HW Exam on Topics Related to REDOX

Due Monday, Nov 22, 2021

1.

In early lectures we developed equation (16) for the reaction given in Eq. (17)

$$2\Delta G^0_{Cu_2O} + RT\ell n \frac{a^2_{Cu_2O}}{a^4_{Cu_2} a_{O_2}} = 0 \qquad (16)$$

Note that Eq. (16) can be written by inspection of the reaction

$$4Cu + O_2 = 2Cu_2O \qquad (17)$$

Note that Eq. (16) was derived assuming that Eq. (17) is held is equilibrium.

Write down, by inspection the equation that will be the equivalent of Eq. (17), for the following reaction

$$n_A A + n_O O_2 = A_{n_A} O_{2n_O}$$

where A is a solid metal and O_2 is oxygen gas.

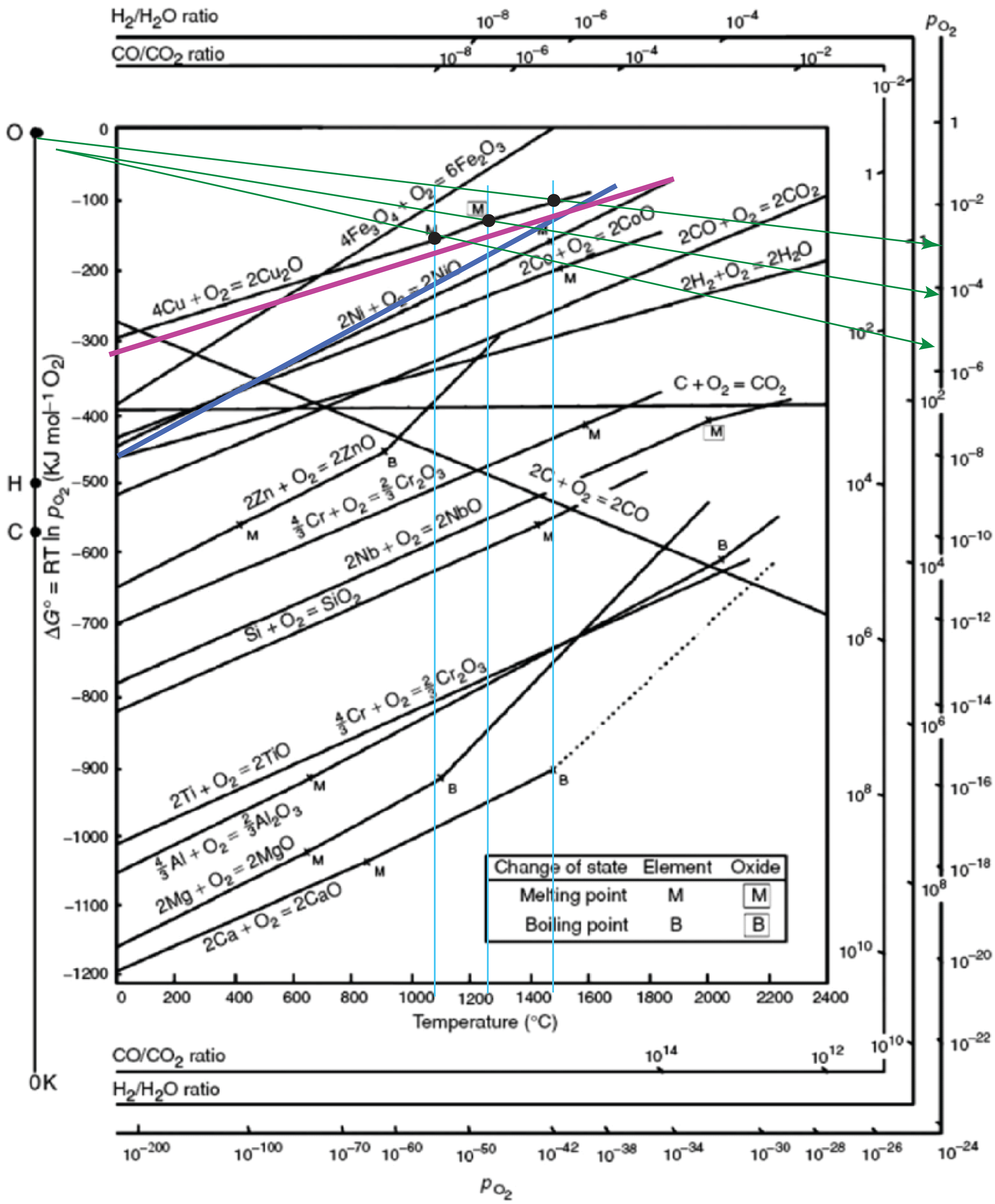
2.

In class we considered internal oxidation of small amount of silicon in a copper-silicon alloy when surrounded by a powder of Cu_2O.

(i) Write down the REDOX reaction that leads to the formation of silica particle within the copper matrix. Explain the nature of the reduction and the oxidation in this reaction.

(ii) Why do the silica particles from within the copper matrix rather then on the surface of the copper specimen.

(iii) Now consider that some nickel is further added to the alloy (in addition to the silicon). What will be the outcome when this alloy is surrounded in powder of Cu_2O and held at 1000 K? (Please consult the Ellingham diagram on the next page)



H_2/H_2O ratio
CO/CO_2 ratio
p_{O_2}
O
H
C
0K
$\Delta G^\circ = RT \ln p_{O_2}$ (KJ mol^{-1} O_2)
Temperature (°C)
$4Fe_3O_4 + O_2 = 6Fe_2O_3$
$4Cu + O_2 = 2Cu_2O$
$2Ni + O_2 = 2NiO$
$2Co + O_2 = 2CoO$
$2CO + O_2 = 2CO_2$
$2H_2 + O_2 = 2H_2O$
$C + O_2 = CO_2$
$2C + O_2 = 2CO$
$2Zn + O_2 = 2ZnO$
$\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$
$2Nb + O_2 = 2NbO$
$Si + O_2 = SiO_2$
$2Ti + O_2 = 2TiO$
$\frac{4}{3}Al + O_2 = \frac{2}{3}Al_2O_3$
$2Mg + O_2 = 2MgO$
$2Ca + O_2 = 2CaO$
Change of state
Element
Oxide
Melting point
Boiling point
M
B

3.

In class we have considered the reaction $4Cu+O_2 = 2Cu_2O$ when the copper is pure, that is its activity is equal to unity, $a_{Cu}=1$.

Now assume the copper is an alloy such that the activity of copper is reduced to $a_{Cu}=0.5$.

In the notes we used the Ellingham diagrams to find the equilibrium vapor pressure of p_{O_2} at 1000 K, for the case of pure copper. The pure copper reaction is shown in the Ellingham diagram on the following page.

On the Ellingham diagram show how the line for $4Cu+O_2 = 2Cu_2O$ will shift when the copper is an alloy with an activity of $a_{Cu}=1$. Draw this new line backed up by quantitative analysis.

Now calculate the equilibrium vapor pressure of oxygen at 1000 K. Is the vapor pressure higher or lower than for the case of pure copper.

Give physical arguments for your answer just above.

4.

Why are all the lines for different oxidation reaction written with one molecule of oxygen?

5.

The line for aluminum oxide lies below the line for chromium oxide. Now consider two scenarios,

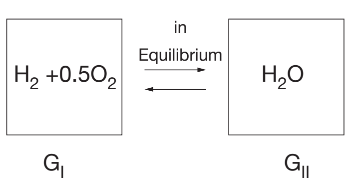
(i) A mixture of aluminum metal and chromium oxide held at 1400°C.

(ii) A mixture of chromium metal and aluminum oxide held at 1400°C.

Which of the above reaction will actually move forward, and why?

6.

Consider an equilibrium reaction among H_2, O_2, and $H_2O(g)$ where the sum of their partial pressures is equal to 1 bar.



The partial pressures are related to one another by

$$\Delta G^o_{H_2O} + RT\ell n\left(\frac{p_{H_2O}}{p_{H_2}p_{O_2}^{1/2}}\right) = 0$$

where ΔG_{H_2O} is the free energy of formation when the constiuents are in their standard state. The valuues as a function of temperature are given in the following table (https://janaf.nist.gov/tables/H-064.html)

	kJ·mol⁻¹
***T*/K**	**$\Delta_f G^\circ$**
0	-238.921
100	-236.584
200	-232.766
298.15	-228.582
300	-228.500
400	-223.901
500	-219.051
600	-214.007
700	-208.812
800	-203.496
900	-198.083
1000	-192.590
1100	-187.033
1200	-181.425

Consider a temperature to be 1000 K.

Make a log-log (to the base 10) plot of the following quantities:

x-axis $\frac{p_{H_2O}}{p_{H_2O}}$ and the y-axis is p_{O_2}.

7.

Write one page or less (in your own words), with no more than three equations, giving the (i)fundamental foundation for the construction of the Ellingham diagrams, and (ii) their application in understanding redox reactions (with an example if you wish).

8.

Derive the equation for "parabolic" oxidation of silicon

$$h^2 = 2k_p t$$

where "h" is the time dependent growth of the oxide layer on the surface of silicon, and k_p is the parabolic rate constant.

Express k_p in terms of coefficient of diffusion of oxygen through silicon oxide overgrowth.