

03D_REDOX Reaction

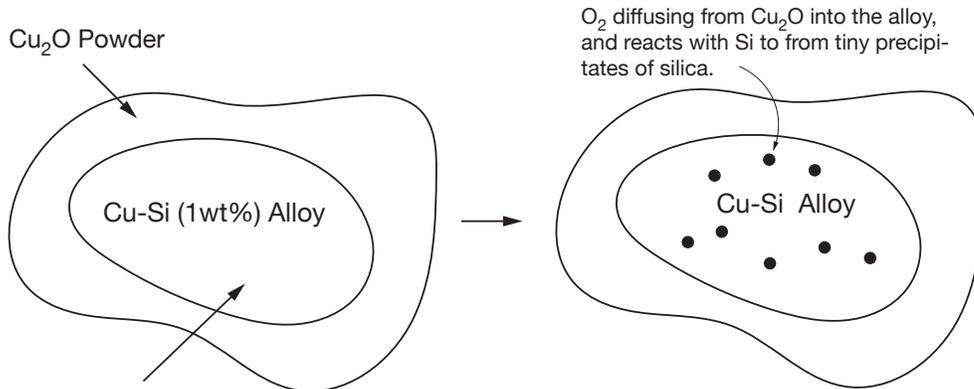
Problem Statement

We are asking whether or not the following reaction will occur, and if so in what temperature range



Note this is a REDOX reaction because

- Cu_2O is reduced to Cu
- while Si is oxidized to SiO_2



- The alloy is made by adding a pinch of silicon (about 1 wt%) to molten copper

Concepts

- Si is in the form of a dilute alloy in copper. It is atomically mixed with copper atoms and is dispersed randomly.
- Reaction in Eq. (1) can occur by the diffusion of oxygen into the copper and internal oxidation of silicon, or by the outward diffusion of Si from within to the surface. It so happens that the diffusion of oxygen is much faster than the diffusion of silicon in copper, therefore the redox reaction produces “internal oxidation”.
- The diffusion flux of oxygen is given the same equation that we used in the sintering problem, except here it is the chemical potential difference in oxygen that drives the oxygen flux,

$$J_{O_2} = \frac{x_{O_2} D_{O_2 \text{ in Cu}}}{\Omega_{Cu} k_B T} \frac{\Delta \mu_{O_2}}{L} \quad (2)$$

Here L is the distance from the surface to the silica particle within copper where silicon is oxidizing. Note the difference from the earlier equation used in sintering analysis, the presence of x_{O_2} , the (equilibrium) molar concentration of oxygen in copper. (Think about it: how can oxygen be transported if it does not dissolve in copper!!)

- All the parameters in Eq. (2) are known, except $\Delta \mu_{O_2}$, which is equal to the difference in the chemical potential of oxygen between the surface and at the surface of the silica particle within copper.

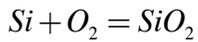
$$\Delta \mu_{O_2} = \mu_{O_2}^{surface} - \mu_{O_2}^{SiO_2/Cu} \quad (3)$$

These chemical potentials are determined by the following reactions held in equilibrium.

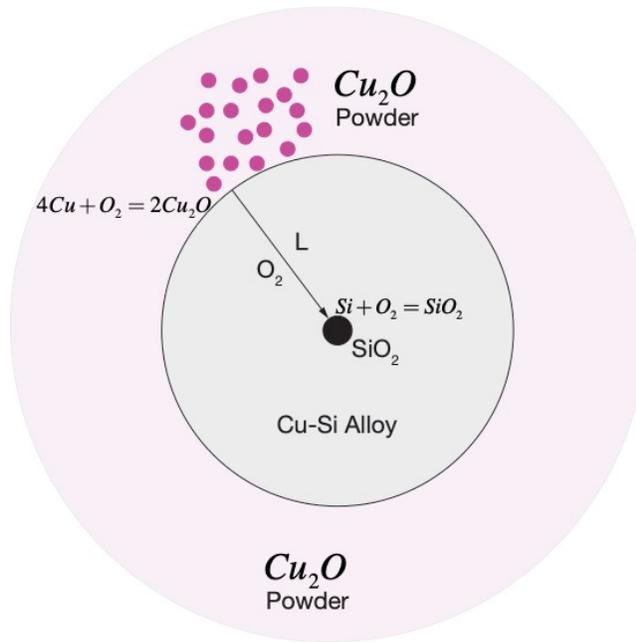
At the surface,



At the interface between the silica particle and the copper matrix,



(5)



Determination of the Chemical Potential of Oxygen

Recall that

$$\mu_{O_2} = \mu_{O_2}^{\circ} + RT \ln p_{O_2}$$

Where $\mu_{O_2}^{\circ}$ is the chemical potential of the standard state assumed to be 1 atm pressure. Therefore if p_{O_2} is measured in atmospheres then

$$\mu_{O_2} = RT \ln p_{O_2}$$

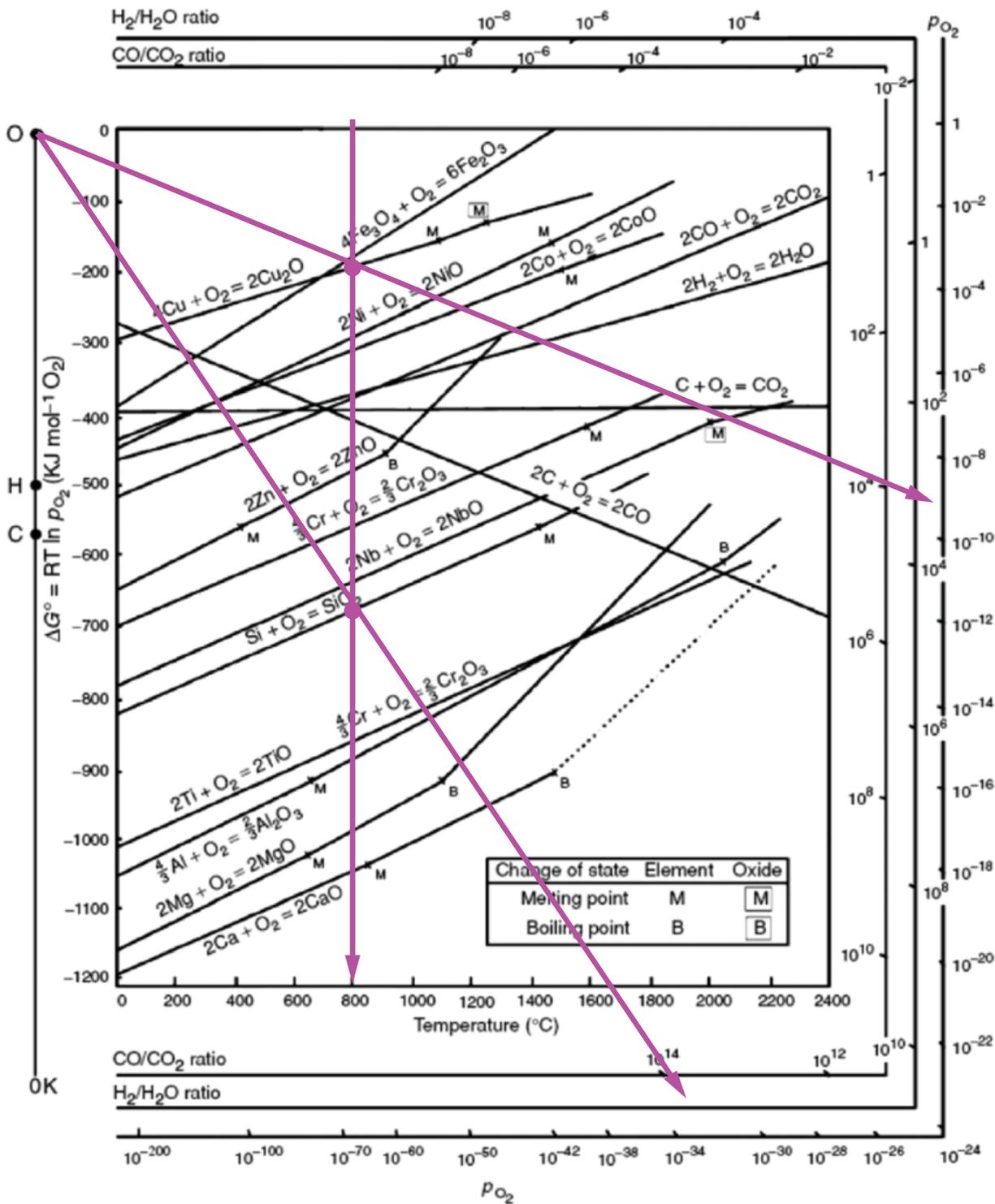
Recall the construction of the Ellingham diagram for example equilibrium condition for Eq. (4) is given by

$$2\Delta G_{Cu_2O}^{\circ} + RT \ln \frac{a_{Cu_2O}^2}{a_{Cu}^4 p_{O_2}} = 0$$

Since copper and cuprous oxide being present in their pure solid state are in their standard state hence their activities are equal to unity, the above equation reduces to.

$$2\Delta G_{Cu_2O}^{\circ} - RT \ln p_{O_2} = 0 \quad (6)$$

The Ellingham diagram gives the partial pressure of oxygen as a function of temperature which satisfies Eq. (6). We are now ready to write down the expressions for the chemical potentials of oxygen at the surface and at the silica/copper interface.



$$\mu_{O_2}^{surface}$$

We can read the partial pressure of oxygen which satisfies $4Cu + O_2 = 2Cu_2O$ in equilibrium from Ellingham at $800^\circ C$ as shown above

$$\mu_{O_2}^{surface} = RT \ln p_{O_2}^{surface} = RT \ln 10^{-9} = \frac{RT}{e}(-9) \quad (7)$$

$$\mu_{O_2}^{SiO_2/Cu}$$

Here we seek equilibrium in the equation $Si + O_2 = SiO_2$, so that

$$\Delta G_{SiO_2}^o + RT \ln \frac{a_{SiO_2}}{a_{Si} p_{O_2}^{SiO_2/Cu}} = 0$$

Here the activity of silica is unity since it exists in its pure state. However the activity of silicon is not unity since it exists as a “dilute” atomically mixed alloy with copper. The activity of Si is given by the molar concentration of Si in copper. Let us assume that the molar concentration is 0.01, then $a_{Si} = .01$. Therefore the equation just above becomes,

$$\Delta G_{SiO_2}^o - RT \ln a_{Si} = RT \ln p_{O_2}^{SiO_2/Cu} \quad (8)$$

Now, if the activity of silicon were to be equal to unity then the $p_{O_2}^{SiO_2/Cu}$ could have been read from Ellingham, and its value, as per this reading would be 10^{-33} atm. But with the activity of silicon being less than unity, we have that

$$\mu_{O_2}^{SiO_2/Cu} = RT \ln p_{O_2}^{SiO_2/Cu} = RT \ln 10^{-33} - RT \ln a_{Si} \quad (9)$$

Where the first term on the right is from Ellingham and the second from the activity of Si. Substituting for the activity of silicon Eq. (9) is equal to

$$\mu_{O_2}^{SiO_2/Cu} = \frac{RT}{e}(-33 + 2) = -31 \frac{RT}{e} \quad (10)$$

The Driving Force for Diffusion of Oxygen in Copper

Combining Eqs (3), (7) and (10), we have the final result

$$\Delta \mu_{O_2} = \mu_{O_2}^{surface} - \mu_{O_2}^{SiO_2/Cu} = \frac{22}{e} RT$$

Remember “e” is to convert \log_e into \log_{10} .

Substituting $R=8.31 \text{ J mol}^{-1}$, and $T=800+273 \text{ K}$, we have that

The energy of the redox reaction is 85.3 kJ mol^{-1} . This is the thermodynamic force that drives the reaction.

$$\Delta \mu_{O_2} = 85.3 \text{ kJ mol}^{-1}.$$

We may now calculate the rate of growth for the silica particles from the flux equation

$$J_{O_2} = \frac{x_{O_2} D_{O_2 in Cu}}{\Omega_{Cu} k_B T} \frac{\Delta \mu_{O_2}}{L}$$

See if you can calculate (even very approximately) the time it would take for a silica particle having a diameter of 100 nm to grow at a distance of 10 μm from the surface.

For the diffusion coefficient of oxygen in copper search the literature in Google Scholar. Here is one of the results,

J. Chem. Phys. **9**, 742 (1941); <https://doi.org/10.1063/1.1750834>

ABSTRACT

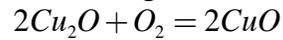
Diffusion equations derived from Fick's law are discussed and applied to experimental data in the literature on the diffusion of oxygen in copper and on reaction rates for chemical reactions in the solid phase. Previous limitations on the applicability of the formulae are removed by the use of a simple graphical method so that the theory can be applied to data to which it was previously inapplicable. It is pointed out that the exact solution to Fick's law obtained is equivalent to the parabolic law in the early stages of the diffusion process. The activation energy for the diffusion of oxygen in copper is found to be 50.5 kcal. per g-atom.

The activation energy is given above to be $50.5 \times 4.18 \text{ kJ mol}^{-1}$. The pre-exponential for the diffusion coefficient may be assumed to be equal to that for volume self diffusion in copper (as we did before). Alternatively you can pull up the paper given by the link above which gives the actual data for the diffusion of oxygen in copper (see Fig. 4) in that paper.

A further question:

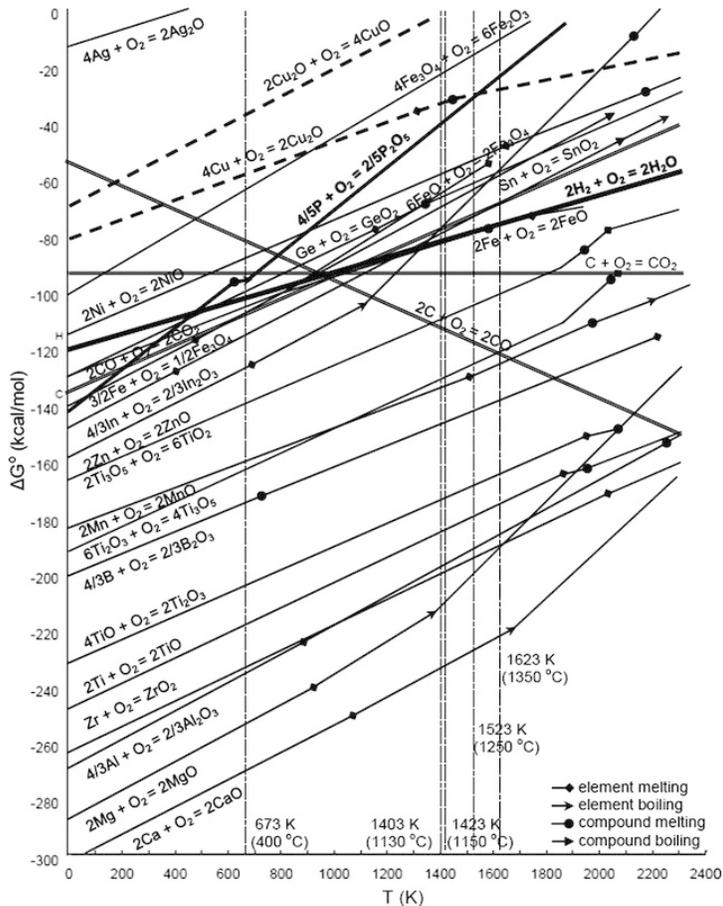
What will happen if the alloy was directly heated in air?

The oxygen activity in air will react first with copper to form the oxide. The oxide will continue to grow and forming a thick layer. Therefore we shall be oxidizing copper rather than the silicon atoms within the copper alloy. Ellingham diagrams will inform you whether you will form Cu_2O or CuO . The answer to this question comes from considering the reaction



Again we can quickly look up the partial pressure of oxygen for Cu_2O and CuO : whichever has the lower partial pressure will oxidize.

The Ellingham diagram below gives the line for the reaction $2\text{Cu}_2\text{O} + \text{O}_2 = 2\text{CuO}$. You can read the oxygen pressure where this reaction is in equilibrium. If the pressure is higher then the reaction will move to the right



HW Question: from the data given in the diagram on the left can you draw the line for the reaction:

