UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2007/2008

April 2008

EBS 323/3 - Pyrometallurgy
[Pirometalurgi]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains EIGHT printed pages and THREE pages APPENDIX before you begin the examination.
[Sila pastikan bahawa kertas peperiksaan ini mengandungi LAPAN muka surat beserta TIGA muka surat LAMPIRAN yang bercetak sebelum anda memulakan peperiksaan ini.]

This paper contains SEVEN questions.
[Kertas soalan ini mengandungi TUJUH soalan.]

Instructions: Answer **FIVE** questions. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.
*[**Arahan:** Jawab **LIMA** soalan. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.]*

Answer to any question must start on a new page.
[Mulakan jawapan anda untuk setiap soalan pada muka surat yang baru.]

You may answer a question either in Bahasa Malaysia or in English.
[Anda dibenarkan menjawab soalan sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.]

1. [a] A lead roasting operation, with the gas phase composition to be determined, is carried out at 1100 K and at 1 atm total pressure.

(i) Calculate the maximum partial pressure of SO_2 at which Pb and PbO can coexist at 1100 K under equilibrium condition (i.e., without forming the lead oxysulfate $PbSO_4.PbO$).

(ii) With the roaster gas composition of 12% SO_2 and 4% O_2 at 1 atm total pressure, is lead sulfate the stable solid phase?

(iii) With 1% O_2 in the gas, what partial pressure of SO_2 is necessary to form the lead oxysulfate $PBSO_4.PbO$?

Operasi pemanasan plumbum dengan komposisi fasa gas akan ditentukan pada suhu 1100 K dan tekanan 1 atm.

(i) Kira tekanan separa maksimum SO_2 dimana Pb dan PbO terbentuk pada suhu 1100 K dibawah keadaan keseimbangan (contoh: tanpa pembentukan plumbum oksisulfat $PbSO_4.PbO$).

(ii) Komposisi gas pemanas 12% SO_2 dan 4% O_2 pada tekanan 1 atm, adakah plumbum sulfat suatu fasa pepejal stabil?

(iii) Dengan 1% O_2 dalam gas, apakah tekanan separa bagi SO_2 yang sesuai untuk membentuk plumbum oksisulfat $PbSO_4.PbO$?

(65 marks/*markah*)

[b] Summarize the preliminary processing steps for the principal sulfide and oxide ores of the common metals.

Ringkaskan langkah pemprosesan awal untuk bijih sulfida dan oksida terpenting daripada logam biasa

(35 marks/*markah*)

...3/-

2. [a] The separation of copper in the matte during the smelting of copper ores is highly efficient. Assuming that Cu_2S and FeS behave ideally in the matte, and noting that the activity of iron oxide in a typical reverberatory slag is of the order of 0.5 (relative to liquid pure FeO), justify this industrial experience on a thermodynamic basis.

Pemisahan kuprum di dalam matte semasa peleburan bijih kuprum adalah sangat cekap. Dengan beranggapan Cu_2S dan FeS berkelakuan unggul di dalam matte dan aktiviti oksida besi di dalam jermang reverbaratori berada dalam tertib 0.5 (relatif kepada cecair tulen FeO), justifikasikan pengalaman industri ini dalam asas termodinamik.

(70 marks/*markah*)

[b] Write the chemical equations involved in the removal of Pb, Sn, S and Fe in the fire refining of copper. What happens to each of the compounds formed?

Tuliskan persamaan kimia yang terlibat dalam penyingkiran Pb, Sn, S, dan Fe dalam pembakaran pembersihan tembaga. Apakah yang akan terjadi kepada setiap sebatian yang terbentuk?

(30 marks/*markah*)

3. [a] A liquid lead bullion initially free of zinc and containing 0.77 wt% Ag is treated by the Parkes process at 500°C with zinc to remove the silver. Assume that the reaction product is pure Ag_2Zn_3, calculate the zinc addition per ton of lead bullion required to remove 98% of the silver.

$2\,Ag\,(l) + 3\,Zn\,(l) = Ag_2Zn_3(s)$ $\Delta G^o_{773} = -127{,}600$ J/g-mole

$\gamma^0_{Zn} = 11$

$\gamma^0_{Ag} = 23$

Atomic weight: Ag=107.9 Pb=207.2 Zn=65.4

Cecair plumbum perak biasanya tidak mengandungi zink dan mengandungi 0.77% berat Ag diperolehi melalui proses Parkes pada suhu 500° C dengan zink untuk menyingkirkan Perak. Dengan menganggap hasil tindakbalas adalah Ag_2Zn_3 tulen, kira pertambahan zink per tan yang diperlukan daripada plumbum perak untuk menyingkirkan 98% perak.

$2Ag(l) + 3Zn(l) = Ag2Zn3$ $\Delta G^o{}_{773} = -127600 J/g-mole$

$\gamma^o{}_{Zn} = 11$

$\gamma^o{}_{Ag} = 23$

Berat atom : Ag=107.9, Pb=207.2, Zn=65.4

(70 marks/*markah*)

[b] Briefly describe economically and technically feasible liquid phase techniques for:

(i) removing cadmium from lead at cadmium concentration below 1 wt%.

(ii) removing bismuth from lead.

Huraikan dengan ringkas dari segi ekonomi dan teknikal fasa cecair yang mungkin tentang:

(i) Penyingkiran cadmium daripada konsentrat plumbum dibawah 1% berat.

(ii) Penyingkiran bismuth daripada plumbum

(30 marks/*markah*)

...5/-

4. [a] Briefly discuss the solution loss and carbon deposition reactions, in accordance with the Boudouard reaction, in the lead blast furnace with respect to:

(i) effect of pressure

(ii) effect of temperature

(iii) reduction reactions

Bincangkan secara ringkas kehilangan larutan dan tindakbalas pengenapan karbon, berdasarkan tindakbalas Boudouard, dalam relau bagas plumbum dengan mempertimbangkan:

(i) Kesan tekanan

(ii) Kesan suhu

(iii) Tindakbalas penurunan

(50 marks/*markah*)

[b] Write short notes on:

(i) Sievert's law and its applications in iron and steel making.

(ii) Self and super fluxed sinters and their role in a blast furnace.

Tuliskan nota ringkas tentang:

(i) Hukum Sieverts dan kegunaannya dalam pembuatan besi dan keluli.

(ii) Self and super fluxed sinters dan peranannya dalam relau bagas.

(50 marks/*markah*)

5. [a] What is the mechanism and the chemical reactions involved in sulfur transfer between slag and hot metal inside a blast furnace? From the fundamental principles, discuss the strategies to be adopted to get low sulfur in the product.

Apakah mekanisma dan tindak balas kimia yang terlibat dalam pemindahan antara jermang (slag) dan logam panas di dalam relau bagas? Daripada prrinsip asas, bincangkan strategi yang diambil untuk memperolehi produk yang rendah sulfur.

(30 marks/*markah*)

[b] Discuss in brief how the productivity of a blast furnace can be improved through high top pressure and oxygen enrichment of blast.

(30 marks/*markah*)

[c] If a blast furnace operator wants to maintain the ratio of CO/CO_2 to be 1.8 : 1, ignoring the amount of CO_2 added by the decomposition of $CaCO_3$, calculate:

(i) The weight of carbon required per ton of iron reduced and

(ii) The volume of air required per ton of iron reduced

Jika operasi relau bagas dikekalkan dengan nisbah CO/CO_2 dengan 1.8 : 1, dengan mengabaikan kandungan CO_2 yang ditambah daripada penguraian $CaCO_3$, kira:

(i) Berat karbon (per ton) diperlukan dan

(ii) Isipadu udara (per ton) diperlukan

(40 marks/*markah*)

6. [a] Outline the principles of LD process of steel making mentioning how is it superior over the open hearth process?

Gariskan prinsip-prinsip proses LD bagi pembuatan keluli dengan menyebutkan sejauh manakah ianya lebih baik berbanding dengan proses palong terbuka (open hearth process)?

(30 marks/*markah*)

[b] Describe briefly with the help of a schematic diagram the cored wire injection process of steel refining. How does this process improve the steel quality?

Huraikan secara ringkas dengan bantuan gambarajah skematik proses suntikan dawai teras (cored wire injection process) pembersihan keluli. Bagaimanakah proses tersebut boleh meningkatkan kuantiti keluli?

(35 marks/*markah*)

[c] What is the mechanism of phosphorus transfer between a slag and metal? Considering the situations found during iron and steel making, compare qualitatively the extents of dephosphorization that may be achieved.

Apakah mekanisma pemindahan fosforus diantara jermang (slag) dan logam? Andaikan keadaan semasa pembuatan besi dan keluli adalah keadaan asal, bandingkan had mutu penyahfosforanan yang mungkin dicapai.

(35 marks/*markah*)

7. [a] Schematically describe the COREX process of iron making. How the COREX-MIDREX combination process is superior over the COREX process?

Huraikan secara skematik proses COREX bagi pembuatan besi. Sejauh manakah gabungan proses COREX-MIDREX lebih baik berbanding proses COREX?

(35 marks/*markah*)

[b] What are the major chemical reactions involved in a gas based DRI process? From theoretical point of view, discuss in brief the major ways and means to improve the productivity of such a process.

Apakah tindak balas kimia utama yang terlibat dalam proses gas asas DRI (gas based DRI process)? Daripada teori, bincangkan secara ringkas langkah-langkah utama dan cara untuk meningkatkan pengeluaran daripada proses demikian.

(35 marks/*markah*)

[c] Why is it important to prevent the re-oxidation of DRI? Discuss the mechanism how a pile of DRI may catch fire during shipping.

Kenapa ianya penting untuk menyah pengoksidaan semula DRI? Bincangkan mekanisma bagaimana himpunan (pile) DRI boleh terbakar semasa penghantaran.

(30 marks/*markah*)

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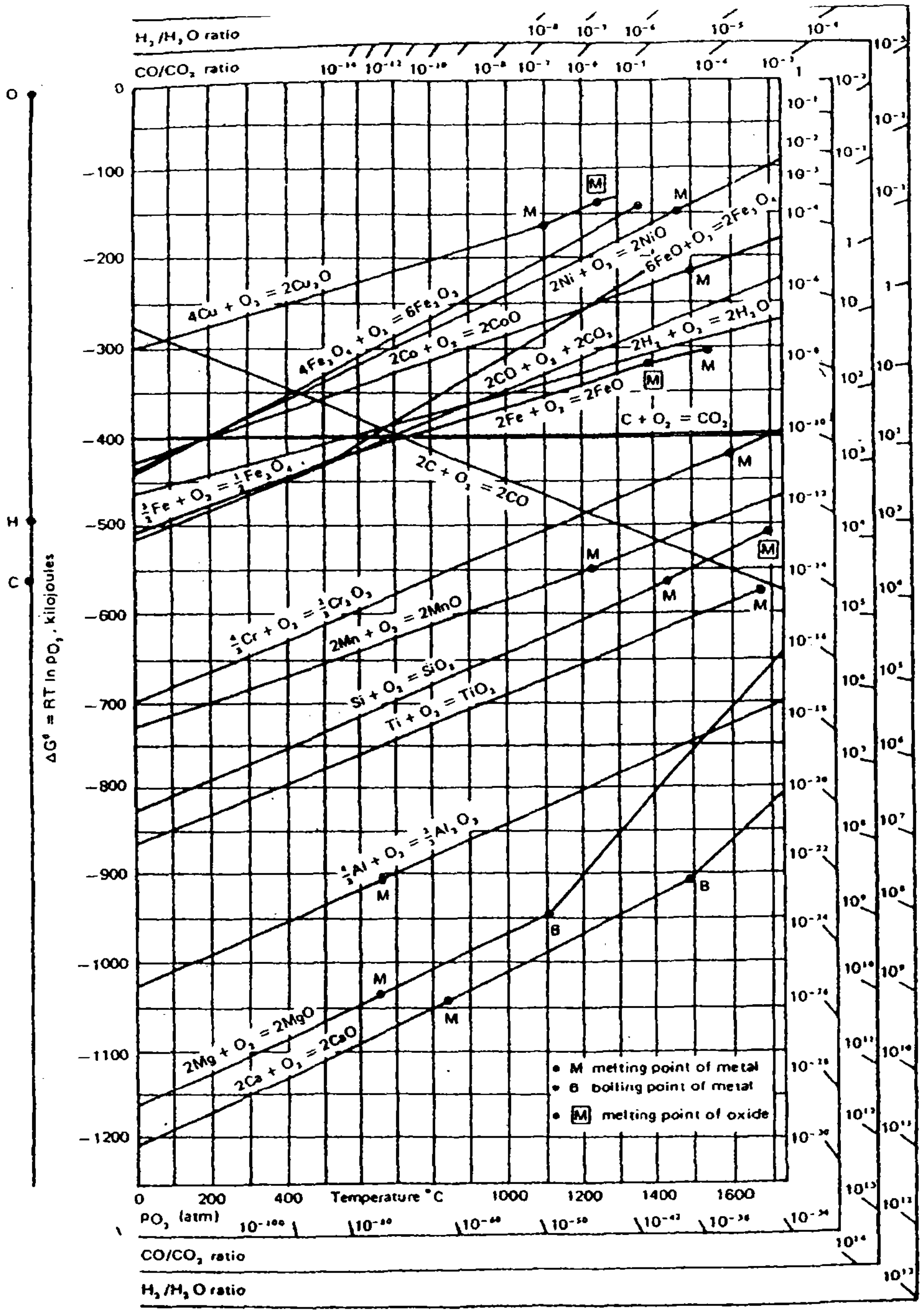
APPENDIX 1

LAMPIRAN 1



The Ellingham diagram for metallurgically important oxides.

APPENDIX 2

LAMPIRAN 2

SELECTION STANDARD GIBBS ENERGIES

Reaction	$\overline{\Delta H^0}$ (joule)	$\overline{\Delta S^0}$ (joule)	Range (°C)
$S_4(g) = 2\ S_2$	62 800	115.5	25–1700
$S_6(g) = 3\ S_2$	276 000	305	25–1700
$S_8(g) = 4\ S_2$	400 000	450	25–1700
$SO(g) = \frac{1}{2} S_2 + \frac{1}{2} O_2$	57 800	−5.0	445–2000
$SO_2 = \frac{1}{2} S_2 + O_2$	362 000	72.7	445–2000
$SO_3(g) = \frac{1}{2} S_2 + \frac{3}{2} O_2$	458 000	163.3	445–2000
$S = S(l)$	1715	4.44	115 m
$S(l) = \frac{1}{2} S_2$	58 600	68.3	115– 445 b
$S_2 = 2\ S(g)$	469 300	161.3	25–1700

Reaction	$\overline{\Delta H^0}$ (joule)	$\overline{\Delta S^0}$ (joule)	Range (°C)
Graphite = Diamond	1440	−4.48	29– 900
$C = C(g)$	713 500	155.5	1750–3800 s
$CH_4(g) = C + 2\ H_2$	91 040	110.7	500–2000
$CO = C + \frac{1}{2} O_2$	110 540	−89.35	−150– 500
$CO = C + \frac{1}{2} O_2$	114 400	−85.77	500–2000
$CO_2 = C + O_2$	395 350	−0.54	500–2000
$CO_2 = C + O_2$	393 500	−2.88	−50– 500
$COS(g) = C + \frac{1}{2} O_2 + \frac{1}{2} S_2$	202 800	−9.96	500–2000
$CS(g) = C + \frac{1}{2} S_2$	−163 000	−88	25–2000
$CS_2(g) = C + S_2$	11 400	−6.5	25–2000

Reaction	$\overline{\Delta H^0}$ (joule)	$\overline{\Delta S^0}$ (joule)	Range (°C)
$2\ PbO \cdot SiO_2 = 2\ PbO \cdot SiO_2(l)$	51 050	50.3	743 m
$2\ PbO \cdot SiO_2(l) = 2\ PbO(l) + SiO_2$	33 500	−6.7	885–1500
$PbO \cdot SiO_2 = PbO \cdot SiO_2(l)$	26 000	25.1	764 m
$PbO \cdot SiO_2 = PbO(l) + SiO_2$	25 100	1.26	885–1500
$Pb = Pb(l)$	4810	8.0	327 m
$Pb(l) = Pb(g)$	182 000	90.1	327–1746 b
$PbO = PbO(l)$	27 500	23.7	886 m
$PbO(l) = Pb(l) + \frac{1}{2} O_2$	181 000	68.0	886–1535 b
$Pb_3O_4 = 3\ Pb(l) + 2\ O_2$	702 500	370	328–1200
$PbO_2 = Pb(l) + O_2$	272 000	194	328– 900
$PbS = Pb(l) + \frac{1}{2} S_2$	163 000	88.0	328–1113 m
$PbO \cdot B_2O_3 = PbO(l) + B_2O_3(l)$	102 500	33.0	885–1535
$PbO \cdot 2\ B_2O_3 = PbO(l) + 2\ B_2O_3(l)$	166 500	79.5	885–1535
$PbSO_4 = PbO + SO_2 + \frac{1}{2} O_2$	401 000	262	25–1090 m

Reaction	$\overline{\Delta H^0}$ (joule)	$\overline{\Delta S^0}$ (joule)	Range (°C)
$Cu = Cu(l)$	13 050	9.62	1085 m
$Cu(l) = Cu(g)$	308 200	108.9	1085–2570 b
$Cu_2O = Cu_2O(l)$	56 820	37.66	1244 m
$Cu_2O = 2\ Cu + \frac{1}{2} O_2$	168 400	71.25	25–1085
$Cu_2O(l) = 2\ Cu(l) + \frac{1}{2} O_2$	119 000	39.5	1236–2000
$CuO = Cu + \frac{1}{2} O_2$	152 300	85.4	25–1085
$Cu_2S_\gamma = 2\ Cu + \frac{1}{2} S_2$	140 700	43.3	25– 435
$Cu_2S_\beta = 2\ Cu + \frac{1}{2} S_2$	132 000	30.8	435–1129 m
$Cu_2S = Cu_2S(l)$	9000	6.40	1129 m
$Cu_{1.737}S_\beta = 1.738\ Cu + \frac{1}{2} S_2$	113 600	26.6	435– 620
$CuS = Cu + \frac{1}{2} S_2$	115 600	76.0	25– 430

Reaction	$\overline{\Delta H^0}$ (joule)	$\overline{\Delta S^0}$ (joule)	Range (°C)
$CuFeS_2 = Cu + Fe + S_2$	278 600	115	557– 700
$Cu_2O \cdot Fe_2O_3 = Cu_2O + Fe_2O_3$	37 700	19.0	25–1100
$CuSO_4 = \frac{1}{2} CuO \cdot CuSO_4 + \frac{1}{2} SO_2 + \frac{1}{4} O_2$	152 600	136	400– 800
$CuO \cdot CuSO_4 = 2\ CuO + SO_2 + \frac{1}{2} O_2$	297 000	250	500– 900
$Fe_\delta = Fe(l)$	13 800	7.61	1536 m
$Fe(l) = Fe(g)$	363 600	116.0	1536–2860 b
$Fe_{0.947}O = Fe_{0.947}O(l)$	31 340	19.0	1370 m
$Fe_{0.947}O = 0.947\ Fe + \frac{1}{2} O_2$	263 700	64.4	25–1370 m
$FeO(l) = Fe(l) + \frac{1}{2} O_2$	256 000	54.7	1371–2000
$Fe_3O_4 = 3\ Fe + 2\ O_2$	1 100 000	307	25–1597 m
$Fe_2O_3 = 2\ Fe + \frac{3}{2} O_2$	814 000	251	25–1500
$FeS = Fe_\gamma + \frac{1}{2} S_2$	164 000	61.0	988–1190 m
$FeS_2 = FeS + \frac{1}{2} S_2$	182 000	188	630– 760
$Fe_2(SO_4)_3 = Fe_2O_3 + 3\ SO_2 + \frac{3}{2} O_2$	772 000	724	400– 800
$Fe_2(SO_4)_3 = 2\ FeSO_4 + SO_2 + O_2$	396 000	352	430– 630
$FeSO_4 = \frac{1}{2} Fe_2O_3 + SO_2 + \frac{1}{4} O_2$	203 500	202.3	500– 630
$2\ FeO \cdot SiO_2 = 2\ FeO \cdot SiO_2(l)$	92 050	61.7	1220 m
$2\ FeO \cdot SiO_2 = 2\ FeO + SiO_2$	36 200	21.0	25–1220 m
$Zn = Zn(l)$	7320	10.6	420 m
$Zn(l) = Zn(g)$	118 000	100.3	420– 907 b
$ZnO = Zn(g) + \frac{1}{2} O_2$	460 240	190.4	907–1700
$ZnS = Zn(l) + \frac{1}{2} S_2$	278 000	108	420– 907
$ZnS(g) = Zn(g) + \frac{1}{2} S_2$	−5020	30.5	1182 b–1700
$ZnO \cdot Fe_2O_3 = ZnO + Fe_2O_3$	9620	3.8	25– 700
$ZnSO_4 = ZnO + SO_2 + \frac{1}{2} O_2$	328 000	267	25– 700

Reaction	$\overline{\Delta H^0}$ (joule)	$\overline{\Delta S^0}$ (joule)	Range (°C)
$Mg = Mg(l)$	8960	9.71	650 m
$Mg(l) = Mg(g)$	129 600	95.1	650–1093 b
$MgSO_4 = MgO + SO_2 + \frac{1}{2} O_2$	371 000	261	670–1050
$2\ MgO \cdot SiO_2 = 2\ MgO \cdot SiO_2(l)$	71 100	32.6	1898 m
$2\ MgO \cdot SiO_2 = 2\ MgO + SiO_2$	67 200	4.31	25–1898 m
$MgO \cdot SiO_2 = MgO \cdot SiO_2(l)$	75 300	40.6	1577 m
$MgO \cdot SiO_2 = MgO + SiO_2$	41 100	6.1	25–1577 m
$MgO = Mg + \frac{1}{2} O_2$	601 000	107.6	25– 650
$MgO = Mg(g) + \frac{1}{2} O_2$	730 000	204	1090–2000
$MgS = Mg + \frac{1}{2} S_2$	410 000	94.4	25– 650
$MgS = Mg(g) + \frac{1}{2} S_2$	540 000	193	1090–1700
$MgO \cdot Al_2O_3 = MgO + Al_2O_3$	35 600	−2.09	25–1400
$MgCO_3 = MgO + CO_2$	116 000	173.4	25– 402 d

APPENDIX 3
LAMPIRAN 3

Summary of Free Energy Equations[a]

$(\Delta G^{0} = a + bT \log T + cT)$

Reaction	a	b	c	Range (°K)	Accuracy
$Ag_2SO_4(l) = 2\,Ag(c) + SO_2 + O_2$	96,640	30.49	−162.44	930 to 1234	500
$\frac{1}{3}Al_2(SO_4)_3 = \frac{1}{3}Al_2O_3(\alpha) + SO_3$	47,090	9.25	−73.51	600 to 1100	500
$\frac{1}{3}Al_2(SO_4)_3 = \frac{1}{3}Al_2O_3(\gamma) + SO_3$	48,670	—	−42.52	700 to 1100	2000
$BeSO_4(\gamma) = BeO + SO_3$	50,180	23.03	−114.14	900 to 1100	500
$CaSO_4 = CaO + SO_2 + \frac{1}{2}O_2$	136,830	41.61	−206.73	1100 to 1638	700
$\frac{3}{2}CdSO_4 = \frac{1}{2}(CdSO_4\cdot 2\,CdO) + SO_3$	38,700	—	−22.0	1100 to 1273	2000
$\frac{1}{3}Ce_2(SO_4)_3 = \frac{2}{3}CeO_2 + SO_2 + \frac{1}{3}O_2$	63,000	—	−50.97	900 to 1200	500
$CoSO_4 = CoO + SO_3$	69,230	27.63	−137.18	890 to 1250	500
$CoSO_4 = \frac{1}{3}Co_3O_4 + SO_2 + \frac{1}{3}O_2$	77,250	32.24	−160.62	1000 to 1100	500
$2\,CuSO_4 = CuO\cdot CuSO_4 + SO_3$	51,780	5.16	−60.60	700 to 1100	500
$CuO\cdot CuSO_4 = 2\,CuO + SO_3$	52,030	5.16	−57.59	800 to 1200	500
$\frac{1}{2}Er_2(SO_4)_3 = \frac{1}{2}(Er_2O_3\cdot SO_3) + SO_3$	57,810	—	−38.56	1000 to 1300	500
$\frac{1}{3}Fe_2(SO_4)_3 = \frac{1}{3}Fe_2O_3 + SO_3$	48,590	8.151	−71.03	700 to 1000	500
$\frac{1}{2}La_2(SO_4)_3 = \frac{1}{2}(La_2O_3\cdot SO_3) + SO_3$	60,480	—	−38.82	1000 to 1300	500
$\frac{1}{2}Lu_2(SO_4)_3 = \frac{1}{2}(Lu_2O_3\cdot SO_3) + SO_3$	57,840	—	−37.71	1000 to 1300	500
$MgSO_4 = MgO + SO_3$	78,560	16.58	−100.69	1000 to 1428	1000
$MnSO_4 = \frac{1}{3}Mn_3O_4 + SO_2 + \frac{1}{3}O_2$	75,890	14.90	−106.69	700 to 1100	500
$MnSO_4(c,l) = \frac{1}{3}Mn_3O_4(?) + SO_2 + \frac{1}{3}O_2$	63,510	—	−47.25	1100 to 1300	?
$Na_2SO_4(c,I) = Na_2O + SO_3$	137,480	14.90	−83.76	600 to 1157	3000
$\frac{1}{2}Nd_2(SO_4)_3 = \frac{1}{2}(Nd_2O_3\cdot SO_3) + SO_3$	56,160	—	−38.03	1000 to 1300	500
$NiSO_4 = NiO + SO_3$	59,290	—	−47.52	900 to 1200	500
$2PbSO_4 = PbSO_4\cdot PbO + SO_3$	74,000	16.81	−97.40	800 to 1139	500
$3(PbSO_4\cdot PbO) = 2(PbSO_4\cdot 2PbO) + SO_3$	87,920	16.81	−104.08	889 to 1223	500
$\frac{5}{3}(PbSO_4\cdot PbO) = \frac{2}{3}(PbSO_4\cdot 4PbO) + SO_3$	80,570	16.81	−95.81	800 to 889	500
$\frac{5}{2}(PbSO_4\cdot 2PbO) = \frac{3}{2}(PbSO_4\cdot 4PbO) + SO_3$	71,380	16.81	−85.47	889 to 1168	500
$PbSO_4\cdot 4PbO = 5PbO + SO_3$	72,870	—	−30.70	800 to 1108	500
$\frac{1}{2}Pr_2(SO_4)_3 = \frac{1}{2}(Pr_2O_3\cdot SO_3) + SO_3$	56,600	—	−37.99	1000 to 1300	500
$\frac{1}{3}Sc_2(SO_4)_3 = \frac{1}{3}Sc_2O_3 + SO_3$	60,980	—	−44.82	1000 to 1300	500
$\frac{1}{2}Sm_2(SO_4)_3 = \frac{1}{2}(Sm_2O_3\cdot SO_3) + SO_3$	56,190	—	−38.82	1000 to 1300	500
$\frac{1}{2}Th(SO_4)_2 = \frac{1}{2}ThO_2 + SO_3$	70,290	25.33	−133.60	700 to 1100	500
$2\,VOSO_4 = V_2O_5 + SO_2 + SO_3$	85,470	18.42	−150.83	700 to 900	500
$\frac{1}{2}Y_2(SO_4)_3 = \frac{1}{2}(Y_2O_3\cdot SO_3) + SO_3$	60,070	—	−39.25	1000 to 1300	500
$\frac{1}{2}Yb_2(SO_4)_3 = \frac{1}{2}(Yb_2O_3\cdot SO_3) + SO_3$	57,150	—	−37.48	1000 to 1300	500