



UNIVERSITY OF MINES AND TECHNOLOGY, TARKWA

FIRST SEMESTER EXAMINATIONS, NOV/DEC 2018

COURSE NO: MR 477

COURSE NAME: METALLURGICAL THERMODYNAMICS

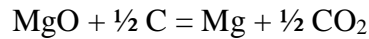
CLASS: BSc IV, MR

TIME: 3 HOURS

Name: _____ Index Number: _____

ANSWER ANY THREE (3) QUESTIONS

Q1. Magnesium can be produced from the *electrolysis of MgO* dissolved in a *fluoride melt* (MgF_2 , BaF_2 , NaF) at 800 °C using an iron cathode and a carbon anode. The cell reaction is



A *back reaction* occurs where part of the metal is *re-oxidised by CO₂* to *MgO* and *CO*.

- Write down balanced equations for the *back reaction* and the *overall reaction* as functions of the *current efficiency, S*. [7 marks]
- Determine the relation between the *current efficiency S* and the *content of CO₂* in the off-gas, stating the validity area for this expression [7 marks]
- What is the *gas composition* when the current efficiency is 85%? [6 marks]
- Calculate the *minimum energy requirement* for the process ($S = 100\%$). Ignore the energy used in heating up the raw materials [6 marks]
- Determine the *actual energy consumption* and the *energy efficiency* for the process when the current efficiency is 85% and the cell voltage is 7.8 V. [7 marks]

	Mg	MgO	CO	CO ₂
ΔH_{800}° [J]	0	-501250	-112600	-395250
M [kg mol ⁻¹]	0.0243	0.0403	0.02801	0.04401

- Q2.**
- Explain the effect of following on the electro-deposition of gold
 - pH [5 marks]
 - ii) sulphide ions [5 marks]
 - Explain the significance of the NaF/AlF₃ ratio in the electrolysis of aluminium. [6 marks]
 - State the main disadvantages
 - pre-baked anodes [5 marks]
 - Soderberg anodes in the electrolysis of aluminium [5 marks]
 - Explain the term *anode effect*, indicating what causes it and how it can be controlled. [7 marks]

- Q3** a) State and explain the main desirable properties of electrolyte for fused salt electrolysis. **[9 marks]**
 b) What are the main similarities between fused salt electrolysis and aqueous solution electrolysis? **[6 marks]**
 c) State the main differences between fused salt electrolysis and aqueous solution electrolysis **[6 marks]**
 d) State the advantages of fused salt electrolysis over aqueous solution electrolysis **[6 marks]**
 e) State the advantages of aqueous solution electrolysis over fused salt electrolysis **[6 marks]**

Q4 In the cathodic deposition of zinc from an $\text{H}_2\text{SO}_4\text{-ZnSO}_4$ solution the limiting current densities i_o are given by the expressions:

$$i_{o,\text{Zn}} = 12 \exp\left(\frac{-43500}{RT}\right) \quad \text{A cm}^{-2}$$

$$i_{o,\text{H}_2} = 133 \exp\left(\frac{-70700}{RT}\right) \quad \text{A cm}^{-2}$$

The overpotentials η for zinc deposition and hydrogen evolution can be expressed as:

$$\eta_{\text{Zn}} = \frac{RT}{2F} \ln\left(\frac{i_{o,\text{Zn}}}{i_{\text{Zn}}}\right) \quad \text{Volt/Decade}$$

$$\eta_{\text{H}_2} = \frac{2RT}{F} \ln\left(\frac{i_{o,\text{H}_2}}{i_{\text{H}_2}}\right) \quad \text{Volt/Decade}$$

The electrolyte has $\text{pH} = 0$ and the activity of Zn^{2+} can be assumed to be 1 at all temperatures. Total cathodic current density is 0.040 A cm^{-2} and the atomic weight of zinc $M_{\text{Zn}} = 65.4 \text{ g mol}^{-1}$. The standard Gibbs energy and enthalpy of formation of $\text{Zn}^{2+}_{(\text{aq})}$ at 298 K are:

$$\Delta G^\circ_f = -147 \text{ kJ mol}^{-1} \text{ and } \Delta H^\circ_f = -154 \text{ kJ mol}^{-1}, \text{ respectively.}$$

- a) Prove that the standard reduction potential for zinc deposition as a function of temperature can be expressed by the relation:

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.798 + 1.218 \times 10^{-4} T \quad \text{[13 marks]}$$

- b) Determine the current efficiency for zinc deposition S_{Zn} at 303 K **[10 marks]**

- c) The table below gives the experimental data for anode potential, specific conductivity and cathodic current efficiency at various temperatures.

T (K)	273	288	303	318	333
E_A (V)	2.700	2.590	2.480	2.360	2.240
k ($\Omega \text{ cm}$) ⁻¹	0.435	0.476	0.526	0.556	0.588
S_{Zn}	0.97	0.95	0.92	0.88	0.83

Derive an expression for the deposition potential of zinc as a function of temperature, T, and current efficiency S_{Zn} and determine the numerical value of the cathodic potential at the temperature 318 K. **[10 marks]**

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