10/14/2019 (Please not two enclosures, JANAF Table and Ellingham

Practice HW2.2-Processing

Consider the following reaction in equilibrium

$$Si + O_2 = SiO_2(quartz) \quad (1)$$

The change in Free Energy for this reaction is

$$\Delta G_{JANAF} = G_{SiO_2(quartz)} - G_{O_2} - G_{Si}$$

Since O_2 and Si are in their standard states we have that

$$\Delta G_{JANAF} = \Delta G_{SiO_2(quartz)} \quad (2)$$

Note the emphasis on quartz. The Free Energy depends not only on the species but also on the phase. Thus the free energy for molten quartz or silica glass will be different from that of quartz. Furthermore there is a phase transformation in quartz at 673°C from a to b quartz so that there is a change in the free energy behavior at the this temperature for SiO_2. (Note that at the transition temperature both phases have the same free energy since they are in equilibrium; therefore the slope of the G vs. T curve changes at this temperature but from the same point).

The equilibrium in Eq. (1) is given by the balance of chemical potentials

$$\mu_{Si} + \mu_{O_2} = \mu_{SiO_2} \quad (3)$$

where

$$\mu_{SiO_2} = \mu^o_{SiO_2} + RT\ell n(a_{SiO_2}) \quad (4)$$

where

$\mu^o_{SiO_2}$ is the standard state.

Writing similar equations for μ_{Si} and for μ_{O_2} into Eq. (3) we obtain

$$(\mu_{SiO_2} - \mu_{Si} - \mu_{O_2}) + RT\ell n \frac{a_{SiO_2}}{a_{Si} a_{p_{O_2}}} = 0 \qquad (5)$$

JANAF Tables gives the values for

(6)

Combining (5) and (6)

$$\Delta G_{SiO_2(quartz)}(T) - RT\ell n(p_{O_2}) = 0 \qquad (6)$$

where $a_{Si} = 1, a_{SiO_2} = 1, \text{and } a_{O_2} = p_{O_2}$

Exercise:

Show how Eq. (6) leads to the line for SiO_2 Ellingham Diagram.

Exercise:

The temperature dependent values for $\Delta G_{SiO_2}(quartz)$ are given in the attached sheet drawn from the JANAF Tables.

Pick a temperature and show that the calculation of equilibrium p_{O_2} from Eq. (6) is consistent with the “quick” reading from the Ellingham diagram.

LIQUID $M_r = 64.0843$

$\Delta_f H°(0\ K) = -897.756\ kJ\ mol^{-1}$

$\Delta_f H°(298.15\ K) = -902.661\ kJ\ mol^{-1}$

$\Delta_{fus}H° = 9.581 \pm 2.1\ kJ\ mol^{-1}$

d from that of quartz using $\Delta_s H°(970\ K) = 1.45 \pm 0.15$ kcal mol^{-1} for high quartz A an oxide melt. This value reduces to $\Delta_f H°(298.15\ K) = 1.96$ kcal mol^{-1} for low cal mol^{-1} with other calorimetric data summarized below. Earlier results were

Reaction	T/K	$\Delta_r H°(T)$ kcal mol^{-1}	$\Delta_r H°(298.15\ K)$ kcal mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal mol^{-1}
A	970	1.45±0.15	1.96	-215.74
B	298	1.78±0.46	1.78	-215.92
A	298-348	-	2.18±0.05	-215.52
A	300	2.27±0.2	2.27	-215.43

SiO_2(quartz, low or high) + $SiO_2(\ell)$

$SiO_2(\ell) + 2\ F_2(g) + SiF_4(g) + O_2(g)$

(5) and Westrum (6) for samples annealed at 1100 and 1070°C, respectively. Data ge 60-160 K and at 300 K but are in agreement elsewhere. The entropy is 0001 cal $K^{-1}mol^{-1}$ and $S°(0\ K) = 1.098$ cal $K^{-1}\ mol^{-1}$. $C_p°$ data (6) for a different by <0.04 cal $K^{-1}\ mol^{-1}$. Earlier data were reviewed by Kelley (8). The residual $S°(1996;0\ K) = 41.258 - 40.160 = 1.098$ cal $K^{-1}\ mol^{-1}$, where 40.160 is obtained um of $\Delta_{fus}S° = 1.14$ cal $K^{-1}\ mol^{-1}$ and $S°(1996\ K) = 40.111$ cal $K^{-1}\ mol^{-1}$ for high 3 cal $K^{-1}\ mol^{-1}$, primarily from the uncertainty in $\Delta_{fus}H°$. etric data of Moser (9) up to 900 K. Enthalpy data of White (10) and Fischer 1500 K is derived from enthalpy data of Southard (12) and White (10). Maximum this range is 0.5%. Enthalpy data of Egan (13) and Kelley (14) deviate from the 1500 K, although large positive deviations appear at lower temperatures. ows a rapid, sigmoidal rise which is suggested by the enthalpy data of Wietzel n region in which $C_p°$ rises to that of the stable liquid. $C_p°$ above 1700 K is -atom^{-1}. This value is consistent with the enthalpy data (15) and with $_2SiO_3$.

96 ± 5 K, while the metastable melting point of high quartz is 1696 ± 50 K. and high cristobalite at T_{fus}. Values ranging from 1.8 to 3.8 kcal mol^{-1} have e diagrams (1).

Jr., Geochim. Cosmochim. Acta, to be published. $\Delta_{sol}H°$.
W. N. Hubbard, J. Phys. Chem. 67, 815 (1963). $\Delta_f H°$.
physical Laboratory, No. 1215, 69 (1953). $\Delta_{sol}H°$.
32, 327 (1959). $\Delta_{sol}H°$.
on and B. P. Stoicheff, Phys. Chem. Solids 12, 53 (1959). $C_p°$ (2.3-19 K).
personal communication, May 19, 1960. $C_p°$(5-300 K)
1967). $C_p°$(60-300 K) measured by Turdakin.
s Bull. 592, 1961.
-936 K).
933). enthalpy (573-1173 K).
1931). enthalpy (321-577 K).
(1941). enthalpy (508-1522 K).
imore, J. Amer. Chem. Soc. 72, 2418 (1950). enthalpy (763-1470 K).
. U. S. Bur. Mines Tech. Paper 686, 1946. enthalpy (400-1500 K).
321). H°(373-1973).

Silicon Oxide (SiO_2) $O_2Si_1(l)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = p° = 0.1 MPa

T/K	$C_p°$ (J $K^{-1}mol^{-1}$)	S° (J $K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ (J $K^{-1}mol^{-1}$)	$H°-H°(T_r)$ (kJ mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f G°$ (kJ mol^{-1})	Log K_f
0	0.000	4.594	INFINITE	-6.896	-897.756	-897.756	INFINITE
100	16.154	15.983	78.952	-6.297	-900.228	-884.112	461.813
200	32.736	33.602	51.618	-3.803	-901.824	-867.314	226.519
298.15	44.183	47.838	47.838	0.000	-902.661	-850.175	148.947
300	44.367	48.202	47.929	0.082	-902.671	-849.850	147.972
400	52.518	62.156	49.776	4.952	-902.893	-832.194	108.673
500	58.082	74.510	53.513	10.499	-902.884	-814.537	85.094
600	62.045	85.468	57.943	16.515	-902.203	-796.949	69.381
700	64.973	95.283	62.587	22.873	-901.548	-779.457	58.164
800	67.208	104.081	67.233	29.486	-900.780	-762.067	49.758
900	68.956	112.112	71.780	36.298	-899.936	-744.777	43.228
1000	70.350	119.452	76.186	43.266	-899.041	-727.585	38.005
1100	71.475	126.211	80.430	50.359	-898.113	-710.484	33.738
1200	72.396	132.471	84.509	57.554	-897.165	-693.469	30.186
1300	73.157	138.298	88.425	64.832	-896.211	-676.533	27.183
1400	73.848	143.743	92.184	72.183	-895.258	-659.670	24.613
1500	74.475	148.852	95.794	79.587	-894.317	-642.876	22.387
1600	80.040	153.767	99.263	87.206	-893.332	-626.148	20.442
1696.000	85.772	158.655	102.487	95.261	-------- II <--> LIQUID --------		
1700	85.772	158.857	102.619	95.604	-941.610	-609.059	18.714
1800	85.772	163.759	105.881	104.181	-939.468	-589.559	17.109
1900	85.772	168.397	109.050	112.759	-937.350	-570.178	15.675
2000	85.772	172.796	112.128	121.336	-935.255	-550.907	14.388
2100	85.772	176.981	115.118	129.913	-933.183	-531.741	13.226
2200	85.772	180.971	118.021	138.490	-931.133	-512.672	12.172
2300	85.772	184.784	120.842	147.067	-929.106	-493.697	11.212
2400	85.772	188.434	123.582	155.645	-927.102	-474.809	10.334
2500	85.772	191.936	126.247	164.222	-925.119	-456.004	9.528
2600	85.772	195.300	128.839	172.799	-923.158	-437.279	8.785
2700	85.772	198.537	131.360	181.376	-921.217	-418.628	8.099
2800	85.772	201.656	133.816	189.953	-919.297	-400.048	7.463
2900	85.772	204.666	136.207	198.531	-917.397	-381.538	6.872
3000	85.772	207.574	138.538	207.108	-915.517	-363.092	6.322
3100	85.772	210.386	140.810	215.685	-913.655	-344.708	5.808
3200	85.772	213.109	143.027	224.262	-911.811	-326.385	5.328
3300	85.772	215.749	145.191	232.839	-909.985	-308.119	4.877
3400	85.772	218.309	147.304	241.417	-908.175	-289.907	4.454
3500	85.772	220.796	149.369	249.994	-906.381	-271.749	4.056
3600	85.772	223.212	151.387	258.571	-1288.754	-243.181	3.528
3700	85.772	225.562	153.360	267.148	-1286.577	-214.168	3.024
3800	85.772	227.849	155.290	275.725	-1284.416	-185.212	2.546
3900	85.772	230.077	157.179	284.303	-1282.269	-156.313	2.094
4000	85.772	232.249	159.029	292.880	-1280.137	-127.470	1.665
4100	85.772	234.367	160.841	301.457	-1278.019	-98.680	1.257
4200	85.772	236.434	162.616	310.034	-1275.914	-69.941	0.870
4300	85.772	238.452	164.356	318.611	-1273.822	-41.252	0.501
4400	85.772	240.424	166.063	327.189	-1271.742	-12.612	0.150
4500	85.772	242.351	167.737	335.766	-1269.674	15.981	-0.186

PREVIOUS: December 1982 CURRENT: June 1987

Silicon Oxide (SiO_2) $O_2Si_1(l)$

CRYSTAL-CRYSTAL-CRYSTAL-LIQUID $M_r = 60.0843$

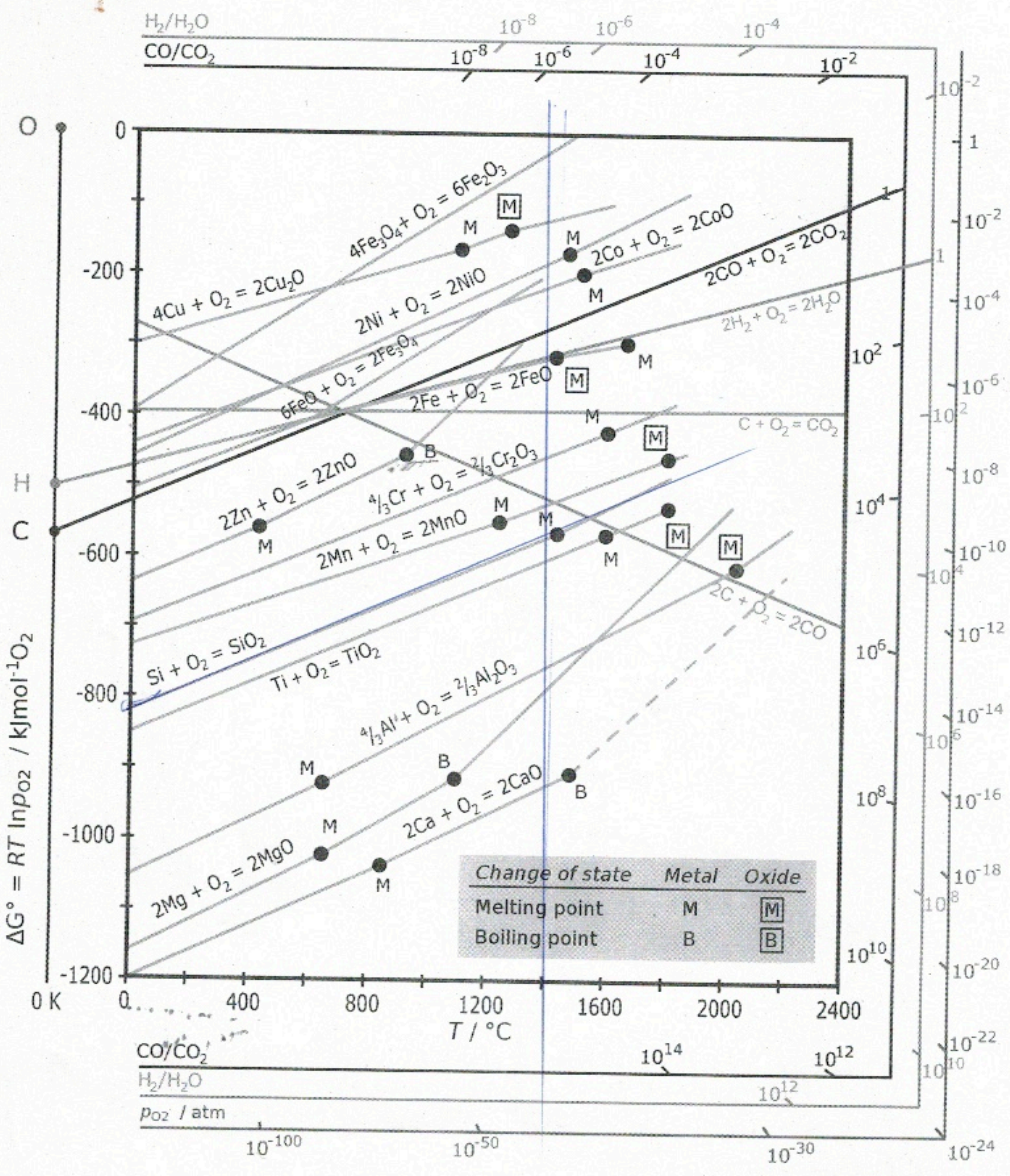
347 K crystal, low quartz (trigonal)
079 K crystal, high quartz (hexagonal)
096 K crystal, high crystabolite
096 K liquid

to the individual tables for details.

Silicon Oxide (SiO_2) $O_2Si_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = p° = 0.1 MPa

T/K	$C_p°$ (J $K^{-1}mol^{-1}$)	S° (J $K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ (J $K^{-1}mol^{-1}$)	$H°-H°(T_r)$ (kJ mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f G°$ (kJ mol^{-1})	Log K_f
0	0.000	0.000	INFINITE	-6.916	-905.872	-905.872	INFINITE
100	15.665	9.694	72.496	-6.280	-908.406	-891.662	465.758
200	32.639	28.067	45.187	-3.820	-910.036	-874.223	228.321
298.15	44.589	41.463	41.463	0.000	-910.857	-856.443	150.045
300	44.789	41.740	41.464	0.083	-910.866	-856.106	149.061
400	53.130	55.874	43.333	5.017	-911.024	-837.812	109.407
500	59.643	68.499	47.127	10.686	-910.692	-819.538	85.617
600	64.417	79.809	51.848	16.898	-910.017	-801.368	69.765
700	68.768	90.063	56.414	23.551	-909.062	-783.331	58.453
800	73.701	99.555	61.220	30.668	-907.794	-765.452	49.879
847.000	76.509	103.840	63.467	34.198		I <--> II	
847.000	67.417	104.700	63.467	34.921		TRANSITION	
900	67.948	108.807	66.017	38.512	-905.918	-747.785	43.400


H₂/H₂O
CO/CO₂
O
H
C
0 K
ΔG° = RT lnp_{O_2} / kJmol⁻¹O₂
T / °C
p_{O_2} / atm
4Fe₃O₄ + O₂ = 6Fe₂O₃
4Cu + O₂ = 2Cu₂O
2Co + O₂ = 2CoO
2Ni + O₂ = 2NiO
2CO + O₂ = 2CO₂
2H₂ + O₂ = 2H₂O
6FeO + O₂ = 2Fe₃O₄
2Fe + O₂ = 2FeO
C + O₂ = CO₂
2Zn + O₂ = 2ZnO
4/3Cr + O₂ = 2/3Cr₂O₃
2Mn + O₂ = 2MnO
2C + O₂ = 2CO
Si + O₂ = SiO₂
Ti + O₂ = TiO₂
4/3Al + O₂ = 2/3Al₂O₃
2Ca + O₂ = 2CaO
2Mg + O₂ = 2MgO
Change of state | Metal | Oxide
Melting point | M | [M]
Boiling point | B | [B]