3E: CO/CO_2 Ratio to Control Oxygen Activity in Ellingham

The Problem Statement

The equilibrium vapor pressure for oxygen for the reaction $Si + O_2 = SiO_2$ at intermediate temperatures can be very low, for example 10^{-17}atm which cannot be experimentally controlled. Instead such low vapor pressures of oxygen can be obtained by using mixtures of CO and CO_2. The problem then is to calculate what $\frac{p_{CO}}{p_{CO_2}}$ will yield a specific value of oxygen activity at a specific temperature. For example on the right let us say we wish to obtain $p_{O_2} = 10^{-14}\, atm$ at a temperature of 1800 °C with mixtures of CO and CO_2. Here is the analysis for that.

Method

Consider the reaction

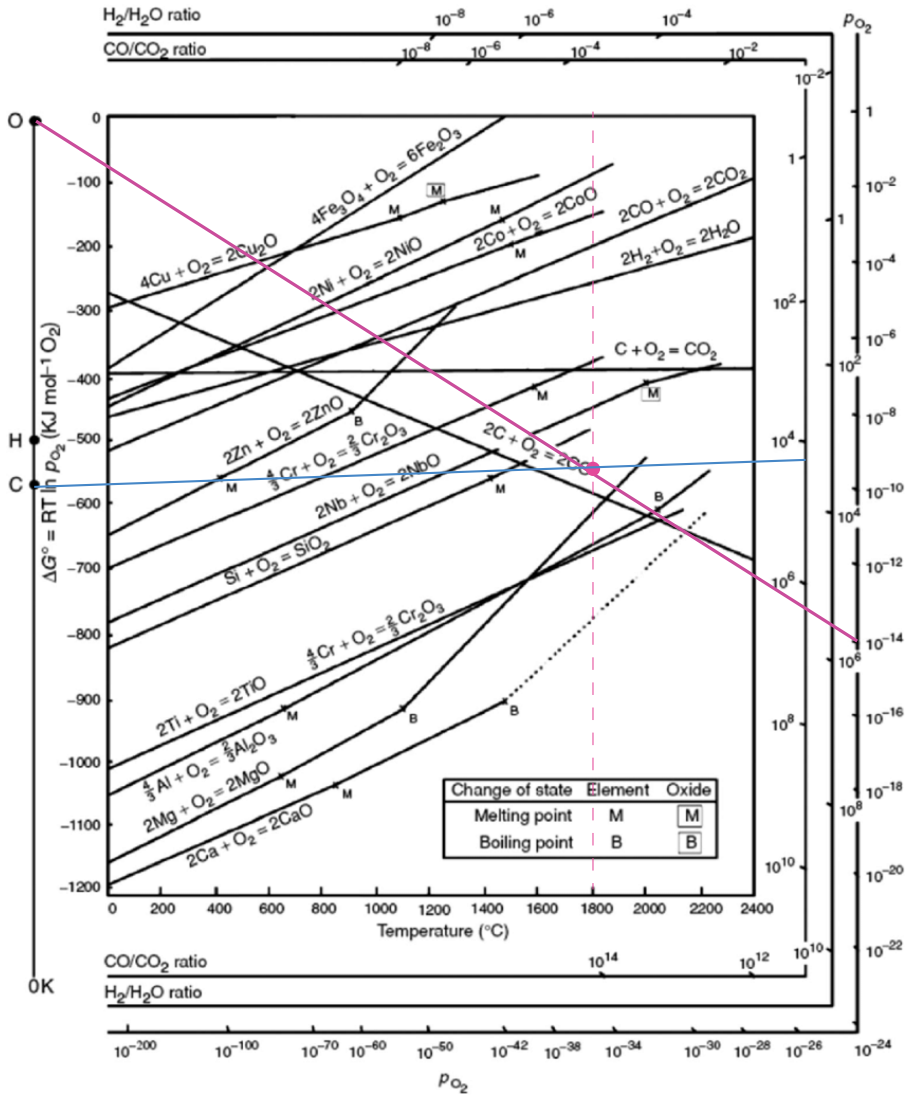
$$2CO + O_2 = 2CO_2 \qquad \text{(i)}$$

in equilibrium. Written in terms of the free energy of formation the equilibrium is prescribed by

$$2\Delta G^0_{CO_2} - 2\Delta G^0_{CO} + RT \ln \frac{p^2_{CO_2}}{p^2_{CO} p_{O_2}} = 0 \quad (2)$$

(to understand Eq. 2 recall that we wrote the equilibrium for the Si + O_2 = SiO_2 in the form $\Delta G^o_{SiO_2} + RT \ln \frac{a_{SiO_2}}{a_{Si} p_{O_2}} = 0$)

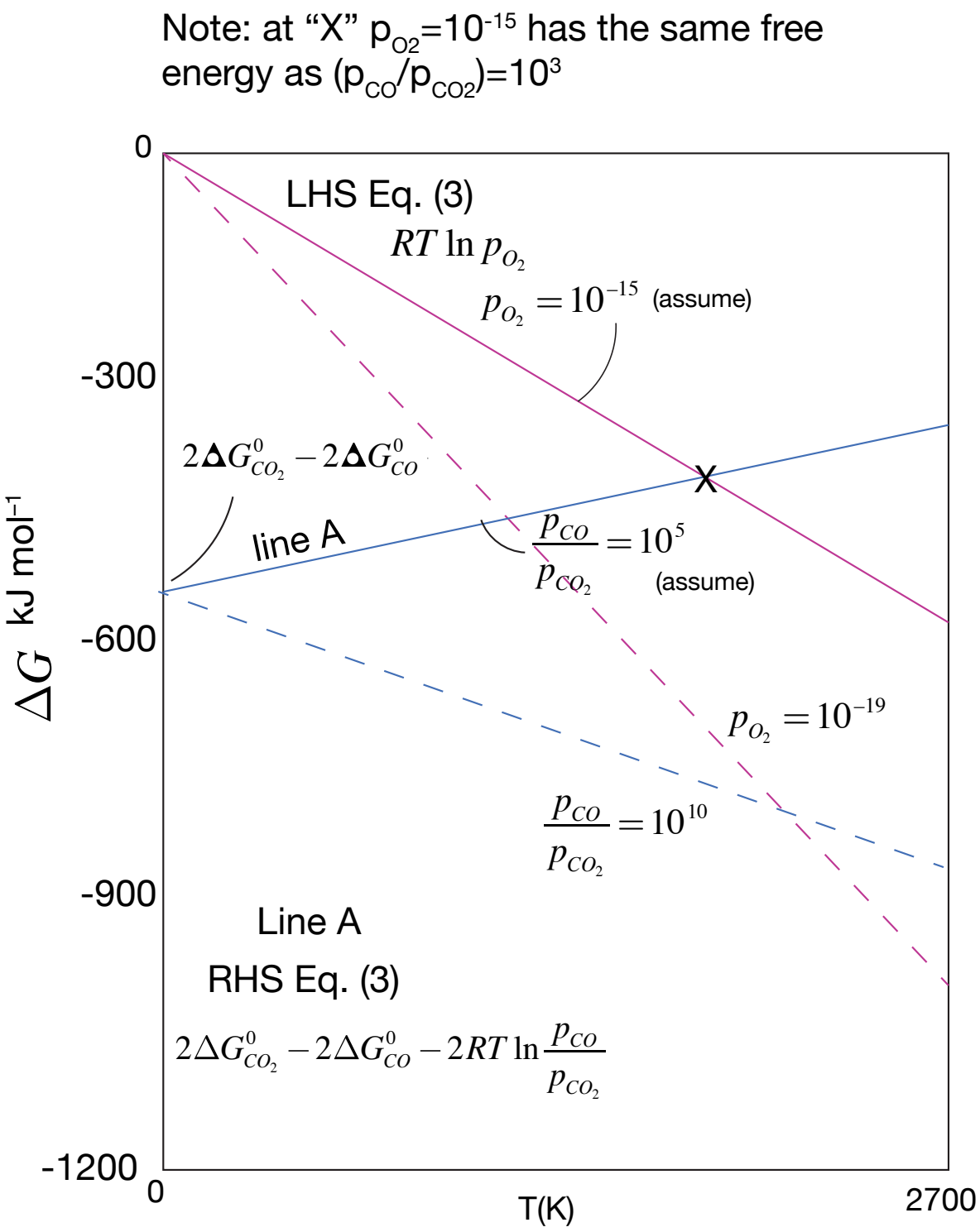
Rearranging terms in Eq. (2) to calculate the ratio p_{CO} / p_{CO_2}



$$RT \ln p_{O_2} = 2\Delta G^0_{CO_2} - 2\Delta G^0_{CO} - 2RT \ln \frac{p_{CO}}{p_{CO_2}} \qquad (3)$$

Note that data for $\Delta G^0_{CO_2}$ and ΔG^0_{CO} are tabulated in JANAF tables (as a function of temperature). Therefore Eq. (3) can be used to calculate the p_{CO}/p_{CO2} ratio for given value of p_{O2} at specific temperature. The question now is how is Eq. (3) displayed graphically in the Ellingham diagram.

We wish therefore to solve Eq. (3) graphically by plotting the left hand side and the right hand side of the equation on the same graph and look for intersection to find the solution as shown below



Notes:

(i) The line for oxygen drops lower as pO2 is decreased

(ii) The line for CO/CO2 rises higher as the ratio is decreased (because of the negative sign of this term in the right hand side of Eq. (3))