

PROGRAM : BACCALAUREUS TECHNOLOGIAE

ENGINEERING: METALLURGY_

METALLURGICAL THERMDYNAMICS III

CODE: THM32-1

DATE : NOVEMBER EXAMINATION

24 NOVEMBER 2016

<u>DURATION</u> : (Y-PAPER) 12:30 - 15:30

<u>WEIGHT</u> : 40:60

FULL MARKS : 100

TOTAL MARKS : 100

EXAMINER: Mr. C BANGANAYI 082016003

MODERATOR : MR M KALEMBA 5112

NUMBER OF PAGES : 3 PAGES + ONE ANNEXURE

INSTRUCTIONS : CALCULATORS ARE PERMITTED (ONLY ONE PER

STUDENT)

<u>REQUIREMENTS</u>: EXAM PAPER TO BE HANDED IN AFTER THE EXAM

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INSTRUCTIONS TO STUDENTS:

ANSWER ALL QUESTIONS.

QUESTION 1:

- a) Using a sketch of G vs T diagram demonstrate why a liquid is more stable than the solid above the melting point of any substance. In your diagram label all important parameters or values including H of liquid and solid at T=absolute zero. (5)
- b) Use the 1st and 2nd law equations to show that:

$$dG=VdP-SdT$$
 (5)

c) Show using diagrams G vs T diagrams how a solid's melting point increases with increase in pressure. State which equation is used to demonstrate this. (5)

QUESTION 2:

- 2.1 Derive the Gibbs free energy equation in terms of standard enthalpy change and standard entropy change and show how this standard free energy change can be given in terms of the equilibrium constant of a reversible reaction (6)
- 2.2 Calculate the equilibrium partial pressure of nitrogen in an inert gas over liquid lithium at 527 °C if the following data are given:

$$3Li + \frac{1}{2} N_2 = Li_3 N \Delta G^o = 76 258 \text{ J. mol}^{-1}$$

$$R = 8.31 \text{ J K}^{-1}.\text{mol}^{-1}$$
(4)

2.3 In a copper converter, the following reaction is believed to occur during the later stages:

$$Cu_2S + 2Cu_2O = 6 Cu + SO_2 (g)$$

$$\Delta G^{o} = -365 - 21.46 \text{ T}$$

Calculate the equilibrium partial pressure of SO_2 at 1 250 °C assuming that both Cu_2S and Cu_2O exist as pure melts (5)

OUESTION 3:

The effect of pressure P on the equilibrium transformation of phases can be expressed through Clausius Clayperon equation i.e. dG=VdP-SdT. Knowing that at equilibrium G^L=G^S for a liquid to solid transformation.

Show that $dT/dP = \Delta V/\Delta S$. Say whether this is positive or negative and what does this mean if it's positive or negative, give example. (15)

QUESTION 4:

Cu-Zn brasses, like many industrial alloys, are based on solid solutions of a base metal, here the FCC Cu. In the equilibrium phase diagram, the Cu-Zn solid solution covers a wide composition range, approaching 38.95 weight percent (wt.%) Zn at a high temperature. In the normal casting fabrication, Cu-Zn alloys exhibit a single α -phase FCC state below 35 wt.% Zn; above this Zn content, the intermetallic β -CuZn (CsCl type) would be formed, which induces precipitation strengthening, but at the expense of the reduced plasticity. For this reason, industrial Cu-Zn alloys contain at most about 40.0 wt.% Zn, which is slightly above the solubility limit of Zn in Cu.

- a) Using e/a (valence electron/atom) ratio concept of metallic bond formation explain why Zn can dissolve up to 40 % in Cu and Cu can only dissolve <1% in Zn (5)
- b) Using a diagram of G vs X_{zn} show by drawing a tangent, the chemical potential (μ) of a Cu 5%Zn solution (5)
- c) Give example of type of phase diagram results from the following interaction parameters (9)
 - (i) $\Omega = 0$
 - (ii) $\Omega = +ve$
 - (iii) Ω = -ve

QUESTION 5

The majority of refining reactions required in liquid metals occur around the liquid slag-liquid metal interface and are commonly known as slag metal reactions.

a) Describe four fundamental functions of slags. (12)

b) Write short descriptions of the properties of slags. (12)

OUESTION 6

Using diagrams describe a positive and a negative deviation from Raoult's law and what causes these deviations (12)

Total 100

FORMULAE-LIST

1.
$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

2.
$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

3.
$$\Delta G^{\circ} = -RT \ln k$$

4.
$$\Delta G_A = RT \ln \gamma_A + RT \ln \left(\frac{M_B}{100 M_A} \right)$$

5.
$$\Delta G^{M} = RT (X_A \ln a_A + X_B \ln a_B)$$

6.
$$\Delta S^{M} = -R \left(X_{A} \ln X_{A} + X_{B} \ln X_{B} \right)$$

7.
$$\Delta H^{M} = RT (X_A \ln \gamma_A + X_B \ln \gamma_B)$$

8.
$$G_A^{XS} = RT \ln \gamma_A$$

9. N =
$$\frac{L}{T} \times \frac{273}{0.022414}$$

10. m =
$$\frac{M}{L}$$

11.
$$\Box c = \sqrt{\frac{8RT}{\pi M}}$$

12. d =
$$\sqrt{\frac{cm}{2\sqrt{2}\pi\mu}}$$

13.
$$\mathcal{U} = \frac{m_A m_B}{m_A + m_B}$$

14.
$$Z_{AB} = N_A N_B d_{AB}^2 \sqrt{8\pi k T u^{-1}}$$

15.
$$\Delta G^{XS} = X_A \Delta G_A^{XS} + X_B \Delta G_R^{XS}$$

16. V = ZAe
$$\frac{-E}{RT}$$

17.
$$\log f_A = \text{wt \% A e}_A^A + \text{wt \% B e}_A^B + \text{wt}$$

% $C e_A^C$ (e = interaction-parameter)

18.
$$S_A = k\sqrt{P_A}$$

19.
$$\ln f_B = X_B e_B^B + X_C e_B^C + X_D e_B^D$$

20.
$$\frac{-d[C]}{dT} = D \frac{[O]_{sat} - [O]}{l\Delta l} \times \frac{12}{16}$$

$$21. \Delta T_{A} = \frac{X_{A}RT_{(f)B}^{2}}{H_{(f)B}}$$

22.
$$\triangle G = -ZFE$$

23.
$$\Delta S = ZF \left[\frac{\partial E}{\partial T} \right]_{P} = S^{M} \text{ (molar)}$$

24.
$$\Delta H_A = -ZF \left[E - T \left(\frac{\partial E}{\partial T} \right) \right] = H^{M_A}$$
 (molar)

25.
$$\Delta G_A = RT \ln a_A + \Delta G^o$$

26.
$$\Delta G = \Delta H - T \Delta S$$

27.
$$t_x = \frac{1}{k} \ln \left(\frac{c_o}{c_o - x} \right)$$

28.
$$k = Ae^{\left(\frac{-E}{RT}\right)}$$

29.
$$t_{0,s} = \frac{1}{kC}$$
 or $\frac{\ln 2}{k}$

30.
$$k = \frac{1}{t} \times \frac{x}{c_0(c_0 - x)}$$