UNIVERSITY OF JOHANNESBURG

PROGRAM	NATIONAL DIPLOMA *EXTRACTION METALLURGY*
SUBJECT	**METALLURGICAL THERMODYNAMICS 2**
CODE	**THM 21-2 (Extraction Metallurgy)** **Main Examination**
DATE	13 JUNE 2015
TIME	08:30
WEIGHT	40:60
TOTAL MARKS	64

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MODERATOR	MARCEL KALEMBA
NUMBER OF PAGES	3 PAGES AND A 3-PAGE ANNEXURE

INSTRUCTIONS

First read carefully through all questions; only then

- Answer all questions in any sequence – but
- Please start answering each question on a new page
- You must clearly demonstrate how you arrived at a given answer, results alone are insufficient
- Finally: Check whether an answer makes sense; is the result likely?
- Calculators are permitted, brains also, but nothing else because
- All data required for calculations are provided in the Annexure

Question 1 [10]

General

1.1 Briefly describe the zeroth law of thermodynamics (2)

1.2 Give the formula for the standard free energy change and describe in words the condition when a reaction is feasible. (2)

1.3 The free energy is composed of two terms that reflect two fundamental forces of nature; shortly describe in words which two fundamental forces are operating and to which terms of the free energy they relate. (2)

1.4 Are exothermic reactions always feasible? (2)

1.5 If gases are involved, what can you generally state about the entropy change of the reaction? Give an example! (2)

Question 2 [8]

Heat

2.1 You have to design a plant that is able to evaporate 55 t/h of water to produce steam at 300°C; the feed water is at 25°C, the steam at 1 atm. How much power do you need? (8)

Assume no losses; use mean heat capacities

Question 3 [12]

Equilibrium constant

Consider the reduction of metal oxides to the respective metals by hydrogen gas:

3.1 Formulate the reaction and define the equilibrium constant K for the reduction of a metal oxide of the composition MO (4)

3.2 Calculate and compare the equilibrium constants at 1000°C for manganese oxide (MnO) and cupric oxide (CuO) (6)

3.3 Based on the values of the equilibrium constants, what qualitative statement can you make as regards the usefulness of this reaction for the industrial production of the two metals? (2)

Question 4 [12]

Gibbs

In an industriai process, the production of MnO from Mn-dioxide, pyrolusite, at 750°C is required.

4.1 Formulate the reaction in which pyrolusite is reduced to MnO with coke and calculate the free energy change for this reduction process at the given temperature. (4)

4.2 Formulate the reaction in which pyrolusite forms MnO by dissociation and calculate the free energy change for this process at the given temperature. (4)

4.3 Express in words which of the two reactions you would choose and why? (4)

Question 5 [22]

Processes

Consider the reduction of magnetite with coke to form iron

5.1 Formulate the overall reaction (2)

5.2 How much coke (in t) would you have to add for the reduction of 1 t of magnetite? Assume stoichiometric requirements and coke to be pure carbon (2)

5.3 Estimate the volume of gas (in m3) that is produced by the reduction of 1 t of magnetite Assume stoichiometric requirements (3)

5.4 If you were to completely combust the produced gas, how much energy could you recover? (4)

5.5 Determine whether the reduction of magnetite is an exo- or endo-thermic process (3)

5.6 As regards the change of entropy for the reaction, what could you predict? (1) Do not calculate yet but give a reason for your answer

5.7 Demonstrate that the reaction is not feasible at standard conditions (3)

5.8 Estimate the temperature at which the reaction becomes feasible. (4)

The end

Substance: Name	Formula	State	Mol Mass g/mol	Enthalpy H°_{298} J/mol	Entropy S°_{298} J/(mol K)	Heat Capacity: Temp Range K	a	b	C_{mean} J/(mol K)
Manganese	Mn	sol	54.9		32.0	298 - 1517	20.7	18.7	28.6
	Mnliq	liq		12 100	40.0	1517 - 2332			46.0
Manganese carbonate	$MnCO_3$	sol	114.9	- 894 100	85.8	298 - 700	58.1	85.4	106
Manganese oxide	MnO	sol	70.9	- 385 221	59.7	298 - 1500	42.9	10.9	52.3
Mn-dioxide, *pyrolusite*	MnO_2	sol	86.9	- 520 029	53.0	298 - 523	35.1	66.0	62.9
Mercury (quicksilver)	Hg	liq	200.6		75.9	298 - 630	28.4	-2.1	27.4
	Hggas	gas		61 291	174.8	630 - 3000			20.8
Mercury oxide, *red mercury*	HgO	sol	216.6	- 90 789	70.3	298 - 800	36.6	27.6	50.8
Mercury sulfide, *cinnabar*	HgS	sol	232.7	- 53 346	82.4	298 - 1098	43.9	15.4	53.5
	HgSgas	gas		127 194	254.2	1098 - 2000	36.6	0.5	37.1
Methane	CH_4	gas	16.0	- 74 873	186.2	298 - 1000	19.3	54.8	54.3
Nickel	Ni	sol	58.7		29.9	298 - 1728	19.1	23.5	33.0
	Niliq	liq		17 472	40.0	1728 - 3187			43.1
Nickel carbonate	$NiCO_3$	sol	118.7	- 694 544	86.2	298 - 700	67.1	68.1	99.0
Nickel carbonyl	$Ni(CO)_4$	gas	170.8	- 602 910	410.6	298 - 2000	152.7	29.1	184.8
Nickel oxide	NiO	sol	74.7	- 239 701	38.0	298 - 2228	20.9	36.5	58.0
Nickel sulfide, *millerite*	NiS	sol	90.8	- 87 864	53.0	298 - 1249	36.5	27.4	51.0
Ni-sulfide, *heazlewoodite*	Ni_3S_2	sol	208.1	- 216 313	133.9	298 - 1062			150
Nitrogen	N_2	gas	28.0		191.6	298 - 1600	28.0	3.1	30.8
Oxygen	O_2	gas	32.0		205.1	298 - 5000	31.9	2.5	38.3
Palladium	Pd	sol	106.4		37.8	298 - 1825	24.2	6.4	29.4
Palladium oxide	PdO	sol	122.4	- 115 478	38.9	298 - 1200	21.0	34.7	45.6
Platinum	Pt	sol	195.1		41.6	298 - 2045	24.3	5.4	30.4
	Ptliq	liq		19 665	51.3	2045 - 4096			34.7
Silicon	Si	sol	28.1		18.8	298 - 1685	19.7	6.1	25.5
	Siliq	liq		50 208	48.6	1685 - 3504			27.2
Silica	SiO_2	sol	60.1	- 910 857	41.5	298 - 1996	29.2	56.8	65.0
	SiO2liq	liq		- 901 292	49.3	1996 - 3000			85.8
Silver	Ag	sol	107.9		42.7	298 - 1234	24.3	2.5	28.0
	Agliq	liq		11 297	51.8	1234 - 2433			33.5
Slag, *calcium ortho silicate*	Ca_2SiO_4	sol	172.2	-2 315 216	120.8	298 - 2403	145.9	40.8	164
	Ca2SiO4liq	liq		-2 244 000	170.8	2403 - 2800			209
Slag, *fayalite*	Fe_2SiO_4	sol	203.8	-1 479 902	145.2	298 - 1490	125.5	60.6	153
	Fe2SiO4liq	liq		-1 387 728	61.9	1490 - 1700			241
Sulfur	S	sol	32.1		32.1	298 - 388	16.8	20.1	23.0
	Sliq	liq		2 122	37.6	388 - 882	30.0	6.8	34.1
	S2gas	gas		128 599	228.2	882 - 5000	35.2	1.9	40.2
Sulfur dioxide	SO_2	gas	64.1	- 296 813	248.2	50 - 500	30.8	31.9	39.0
	SO2hi	hi				500 - 5000	52.5	3.0	60.7
Tin *grey*	Sngr	sol		- 2 092	44.1	298 - 398	25.8		25.8
Tin *white*	Sn	sol	150.7		51.2	298 - 505	21.6	18.1	28.8
	Snliq	liq		7 029	65.1	505 - 800			25.5
Tin dioxide, *cassiterite*	SnO_2	sol	150.7	- 577 631	49.0	298 - 1903	58.7	18.2	78.8
Water	Ice	sol		-279 850		< 273			37.0
	H_2O	liq	18.0	- 285 830	69.9	298 - 373	73.0	7.9	75.5
	H2Ogas	gas		- 241 827	188.8	373 - 1600	30.1	10.0	38.5
Zinc	Zn	sol	65.4		41.6	298 - 693	22.2	10.5	27.1
	Znliq	liq		7 322	52.2	693 - 1 180			31.4
	Zngas	gas		130 415	161.0	1 180 - 2 000			20.8
Zinc carbonate, *smithonite*	$ZnCO_3$	sol	125.4	- 812 780	82.4	298 - 500	38.9	138.1	93.0
Zinc oxide, *zincite*	ZnO	sol	81.4	- 350 460	43.6	298 - 2248	41.4	9.5	53.3
Zinc sulfide, *sphalerite*	ZnS	sol	97.4	- 201 669	57.7	298 - 1293	44.7	10.6	52.8

Substance: Name	Formula	State	Mol Mass g/mol	Enthalpy H°_{298} J/mol	Entropy S°_{298} J/(mol K)	Heat Capacity: Temp Range K	a	b $\times 10^{-3}$	C_{mean} J/(mol K)
Acetylene	C_2H_2	gas	26.0	226 731	201.0	298 - 3000	50.2	14.2	72.9
Aluminium	Al	sol	27.0		28.3	298 - 933	19.8	14.4	28.5
	Alliq	liq		10 711	39.8	933 - 2790			31.7
Aluminium oxide, *alumina*	Al_2O_3	sol	102.0	-1 675 274	50.9	298 - 800	58.2	83.5	101
	Al_2O_3 hi					800 - 2327	112.2	12.7	133
Cadmium	Cd	sol	112.4		51.8	298 - 594	22.3	12.2	27.4
	Cdliq	liq		6 192	62.2	594 - 1040			29.7
	Cdgas	gas		111 796	167.7	1040 - 1500			20.8
Cadmium carbonate	$CdCO_3$	sol	172.4	- 751 865	92.5	298 - 600	43.1	131.8	99.9
Cadmium oxide	CdO	sol	128.4	- 258 990	54.8	298 - 1500	43.0	9.7	51.5
Calcium oxide, *lime*	CaO	sol	56.1	- 635 089	38.1	298 - 3200	46.0	6.0	56.0
Ca-carbonate, *calcite*	$CaCO_3$	sol	100.1	-1 206 921	92.9	298 - 1200	74.8	50.2	110
Carbon, *graphite*	C	sol	12.0		5.7	298 - 1100	4.9	17.2	16.3
Carbon monoxide	CO	gas	28.0	- 110 541	197.7	298 - 5000	30.9	1.9	33.0
Carbon dioxide	CO_2	gas	44.0	- 393 505	213.8	298 - 500	26.0	37.2	35.6
	CO_2hl					500 - 5000	51.9	3.0	60.1
Chromium	Cr	sol	52.0		23.6	298 - 2130	20.3	12.1	30.0
	Crliq	liq		16 900	31.6	2130 - 2945			39.3
Chromium(III)-oxide	Cr_2O_3	sol	152.0	-1 139 701	81.2	298 - 2603	114.8	11.2	131
Iron-chrome spinel *chromite*	Fe $[Cr_2O_4]$	sol	223.8	-1 458 124	142.0	298 - 2123	140.1	35.5	183
Copper	Cu	sol	63.5		33.2	298 - 1358	22.0	7.4	28.0
	Culiq	liq		13 138	42.8	1358 - 2843			32.8
Copper(I)-oxide, *cuprite*	Cu_2O	sol	143.1	- 170 707	92.3	298 - 1508	56.4	25.8	79.7
	Cu2Oliq	liq		- 105 939	135.0	1508 - 2000			99.9
Copper(II)-oxide, *tenorite*	CuO	sol	79.5	- 156 063	42.6	298 - 1397	40.8	13.9	48.6
Chalcopyrite	$CuFeS_2$	sol	183.5	- 190 372	125.0	298 - 830	78.6	63.6	114
Cu(I)-sulfide, *chalcocite*	Cu_2S	sol	159.1	- 81 170	116.2	298 - 1400	47.9	97.2	85.7
Cu-Matte	Cu2Sliq	liq		- 68 325	125.3	1400 - 2000			89.7
Cu(II)-sulfide, *covellite*	CuS	sol	95.6	- 53 095	66.5	298 - 1300	44.4	11.0	53.0
Hydrogen	H_2	gas	2.0		130.7	298 - 5000	28.2	2.7	35.0
Iron	Fe	sol	55.8		27.3	298 - 1811	23.1	16.0	38.7
	Feliq	liq		13 807	34.9	1811 - 3158			45.0
Iron(II)-oxide, *wüstite*	FeO	sol	71.8	- 267 270	57.6	298 - 1650	47.9	10.7	58.0
		liq		- 243 212	72.2	1650 - 3687			68.2
Iron(II)(III)-oxide, *magnetite*	Fe_3O_4	sol	231.5	-1 118 383	146.1	298 - 1870	75.5	240.1	207
Iron-iron spinel Fe $[Fe_2O_4]$	Fe3O4liq	liq		- 980 311	220.0	1870 - 2000			213
Iron(III)-oxide, *hematite*	Fe_2O_3	sol	159.7	- 824 248	87.4	298 - 1700	78.1	99.8	142.0
Iron carbonate, *siderite*	$FeCO_3$	sol	115.9	- 740 568	92.9	298 - 800	48.7	112.1	106.0
Iron sulfide, *pyrrhotite*	FeS	sol	87.9	- 105 441	60.8	298 - 1465	31.0	63.0	68.0
Fe-Matte	FeSliq	liq		- 72 977	82.3	1465 - 3000			62.6
Iron sulfide, *pyrite*	FeS_2	sol	120.0	- 171 544	52.9	298 - 1000	56.0	27.8	73.0
Lead	Pb	sol	207.2		64.8	298 - 600	24.2	8.7	28.1
	Pbliq	liq		4 770	72.7	600 - 1200			29.7
Lead oxide, *litharge*	PbO	sol	223.2	- 218 062	68.7	298 - 1159	41.8	16.1	53.1
	PbOliq	liq		- 192 540	90.7	1159 - 2000			65.0
Lead sulfide, *galena*	PbS	sol	239.3	- 98 634	91.3	298 - 1386	46.6	9.5	54.0
	PbSliq	liq		- 79 806	104.9	1386 - 2000			66.9
Lead sulfate, *anglesite*	$PbSO_4$	sol	303.3	- 923 137	149.5	298 - 1139	66.5	110.0	144.0
Magnesium	Mg	sol	24.3		32.7	298 - 922	21.4	11.8	28.5
	Mgliq	liq		8 954	42.4	922 - 1361			32.6
	Mggas	gas		146 440	148.6	1361 - 2000			20.8
Mg-carbonate, *magnesite*	$MgCO_3$	sol	84.3	-1 095 798	65.7	298 - 700	47.8	99.0	94.0
Mg-oxide, *periklase*	MgO	sol	40.3	- 601 241	26.9	298 - 3105	42.8	6.0	53.0

Variable, constant or function				Unit of measurement			
t	time			s	second	=	1 / 60 min
			also measured in	1 h	hour	=	3600 s
			also measured in	1 d	day	=	24 h
m	mass		SI	1 kg		=	1000 g
			also	1 t		=	1000 kg
n	mole		for chemical calculations	mol		=	m / M mol
M	Mole mass		*tabulated*	g / mol			
V	volume			1 m^3	cubicmeter	=	1000 L *liter*
V_{mol}	mol volume		volume occupied by 1 mol of *an ideal gas* at 273 K			=	22.4 L / mol
d	density	=	m / V mass / volume	t / m^3		or	kg / L
			density of water at 4°C			=	1 kg / L
p	pressure		SI	1 Pa	Pascal	=	1 N / m^2
			old but useful	1 atm	atmosphere	=	101 325 Pa
T	temperature		also measured in °C	K	Kelvin	=	273 + °C
E	energy	E_{me}	*mechanical*	1 Nm	Newtonmeter	=	1 J
		E_{ms}	*volume work* pV	1 atm x L	Literatmosphere	=	101.3 J = Pa m^3
		E_{th} or Q	*thermal*	1 J	Joule	=	1 Ws
		E_{el}	*electrical*	1 Ws	Wattsecond	=	1 J
P	power	=	energy / time	1 J/s		=	1 W *Watt*
H_T	enthalpy	heat content at constant pressure		J / mol		=	U + pV
S_T	entropy	=	Q_{rev} / T	J / (mol K)			
G^o_T	Gibbs free energy	=	$H^o_T - T S^o_T$	J / mol	under standard conditions		
G_T		=	G^o_T + RT *ln* K	J / mol	under *non-standard* conditions		
H^o_{298} S^o_{298} G^o_{298}		enthalpy, entropy or free energy values under standard conditions at room temperature					
ΔH ΔS ΔG		change of enthalpy, entropy or Gibbs free energy in reactions				Σ products – Σ reactants	
ΔH^o_T ΔS^o_T ΔG^o_T		change of enthalpy, entropy or Gibbs free energy under standard condtions at temp. T					
ΔG_T		=	ΔG^o_T + R T *ln* K = $\Delta H^o_T - T\Delta S^o_T$ + RT *ln* K		*General reaction isotherm*		
K	equilibrium constant			no units		Π products / Π reactants	
C ≡ C_p	heat capacity		at constant pressure	J / (mol K)			
C_T	molar h.c. at T	=	$\int (a + b10^{-3} T)\, dT$	J / (mol K)	to be integrated from T_{lo} to T_{hi}		
C_{mean}	mean h.c.	=	Q / ΔT	J / (mol K)	valid over entire temperature interval		
R	universal gas constant			8.314 J / (mol K)			
F	Faraday constant			96 484 Cb / mol = As / mol		=	26.8 Ah/mol
N_A	Avogadro Number		number of particles or molecules *per mole* of matter			=	6E+23 / mol
Oxygen in air		oav =	21.0% by volume		oam	=	23.2% by mass
Water		M =	18.0 g / mol		1 L = 1 kg	=	55.5 mol/L
Consumption of electrical energy			1 kWh	=	1000 x 3600 Ws = J	=	3.6 MJ

μ	10^{-6}	*micro*	e.g.	1 μL	microliter	=	10^{-6} L		
m	10^{-3}	*milli*		1 ms	millisecond	=	10^{-3} s		
	$10^0 = 1$	unit							
k	10^3	*kilo*		1 km	kilometer	=	10^3 m		
M	10^6	*mega*		1 Mg	megagram	=	10^6 g	=	1 t
G	10^9	*giga*		1 GJ	gigajoule	=	10^9 J		