National Exams May 2018

10-Met-A7, Corrosion and Oxidation

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 an OPEN BOOK EXAM.
   One of two calculators is permitted - any Casio or Sharp approved model.

3. FIVE (5) questions constitute a complete exam paper.
   The first five questions as they appear in the answer book for which answers are provided will be marked.

4. Each question is of equal value in total. The breakdown of marks is also provided for each part of a question.

5. Questions require an answer in one of three forms:

   i. An essay format. Clarity and organization of the answer are important.
   ii. A mathematical calculation. Showing all steps progressively towards the final answer are important
   iii. A contrast and comparison. Complete the table provided writing only in the space allocated.

6. The examination paper **must** also be returned along with any examination booklets as some answers must be completed on the examination paper itself.

7. A list of constants to be used in calculations is provided at the end of the examination along with a list of definitions with appropriate units.

Question 1: 20 (20 Marks)

A direct methanol fuel cell has the following reactions:

ANODE $CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$
CATHODE $3/2\ O_2 + 6H^+ + 6e^- = 3H_2O$
CELL $CH_3OH + 3/2O_2 = CO_2 + 2H_2O$

Specie	ΔH° (kJ/mole)	ΔS° (J/mole·K)
CH_3OH	-245.98	239.83
O_2	0	205.14
CO_2	-393.51	213.80
H_2O	-285.83	69.95

(a) Calculate the overall enthalpy of the reaction. **(5 Marks)**

(b) Calculate the overall entropy of the reaction. **(5 Marks)**

(c) Calculate the overall free energy of the reaction. **(5 Marks)**

(d) Calculate the standard cell potential of the reaction. **(5 Marks)**

Question 2: (20 Marks)

Complete the following table on this page comparing the different forms of localized corrosion following the format of the examples provided below.

Type of Corrosion	Method of Corrosion Prevention (with explanation)
Crevice	1. 2. 3.
"_____"	1. Alloying with elements (Ti, Nb) to prevent depletion of the passive film former (Cr) within interfaces 2. Providing a suitable thermal treatment to prevent sensitization 3. Limiting the concentration of carbon to < 0.03 wt.%C
Pitting	1. 2. 3.
Galvanic	1. 2. 3.

Question 3: (20 Marks)

(a) Complete the following table on this page comparing various ***reference electrodes*** following the format of the examples provided. **(5 marks)**

Name	Half Cell Reaction	Potential (V vs. SHE)	Applicable Environment
Saturated Calomel		**+0.241**	
Standard Hydrogen	**$2H^+ + 2e^- = H_2$**		
Ag-AgCl		**+0.222**	**Biological media**

(b) What are three features present in the "*galvanic series*" that are ***absent*** in the "*electromotive force series*"? Answer in the space provided below. **(3 marks)**

1. _____

2. _____

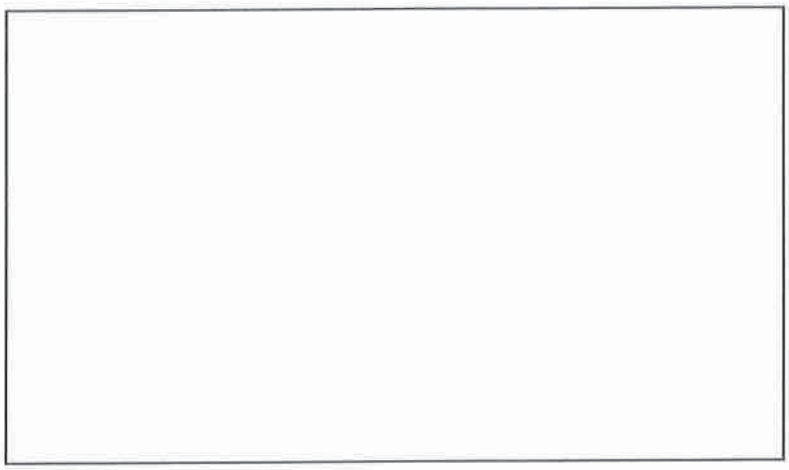
3. _____

(c) Describe the mechanism of crevice corrosion and explain why this form of corrosion is termed "autocatalytic". **(12 marks)**

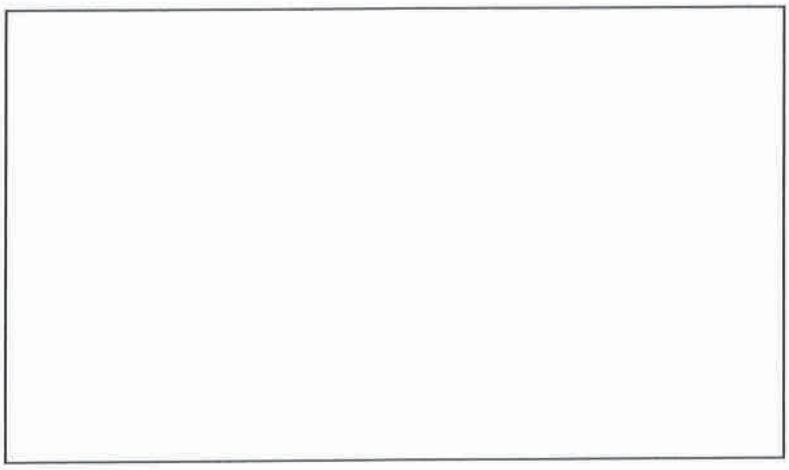
Question 4: (20 Marks)

Illustrate the following corrosion phenomena using a potential – log i diagram using an anodic polarization curve for stainless steel in an acid environment undergoing active-passive-transpassive dissolution as a **reference.** Clearly label all **relevant** thermodynamic and kinetic parameters of E_{corr}, i_{corr}, E_{pp}, E_b, i_{cc}, i_p, on each figure and note the relevant changes in these parameters. Use a solid line (---) for your reference curve and a dotted line for the new curve (- - -). Construct your answer in the square box provided for each part.

(a) A decrease in the Cl^- ion concentration in the environment. **(5 marks)**



(b) Addition of alloying elements that enhance passivity. **(5 marks)**



(c) The effect of increasing temperature on an active-passive-transpassive alloy system. **(5 marks)**

(d) The effect of increasing the acidity on an active-passive-transpassive alloy system. **(5 marks)**

Question 5: (20 Marks)

The table below summarizes the electrochemical parameters for the redox reactions of Pb and Sn that are utilized in Pb-Sn solder alloys:

	E_0 (V vs. SHE)	i_0 (A/cm^2)	β (mV/decade)	i_{LIM} (A/cm^2)
$Pb^{2+} \leftrightarrow Pb$	-0.8	1×10^{-8}	80	0.7
$Sn^{2+} \leftrightarrow Sn$	-0.9	8×10^{-6}	100	0.1
$H^+ \rightarrow H_2$	0.0	3×10^{-8}	200	-
$O_2 \rightarrow H_2O$	1.229	1×10^{-7}	240	0.002

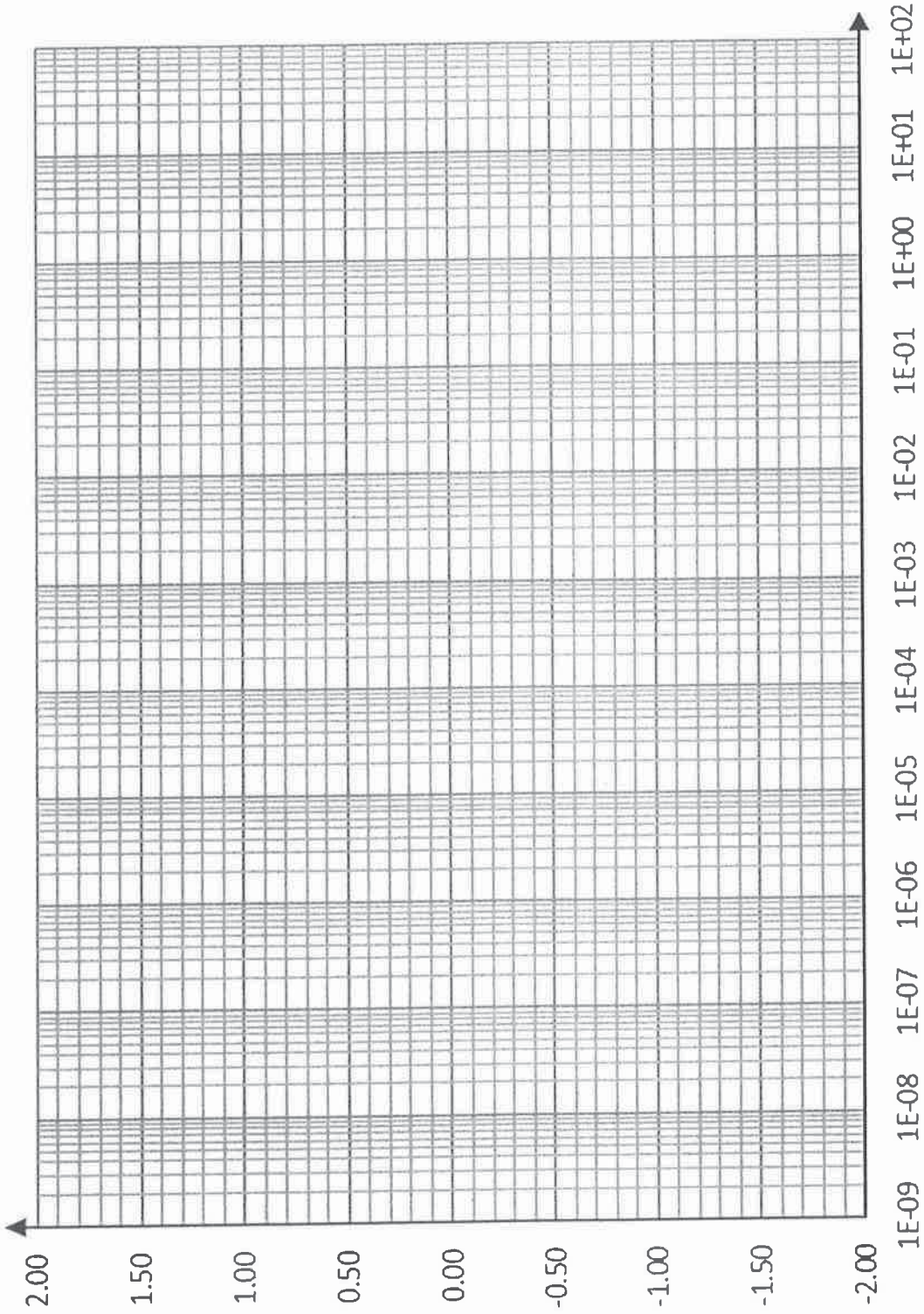
a) Plot the polarization curves for all four reaction through the whole range of current/voltage indicated on the graph paper provided. **(9 marks)**

b) Using mixed potential theory, determine the overall anode and cathode lines. **(5 marks)**

c) Find the overall E_{corr} and i_{corr} from the graph. **(2 marks)**

d) At the open circuit potential, find the current flowing on each anode and cathode reaction from the graph. Indicate whether it is an anode or a cathode and complete the table below. **(4 marks)**

Reaction	i (A/cm^2)	Anode or cathode?
$Pb^{2+} \leftrightarrow Pb$		
$Sn^{2+} \leftrightarrow Sn$		
$H^+ \rightarrow H_2$		
$O_2 \rightarrow H_2O$		


2.00
1.50
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-0.50
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-2.00
1E-09
1E-08
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1E-06
1E-05
1E-04
1E-03
1E-02
1E-01
1E+00
1E+01
1E+02

Question 6: (20 Marks)

(a) What are the three major ***mechanisms*** involved in the environmental degradation of polymeric materials? Answer in the space provided below. **(6 marks)**

i. _____

ii. _____

iii. _____

(b) What polymer classifications (Elastomer (E), Thermoplastic (TP), Thermosetting (TS)) would you recommend for the following case scenarios: **(5 marks)**

i. A portable toilet used for camping ____

ii. A container to store oil based paint ____

iii. An o-ring for preserving jam in a jar ____

iv. An Apple iPad™ case ____

v. A bottle for making soap to wash your hands ____

(c) Justify your choice of polymer for any **one** of the answers in Part (b). **(9 marks)**

Question 7: (20 Marks)

(a) Calculate the Pilling-Bedworth (PB) ratio for the metals Al and Mg given the following set of data. **(8 marks)**

Element	Molecular weight of the oxide (g/mol)	Density of the Oxide (g/cm^3)	Atomic weight of the metal (g/mol)	Density of the Metal (g/cm^3)
Mg	40.304	3.60	24.305	1.738
Al	101.96	3.987	26.981	2.70

(b) Based on your answer to Part (a), which material should be more protective in high temperature oxidation and why? **(6 marks)**

(c) What are 3 limitations in the use of the PB ratio in the prediction of the oxidation resistance of a material? **(6 marks)**

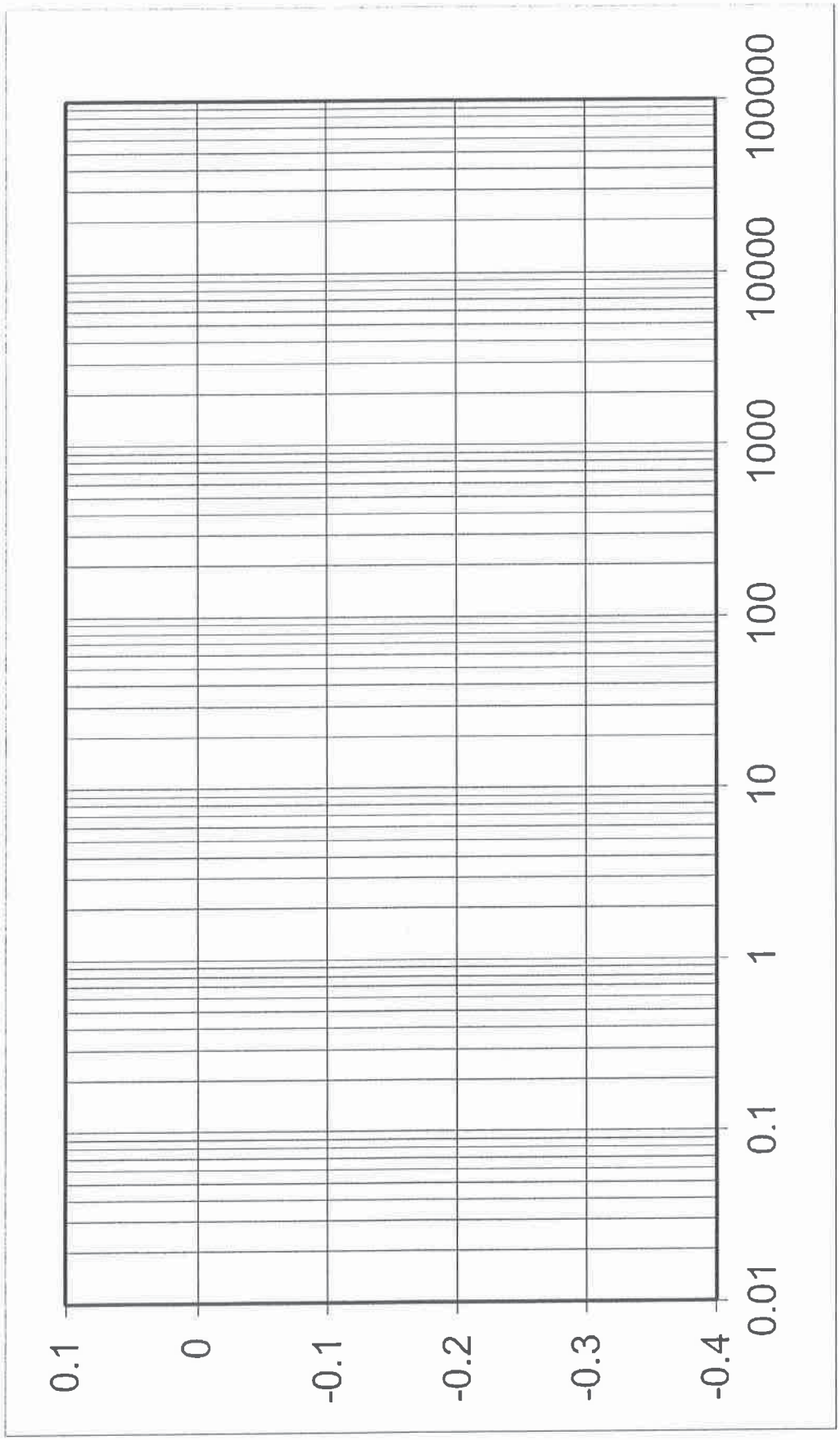
Question 8: (20 Marks)

a) Explain the principle of cathodic protection as a means of corrosion control. (5 marks)

b) Determine the cathodic overpotential necessary to reduce the corrosion rate on a metal from 500 $\mu A/cm^2$ to 1 0.5$\mu A/cm^2$, having the following kinetic behavior about the corrosion potential. Use the graph paper to calculate your answer. (5 marks)
   a. Given: $\beta_a = 0.100V/decade$ and $\beta_c = 0.200V/decade$.

c) Determine the actual corrosion potential of the metal $\mu A/cm^2$. (5 marks)

d) What applied current would be necessary to apply cathodically in order to provide protection of the metal? (5 marks)


0.1
0
-0.1
-0.2
-0.3
-0.4
0.01
0.1
1
10
100
1000
10000
100000

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PHYSICAL CONSTANTS TO USE IN THE EXAMINATION

Constant	*Symbol*	*Value*	*Units*
Avogadro's Number	N	6.02217×10^{23}	mol^{-1}
Boltzmann's Constant	k	1.38062×10^{-23}	$J\ K^{-1}$
Fund. Electronic Charge	e_o	1.60219×10^{-19}	C
Faraday's Constant	F	9.64867×10^{4}	$C\ mol^{-1}$
Gas Constant	R	8.31441 1.98720 0.08206	$J\ K^{-1}\ mol^{-1}$ $cal\ K^{-1}\ mol^{-1}$ $liter\text{-}atm\ K^{-1}\ mol^{-1}$
Permittivity of Free Space	ε_o	8.85418×10^{-12}	$F\ m^{-1}$

DEFINITIONS

Quantity	*Units*	*Symbol*	*Relation*
Electric Capacitance	farads	F	$C\ V^{-1}$
Electric Charge	coulombs	C	A s
Electric Current	amperes	A	$V^{-1}\ W$
Electric Potential	volts	V	$A^{-1}\ W$
Electric Resistance	ohms	Ω	$V\ A^{-1}$