

COLLEGE OF ENGINEERING  
Department of Metallurgical & Materials Engineering  
The University of Alabama

Dr. R. G. Reddy

MTE 562

Thermodynamics

Final Exam

Q.1

(5 pts) a.

Explain the following:

1. First Law of Thermodynamics
1. Enthalpy Change of Phase Transformations

(15 pts) b.

For solid silver, the molar heat capacity at constant pressure is given by

$$C_p = 21.3 + (8.535 \times 10^{-3} T) + (1.506 \times 10^{-5} T^2) \quad \text{J/g atom K}$$

Find the quantity of heat required to raise the temperature of 1 g atom of silver from 25°C to 900°C.

Q.2

(5 pts) a.

Explain the following:

1. Activity of a component i ( $a_i$ )
2. Alternative Standard States of a component i in a dilute metallic solution

(5 pts) b.

Show that Gibbs Duham equation for a binary system is

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 = 0 \quad (\text{constant } P \text{ and } T)$$

where  $\gamma_i$  is the activity coefficient of component i and  $X_i$  is the mole fraction of component i

(10 pts) c.

For 20 atom% cobalt in liquid copper- cobalt solution, partial enthalpy of mixing of cobalt ( $\Delta \bar{H}_{Co}^M$ ) is 16736 J/mole at 1300°C. Calculate the activity of cobalt at 20 atom%. Assume these solutions follow the regular solution model

Q.3

(5 pts) a.

Briefly describe experimental methods for the determination of Standard Gibbs Energy Changes of a reaction

(15pts) b.

For the given reaction:  $\text{Cu}_2\text{O} (s) + \text{C} (s) = 2\text{Cu} (s) + \text{CO} (g)$   
using the attached Gibbs energy- temperature diagrams (Ellingham):

- 1) Calculate the Standard Gibbs energies of the above reaction at 400°C and 1000°C.
- 2) Express the Standard Gibbs energy of the reaction as a function of temperature over a temperature range of 400°C to 1000°C.

$\Delta G^\circ$

Q.4

- (5 pts) a. Show that for an infinite dilute solution, mole fraction as standard state, activity coefficient of a solute component 1 is expressed as

$$\ln f_1 = X_1 \epsilon_1^1 + X_2 \epsilon_1^2 + X_3 \epsilon_1^3 + \dots + X_j \epsilon_1^j$$

Where  $X_i$  is mole fraction of solute  $i$  and  $\epsilon_i^j$  interaction parameter

- (15 pts) b. A steel melt contains 0.80 wt% C, 1.30 wt% Si, and 0.10 wt% S. Calculate the activity of sulfur ( $a_S$ ) in the melt at 1600°C.

Interaction parameters data is given in the **Attached Table 1**.

Q.5

- (5 pts) a. Show that Gibbs-Helmholtz equation is

$$\Delta H_{p,T} = -ZF [E - T(\partial E / \partial T)_p]$$

where  $F$  is the faraday constant;  $Z$  moles of electrons,  $E$  volts of reversible emf.

- (15 pts) b. Construct a cell for  $\text{Ag} + \text{Fe}^{3+} = \text{Ag}^+ + \text{Fe}^{++}$  at 25° C using the nitrate salts. Calculate (a)  $E^\circ$  for the above reaction and (b)  $K_i = (m_+)(m_{++}) / (m_{3+})$  at infinite dilution

The standard emf data is given in the attached **Table-14.1**:

Table 1.

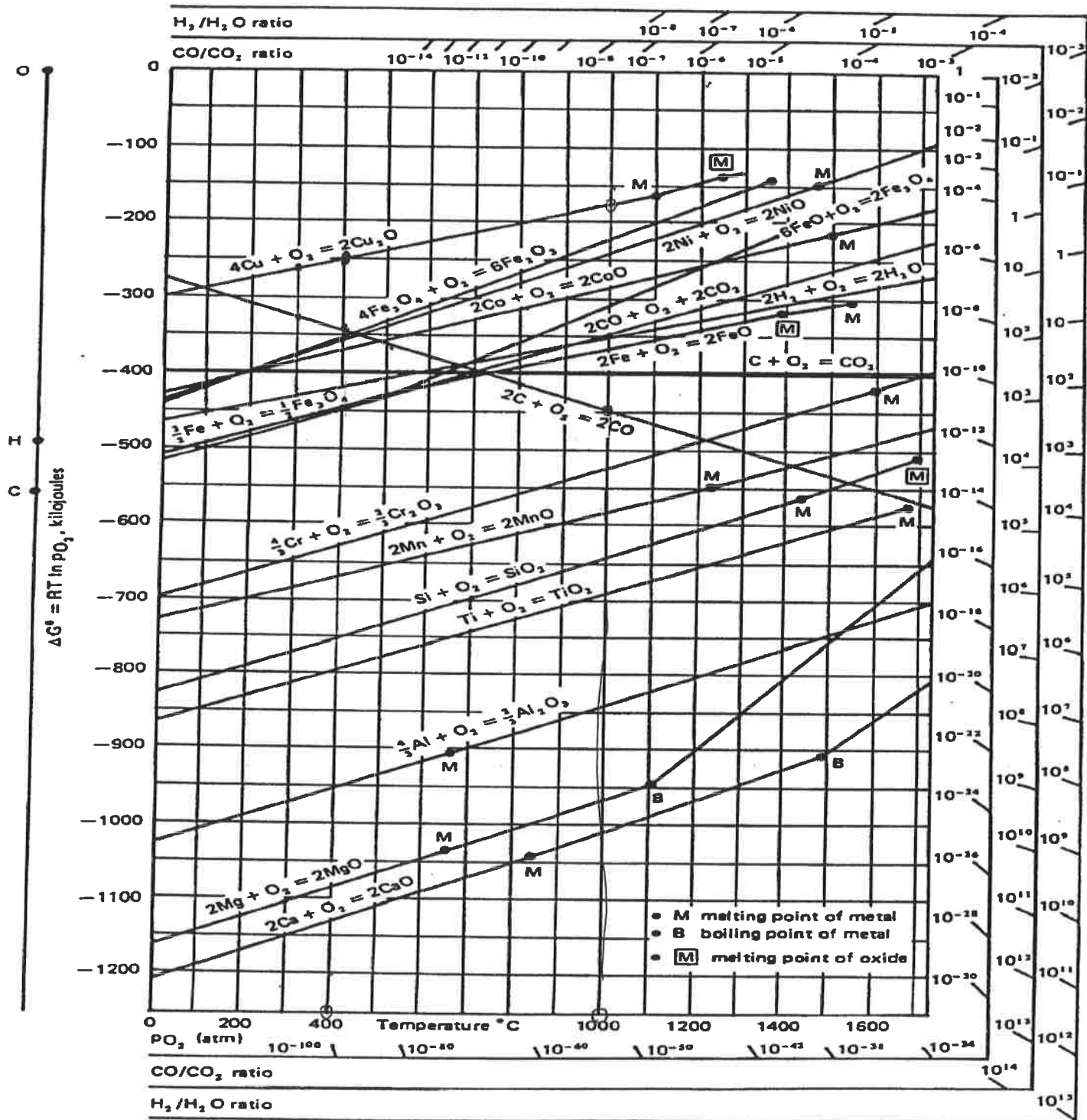
**Table**      **Interaction coefficients  $e_X^Y \times 10^2$  in liquid steel†**

Dis- solved element X	Added element Y								
	Al	C	Cr	Cu	Mn	N	O	S	Si
C	4.8	22	-2.4	1.6		11.1	-9.7	9	10
H	1.3	6	-0.22	0.05	-0.14			0.8	2.7
N	0.3	13	-4.5	0.9	-2.0	0	5.0	1.3	4.7
O	-94	-13	-4.1	-0.9	0	5.7	-20	-9.1	-14
P						11.3	13.5	4.3	9.5
S	5.8	24	-2.2	-1.2	-2.5	3.0	-18	-2.8	6.6
Si	6.3	24		≈0	0	9.3	-25	5.7	32

† From: J. F. Elliott, et al.: "Thermochemistry for Steelmaking," vol. II, Addison-Wesley Publ. Co. Inc., Reading, Mass., 1963.

**Table 14.1** Selected values of standard emf of half-cells,  $E^\circ$ , at 25°C;  $E^\circ$  is also called oxidation potential. Selected values from a table by P. Vanysek in Gen. Ref. (25) for one atm, corrected below to one bar by using (14.23). All metals and salts are in solid state except as indicated, the solvent is water.

<i>Electrode Reaction</i>	<i>E° , Volts</i>	<i>Electrode Reaction</i>	<i>E° , Volts</i>
$\text{Li} = \text{Li}^+ + e^-$	3.0403	$\text{Ag} + \text{Br}^- = \text{AgBr} + e^-$	-0.07116
$\text{K} = \text{K}^+ + e^-$	2.931	$\text{Cu}^+ = \text{Cu}^{++} + 2e^-$	-0.153
$\text{Ca} = \text{Ca}^{++} + 2e^-$	2.868	$\text{Ag} + \text{Cl}^- = \text{AgCl} + e^-$	-0.22216
$\text{Na} = \text{Na}^+ + e^-$	2.71	$2\text{Hg(l)} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2 + 2e^-$	-0.26791
$\text{La} = \text{La}^{3+} + 3e^-$	2.379	$\text{Cu} = \text{Cu}^{++} + 2e^-$	-0.3417
$\text{Mg} = \text{Mg}^{++} + 2e^-$	2.372	$2\text{OH}^- = \text{H}_2\text{O} + 0.5\text{O}_2(\text{g}) + 2e^-$	-0.401
$\text{Al} = \text{Al}^{3+} + 3e^-$	1.662	$2\text{I}^- = \text{I}_2 + 2e^-$	-0.5353
$0.5\text{H}_2(\text{g}) + \text{OH}^- = \text{H}_2\text{O} + e^-$	0.82877	$2\text{Hg(l)} + \text{SO}_4^{--} = \text{Hg}_2\text{SO}_4 + 2e^-$	-0.6123
$\text{Zn} = \text{Zn}^{++} + 2e^-$	0.7620	$\text{Fe}^{++} = \text{Fe}^{3+} + e^-$	-0.771
$\text{Fe} = \text{Fe}^{++} + 2e^-$	0.447	$2\text{Hg(l)} = \text{Hg}_2^{++} + 2e^-$	-0.7971
$\text{Cd} = \text{Cd}^{++} + 2e^-$	0.4031	$\text{Ag} = \text{Ag}^+ + e^-$	-0.7994
$\text{Co} = \text{Co}^{++} + 2e^-$	0.28	$\text{Hg}_2^{++} = 2\text{Hg}^{++} + 2e^-$	-0.920
$\text{Ni} = \text{Ni}^{++} + 2e^-$	0.257	$2\text{Br}^- = \text{Br}_2(\text{l}) + 2e^-$	-1.066
$\text{Ag} + \text{I}^- = \text{AgI} + e^-$	0.15241	$2\text{H}_2\text{O} = \text{O}_2(\text{g}) + 4\text{H}^+ + 4e^-$	-1.229
$\text{Sn(white)} = \text{Sn}^{++} + 2e^-$	0.1377	$2\text{Cl}^- = \text{Cl}_2(\text{g}) + 2e^-$	-1.35810
$\text{Pb} = \text{Pb}^{++} + 2e^-$	0.1260	$2\text{F}^- = \text{F}_2(\text{g}) + 2e^-$	-2.866
$\text{H}_2(\text{g}) = 2\text{H}^+ + 2e^-$	0.000		



The Ellingham diagram for Metallurgically important oxides