and 3, and explain the reason for the apparent contradictory behaviour shown by MgO. (6 marks)

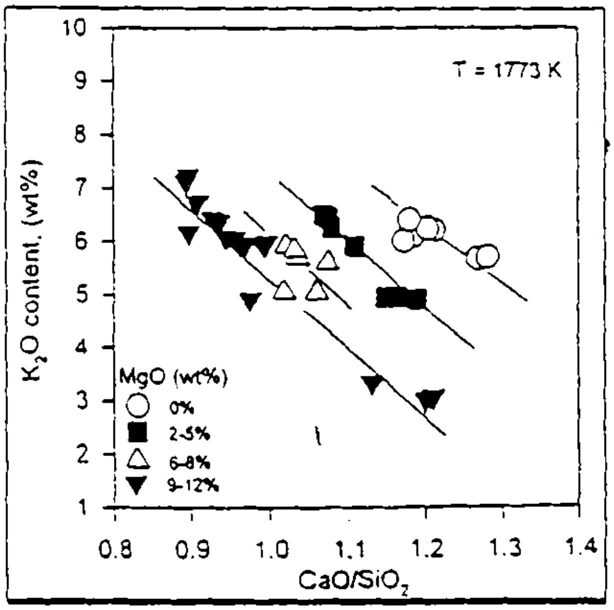


Figure 2

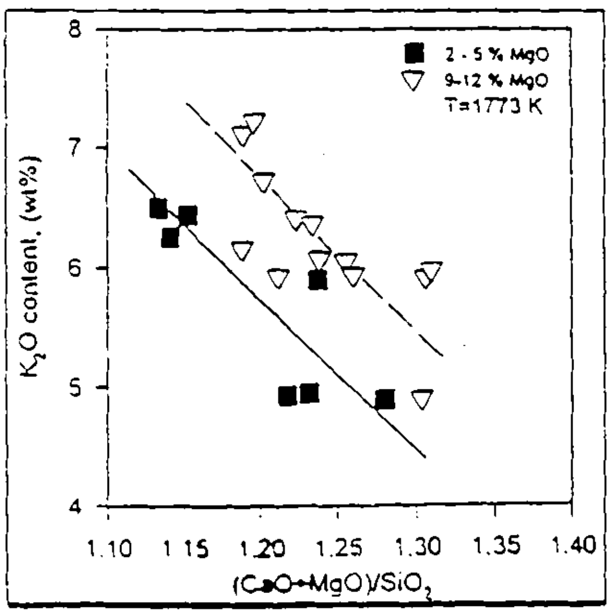


Figure 3

(b) Sketch a graph of K_2O capacity versus optical basicity for slags containing CaO, MgO, Al_2O_3 and SiO_2 and explain why optical basicity is a better method for measuring slag character than the basicity ratios used in Figures 2 and 3. (4 marks)

(c) Indicate on the graph you have drawn, the equivalent relationship for sulphide capacity and explain why the relationships are different. (4 marks)

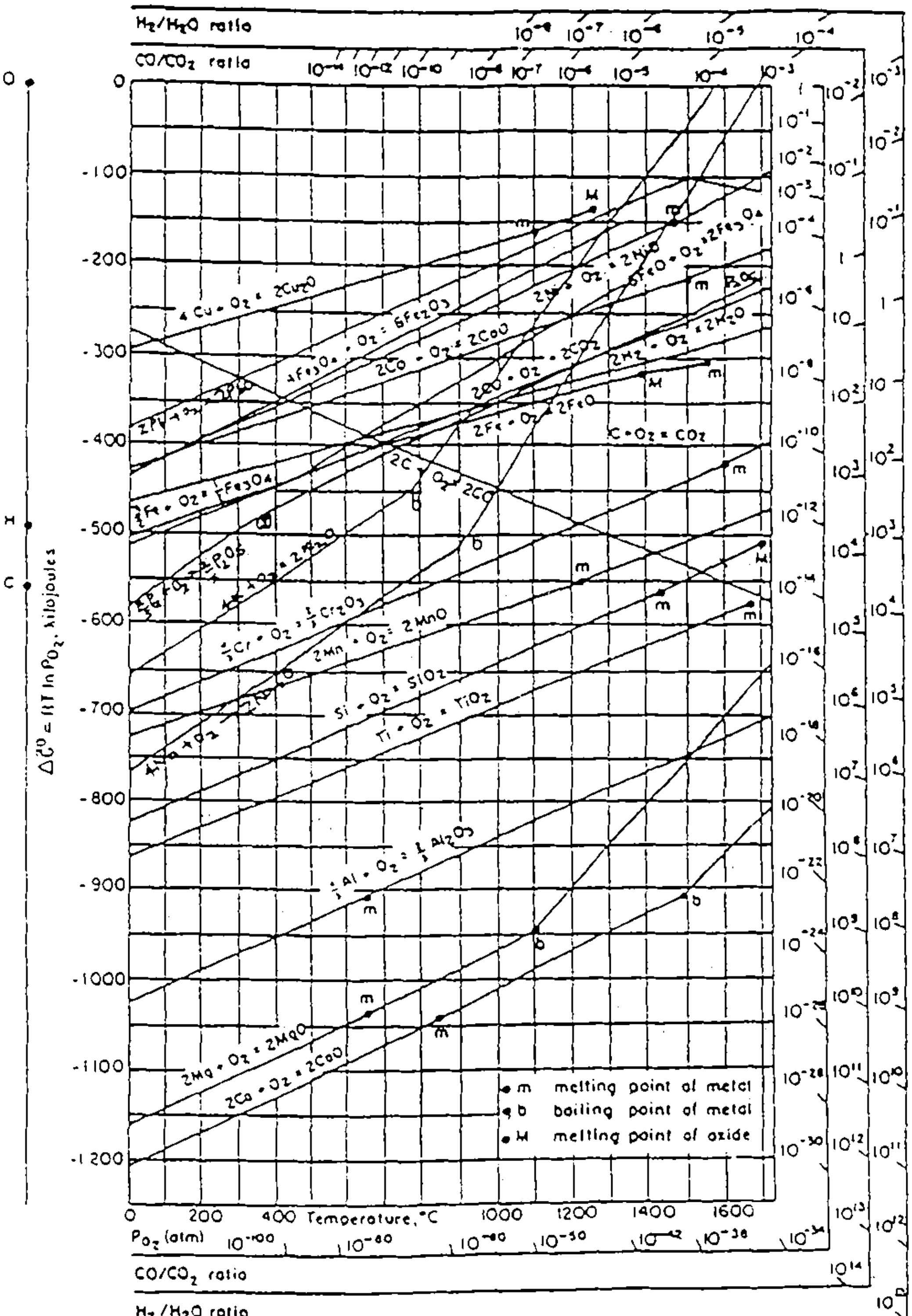
(d) Calculate the optical basicity of an oxide melt containing 40% CaO, 40% SiO_2 and 20% MgO. (6 marks)

Use the following data sheets as required

Atomic weights
Si: 28.09
Cu: 63.54
O: 16
Fe: 55.85
Ca: 40.08
Mg: 24.31

Optical Basicities
CaO: 1
MgO: 0.78
SiO_2: 0.48

R = 8.314J/mol.K = 1.978cal/mol.K



H2/H2O ratio
CO/CO2 ratio
ΔG° = RT ln PO2, kilojoules
Temperature, °C
PO2 (atm)
4Cu + O2 = 2Cu2O
4Fe3O4 + O2 = 6Fe2O3
2Co + O2 = 2CoO
2Ni + O2 = 2NiO
6FeO + O2 = 2Fe3O4
2CO + O2 = 2CO2
2H2 + O2 = 2H2O
2Fe + O2 = 2FeO
C + O2 = CO2
2C + O2 = 2CO
3/2 Fe + O2 = 1/2 Fe3O4
4/3 Cr + O2 = 2/3 Cr2O3
2Mn + O2 = 2MnO
Si + O2 = SiO2
Ti + O2 = TiO2
4/3 Al + O2 = 2/3 Al2O3
2Mg + O2 = 2MgO
2Ca + O2 = 2CaO
m melting point of metal
b boiling point of metal
M melting point of oxide

INTERACTION COEFFICIENTS $e_i^{(j)} \times 10^{2}$*
FOR DILUTE SOLUTIONS OF ELEMENTS DISSOLVED IN LIQUID IRON AT 1600°C

Dissolved element(i)	Added element (j)												
	Al	As	Au	B	C	Cb	Co	Cr	Cu	H	Mn	Mo	N
Al	4.8	—	—	—	11	—	—	—	—	*34*	—	—	*0.5*
As	—	—	—	—	—	—	—	—	—	—	—	—	*9.6*
Au	—	—	—	—	—	—	—	—	—	—	—	—	—
B	—	—	—	—	—	—	—	—	—	*53*	—	—	—
C	*4.8*	—	—	—	22	−6.0	1.2	−2.4	1.6	*72*	—	−0.9	*11.1*
Cb	—	—	—	—	*−46*	8.3	—	—	—	*−21*	—	—	*−44.4*
Co	—	—	—	—	*6*	—	—	—	—	*11*	—	—	*4.7*
Cr	—	—	—	—	*−10*	—	—	—	—	*−11*	—	—	*−16.6*
Cu	—	—	—	—	*8.5*	—	—	—	−2.1	*3.1*	—	—	*4.1*
H	1.3	—	—	5.0	6.0	−0.23	0.18	−0.22	0.05	0	−0.14	—	—
Mn	—	—	—	—	—	—	—	—	—	*−7.7*	—	—	*−7.8*
Mo	—	—	—	—	*−7*	—	—	—	—	—	—	—	*−7.8*
N	0.3	1.8	—	—	13	−6.7	1.1	−4.5	0.9	—	−2.0	−1.1	0
Ni	—	—	—	—	*5.9*	—	—	—	—	*0*	—	—	*4.2*
O	−94	—	−0.4	—	−13	−14	0.7	−4.1	−0.9	—	0	0.35	*5.7*
P	—	—	—	—	—	—	—	—	—	*34*	—	—	*11.3*
Pt	—	—	—	—	—	—	—	—	—	—	—	—	—
S	5.8	—	—	—	*24*	—	—	−2.2	−1.2	*26*	−2.5	—	*3.0*
Sb	—	—	—	—	—	—	—	—	—	—	—	—	*7.8*
Se	—	—	—	—	—	—	—	—	—	—	—	—	*0*
Si	*6.3*	—	—	—	24	—	—	—	*~0*	*76*	0	—	*9.2*
Sn	—	—	—	—	28	—	—	—	—	*62*	—	—	*5.9*
Ta	—	—	—	—	—	—	—	—	—	*−360*	—	—	*−44*
Ti	—	—	—	—	—	—	—	—	—	*−385*	—	—	*−210*
V	—	—	—	—	*−16*	—	—	—	—	—	—	—	*−36*
W	—	—	—	—	*−4.7*	—	—	—	—	—	—	—	*−2.6*

* $e_i^{(j)} = \dfrac{\partial(\log f_i)}{\partial(\%\, j)} = \dfrac{0.2425}{M_i}\cdot \epsilon_i^{(j)} = \dfrac{M_i}{M_j}\cdot e_j^{(i)}$ at infinite dilution of dissolved elements: f = activity coefficient; %j = weight percent of (j); M = atomic weight (of i or j).

Note: Plain numbers are obtained from values reported in the literature. Italic numbers are obtained by calculation from the reciprocal relationship noted above.

INTERACTION COEFFICIENTS $e_i^{(j)} \times 10^{2}$*
FOR DILUTE SOLUTIONS OF ELEMENTS DISSOLVED IN LIQUID IRON AT 1600°C

Dissolved element(i)	Added element (j)												
	Ni	O	P	Pt	S	Sb	Se	Si	Sn	Ta	Ti	V	W
Al	—	−160	—	—	4.9	—	—	6.0	—	—	—	—	—
As	—	—	—	—	—	—	—	—	—	—	—	—	—
Au	—	−4.5	—	—	—	—	—	—	—	—	—	—	—
B	—	—	—	—	—	—	—	—	—	—	—	—	—
C	1.2	−9.7	—	—	9	—	—	10	280	—	—	−3.8	−3.3
Cb	—	82	—	—	—	—	—	—	—	—	—	—	—
Co	—	2.6	—	—	—	—	—	—	—	—	—	—	—
Cr	—	−13	—	—	−3.55	—	—	—	—	—	—	—	—
Cu	—	−3.8	—	—	−2.4	—	—	~0	—	—	—	—	—
H	0	—	1.1	—	0.8	—	—	2.7	0.53	−2	−8	—	—
Mn	—	0	—	—	−4.3	—	—	0	—	—	—	—	—
Mo	—	2.1	—	—	—	—	—	—	—	—	—	—	—
N	1.0	5.0	5.1	—	1.3	0.9	0	4.7	0.7	−3.4	−63	−10	−0.2
Ni	−0.0	2.1	—	—	0	—	—	1.0	—	—	—	—	—
O	0.6	−20	7.0	0.4	−9.1	—	—	−14	0	—	−19	−27	0.8
P	—	13.5	—	—	4.3	—	—	9.5	—	—	—	—	—
Pt	—	3.5	—	—	—	—	—	—	—	—	—	—	—
S	0	−18	4.5	—	−2.8	—	—	6.6	—	—	—	—	—
Sb	—	—	—	—	—	—	—	—	—	—	—	—	—
Se	—	—	—	—	—	—	—	—	—	—	—	—	—
Si	0.5	−25	8.6	—	5.7	—	—	32	—	—	—	—	—
Sn	—	0	—	—	—	—	—	—	—	—	—	—	—
Ta	—	—	—	—	—	—	—	—	—	—	—	—	—
Ti	—	−56	—	—	—	—	—	—	—	—	—	—	—
V	—	−86.4	—	—	—	—	—	—	—	—	—	—	—
W	—	9.7	—	—	—	—	—	—	—	—	—	—	—

STANDARD FREE ENERGY OF SOLUTION OF VARIOUS ELEMENTS IN LIQUID IRON

M(pure) = M(1% solution, hypothetical)

Element, state	γ°_{1873}*	ΔF°, cal/gm · atom
Aluminum (l)	0.063	$-10{,}300 - 7.71T$
Carbon (graphite)	—	$5{,}100 - 10.00T$
Chromium (s)	1	$5{,}000 - 11.31T$
Cobalt (l)	1	$- 9.31T$
Copper (l)	8.5	$8{,}000 - 9.40T$
Hydrogen, $\frac{1}{2}H_2$ (g) = $\underline{H}$ (%)	—	$8{,}720 + 7.28T \pm 260$
$\frac{1}{2}H_2$ (g) = $\underline{H}$ (ppm)	—	$8{,}720 - 11.02T \pm 260$
Manganese (l)	1	$- 9.11T$
Molybdenum (s)	1	$5{,}800 - 13.3T$
Nickel (l)	0.66	$-5{,}000 - 7.42T$
Nitrogen, $\frac{1}{2}N_2$ (g) = $\underline{N}$ (%)	—	$860 + 5.71T \pm 100$
Oxygen, $\frac{1}{2}O_2$ (g) = $\underline{O}$ (%)	—	$-28{,}000 - 0.69T$
FeO (l) = $\underline{O}$ (%) + Fe (l)	—	$+28{,}900 - 12.51T$
Phosphorus, $\frac{1}{2}P_2$ (g) = $\underline{P}$ (%)	—	$-29{,}200 - 4.6T$
Silicon (l)	0.0011	$-28{,}500 - 6.09T$
Sulfur, $\frac{1}{2}S_2$ (g) = $\underline{S}$ (%)	—	$-31{,}520 + 5.27T$
Titanium (s)	0.011	$-13{,}100 - 10.7T$†,‡
Tungsten (s)	1	$8{,}000 - 13.4T$‡
Vanadium (s)	0.18	$-3{,}700 - 7.5T$‡
Zirconium (s)	0.011	$-12{,}800 - 12.0T$†

* For reference state and standard state of the pure substance, composition in atom fraction.
† Calculated assuming regular solution behavior.
‡ Estimated on basis of heat and entropy of melting at 1600°C.