The Overarching Questions

We shall consider all three types of equations in the previous lecture, that is, solid-gas, amongst gases, and solid-solid.

However, the process is illustrated by considering the reaction for the oxidation/reduction of copper oxide.

Oxidation of a metal

Consider oxidation of copper

$$4Cu + O_2 \rightleftarrows 2Cu_2O \tag{1}$$

How to be determine whether the reaction will go to the right (oxidation) or to the left (reduction)?

The approach is the calculate the equilibrium between the three constituents in the reaction, the metal, the gas and the oxide.

The above equilibrium is defined by a specific vapor pressure of O_2 (at a specific temperature). The vapor pressure expressed as a partial pressure in units of atm (1 atm = 100 kPa); it is also called the "activity" of the gas phase.

By definition the activities of pure Cu and pure Cu_2O are equal to unity.

A visual description of the direction of the reaction in Eq. (1) is as following,

If $p_{O_2}^*$ is the activity of oxygen when equation (1) is at an equilibrium, then if

$p_{O_2} < p_{O_2}^*$ then the reaction will move to the left, that is Cu_2O will reduce. (2)

if

$p_{O_2} > p_{O_2}^*$ then copper will oxidize. (3)

I usually visualize the reaction like a scale.. if the left hand side is lower then it pulls the reaction to the left, if it is higher is pushes the equation to the right.

Therefore the problem reduces to finding the value of $p_{O_2}^*$ where Eq.(1) is held in equilibrium. This is done graphically in Ellingham diagrams. The diagrams are a graphical solutions to equations from chemical potentials.

Equations that are the Foundation of Ellingham Diagrams

The equilibrium condition for the equation $4Cu + O_2 \rightleftarrows 2Cu_2O$ can be written in terms of the chemical potentials.

Note that the equation has three species

Cu, O_2, Cu_2O, each with their distinct chemical potentials, μ_{Cu} , and so on.

Now the chemical potentials depend primarily on two "things", (i) temperature, and (ii) chemical composition. For example if instead of pure copper you have an alloy of Cu+Al, the the chemical potential of copper in the alloy will be different (actually lower) than the

chemical potential of pure copper. Therefore the chemical potential is defined relative the **pure form or state** of a condensed phase (it may be a solid or a liquid). It can be shown that the general chemical potential of copper may be written as (please take this for a fact from old scientific literature)

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

Note the units for each term in the above equation. Activity is dimensionless (as it must be since the logarithm of a physical quantity cannot have units since a log function can be expanded into a power series). RT has units of Jmol^{-1}, therefore the chemical potentials also have units of Jmol^{-1} (if we write k_BT instead of RT, then the units would be J molecule or J per atom, remmber that R is equal to the product of k_B and N_A the Avogadro's number).

Chemical potentials for O_2 and Cu_2O will have the same form as Eq. (5).

Now, the equilibrium condition for Eq. (1) can be written in terms of the chemical potentials as follows,

$$4\mu_{Cu} + \mu_{O_2} = 2\mu_{Cu_2O} \tag{5}$$

Filling in for the chemical potentials from equivalents of Eq. (4), we have that

$$4\mu^o_{Cu} + 4RT\ell n(a_{Cu}) + \mu^o_{O_2} + RT\ell n(a_{O_2}) = 2\mu^o_{Cu_2O} + 2RT\ell n(a_{Cu_2O}) \tag{6}$$

Pay attention to what is on the right and what is on the left hand side of Eq. (6). Remember that chemical potential represent the energy state of a species. Therefore,

If the total energy of the right hand side, say ΔG_{RHS} and of the left hand side is ΔG_{LHS}, so that

$$\Delta G_{RHS} = 2\mu^o_{Cu_2O} + 2RT\ell n(a_{Cu_2O}) \tag{7}$$

and,

$$\Delta G_{LHS} = 4\mu^o_{Cu} + 4RT\ell n(a_{Cu}) + \mu^o_{O_2} + RT\ell n(a_{O_2}) \tag{8}$$

Then the reaction $4Cu + O_2 \rightleftarrows 2Cu_2O$,

Will be in equilibrium if

$$\Delta G_{RHS} = \Delta G_{LHS}, \text{ as prescribed by Eq. (5)} \tag{9}$$

However, if

$$\Delta G_{RHS} < \Delta G_{LHS} \text{ then the metal would oxidize} \tag{10}$$

or if

$$\Delta G_{RHS} > \Delta G_{LHS} \text{ then the metal oxide will reduce} \tag{11}$$

The convention is to write the change in the free energy of reactions as RHS minus the LHS:

$$\Delta G = \Delta G_{RHS} - \Delta G_{LHS} \tag{12}$$

If ΔG is negative then energy is released to the environment (since what is left after the reaction is less than what was there before the reaction), and the reaction is termed as being exothermic.

If ΔG is positive then energy is consumed from the environment (since what is created – left after the reaction –is more than what was there before the reaction), and the reaction is termed as being endothermic.

Please remember the above conventions and defintions since endothermic and exothermic are widley used to communicate how a reaction interacts with the environment.

Now we return to the chemical potentials in

$$4\mu^o_{Cu} + 4RT\ell n(a_{Cu}) + \mu^o_{O_2} + RT\ell n(a_{O_2}) = 2\mu^o_{Cu_2O} + 2RT\ell n(a_{Cu_2O})$$ (same as Eq. 6 above)

Taking the difference between RHS and the LHS, we have that,

$$\left[2\mu^o_{Cu_2O} - 4\mu^o_{Cu} - \mu^o_{O_2}\right] + 2RT\ell n(a_{Cu_2O}) - 4RT\ell n(a_{Cu}) - RT\ell n(a_{O_2}) = 0$$ (13)

or, collecting the terms in natural log, we have that

$$\left[2\mu^o_{Cu_2O} - 4\mu^o_{Cu} - \mu^o_{O_2}\right] + RT\ell n \frac{a^2_{Cu_2O}}{a^4_{Cu_2} a_{O_2}} = 0$$ (14)

The terms in the brackets represent the energy of the reaction when the consituents are in their standard states. There these terms can be catalogued in handbooks. Indeed they are in what are called JANAF Tables (we shall come to them later). But succinctly since Cu_2O is derived from two funamental consituents, we say that

$$2\Delta G^0_{Cu_2O} = 2\left[\mu^o_{Cu_2O} - 2\mu^o_{Cu} - 0.5\mu^o_{O_2}\right]$$ (15)

Note that $\Delta G^0_{Cu_2O}$ is called the energy of formation of one mole of the oxide (from the standard states is implied in this statement).
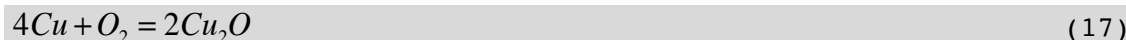
Where $\Delta G^0_{Cu_2O} = \left[\mu^o_{Cu_2O} - 2\mu^o_{Cu} - 0.5\mu^o_{O_2}\right]$

$\Delta G^0_{Cu_2O}(T\,in\,Kelvin)$ is called the energy for formation (of Cu_2O, in the presence instance) found in tables in "JANAF".

Now Eq. (14), can be written as

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

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

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

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

Development of Ellingham from Equations in the Gray-Box

•Step One: assume all "solid" constituents to be pure, thus we can set their activity to be unity (by definition).

•Equate $a_{O_2} = p_{O_2}$ again from the standard state (where the activity is equal to unity for a pressure of one atm)
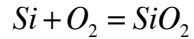
Thus Eq. (16) becomes,

$$2\Delta G^0_{Cu_2O} = RT\ell n(p_{O_2})$$ ****   (18)

The equation for any reaction to be displayed in Ellingham must have the right hand side be exactly equal to $RT\ell n(p_{O_2})$ for a graphical solution to Eq. (18).

The left hand side can vary depending on the stoichiometry of the reaction.
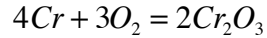
•For example consider

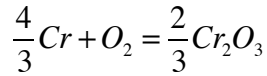$$Si + O_2 = SiO_2$$

In this case Eq. (18) becomes

$$\Delta G^0_{SiO_2} = RT\ell n(p_{O_2}) \qquad\qquad (19)$$

Note how why the factor of 2 in front of the energy of formation, $\Delta G^0_{Cu_2O}$, in Eq. (18) is not present in Eq. (19).

•As a more complex reaction consider oxidation of Cr

$$4Cr + 3O_2 = 2Cr_2O_3$$

Now, we first write the equation so that only one mole of oxygen is involved. Thus we have that

$$\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$$

Now the equivalent of Eqns (18) and (19) becomes

$$\frac{2}{3}\Delta G^0_{Cr_2O_3} = RT\ell n(p_{O_2}) \qquad\qquad (20)$$

Note that in all instances (equations 18, 19, and 20), the right hand side is the same.

The left hand side is a multiple of the Energy of Formation of the Oxide from the standard state of the consistuents, that is ΔG^0_{oxide} as given in the JANAF Tables; these values are given for the energy of formation for one mole of the oxide.

These values for the three cases, drawn from the weblinks below are quoted below.

https://janaf.nist.gov/tables/Cr-014.html; for Cr_2O_3 (crystal)

https://janaf.nist.gov/tables/O-038.html; for SiO_2(glass)

https://janaf.nist.gov/tables/Cu-019.html; for Cu_2O (crystal)

The Data from JANAF are given on the next page.

•Note that all values are negative at all temperature, meaning that the reactions given in Eqns (18), (19) and (20) are all exothermic.

You can obtain the data for the energy of formation per molecule of the oxide from its constituents (in the standard state) from the JANAF website given above.

•To solve equations (18)-(20) you would need to take multiples of the free energy of formation for one molecule as given in JANAF. Thus they will be $2*\Delta G^o_{Cu_2O}$, or $1*\Delta G^o_{SiO_2}$, or

$\frac{2}{3}\Delta G^0_{Cr_2O_3}$.

Cr2O3		Cu₂O		SiO₂	
T(K)	DG (kJ/mole)	T(K)	DG (kJ/mole)	T(K)	DG (kJ/mole)
0	-1128.844	0	-168.952	0	-897.756
100	-1107.252	100	-162.621	100	-884.112
200	-1080.195	200	-155.348	200	-867.314
298.15	-1053.066	298.15	-147.886	298.15	-850.175
300	-1052.56	300	-147.745	300	-849.85
400	-1025.421	400	-140.092	400	-832.194
500	-998.699	500	-132.484	500	-814.537
600	-972.333	600	-124.944	600	-796.949
700	-946.252	700	-117.478	700	-779.457
800	-920.401	800	-110.087	800	-762.067
900	-894.736	900	-102.767	900	-744.777
1000	-869.217	1000	-95.517	1000	-727.585
1100	-843.808	1100	-88.331	1100	-710.484
1200	-818.475	1200	-81.208	1200	-693.469
1300	-793.188	1300	-74.144	1300	-676.533
1400	-767.918	1400	-66.321	1400	-659.67
1500	-742.639	1500	-57.438	1500	-642.876

Ellingham given graphical Solutions to the oxidation reactions

A general form of Eqns (18,19, 20) can be written as

$$x\Delta G_{oxide}^{JANAF} = RT\ell n(p_{O_2}) \qquad (21)$$

Where x=2/3 for Cr₂O₃, x=1 for SiO₂, and x=2 for Cu₂O.

The method is to plot the left hand side against temperature, and the right hand side for different values of p_{O_2}. Where the intersect is the solution to Eq. (21).

This is illustrated by the sketches on the right.

Caution: what is written as ΔG_o(T) in the sketch is actually $x\Delta G_{oxide}^{JANAF}$; for example for

Cr₂O₃, $\qquad \Delta G_o^{ellingh} = \dfrac{2}{3}\Delta G_{Cr_2O_3}^{JANAF}$
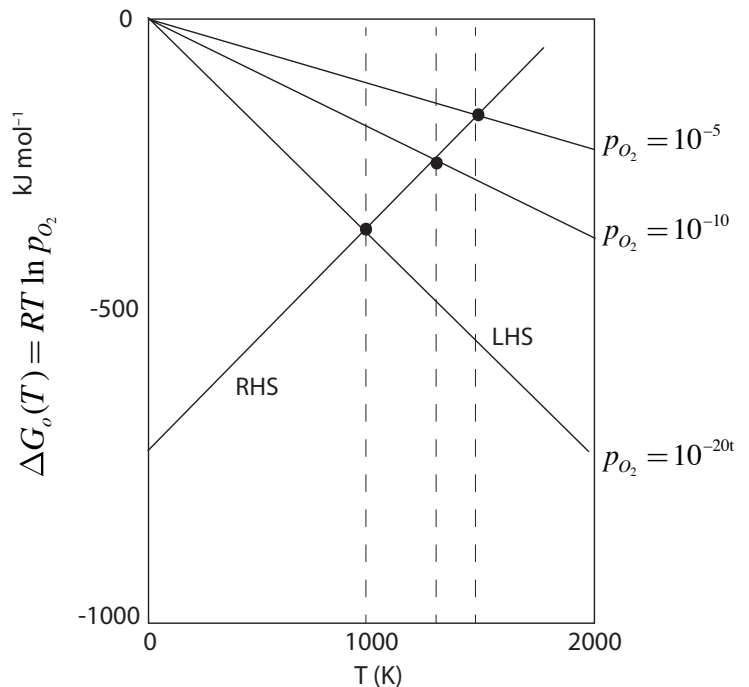
Reading Ellingham Diagrams

Case I: Si+O₂=SiO₂

What is the pO_2 for the $Si+O_2=SiO_2$ to be in equilibrium at a given temperature?

The way to read Ellingham is shown on the right.

The red line shows the data from JANAF for the energy of formation of SiO_2 from the standard states.

The blue lines are the temperatures where we wish to calculate the equilibrium p_{O_2} values:

1000 ºC, 1200 ºC and 1400 ºC.

The lines in green are the plots for $RT\ell n(p_{O_2})$ which are drawn through the points on RED LINE to find to oxygen pressure for each of the three temperaturess. The answers are
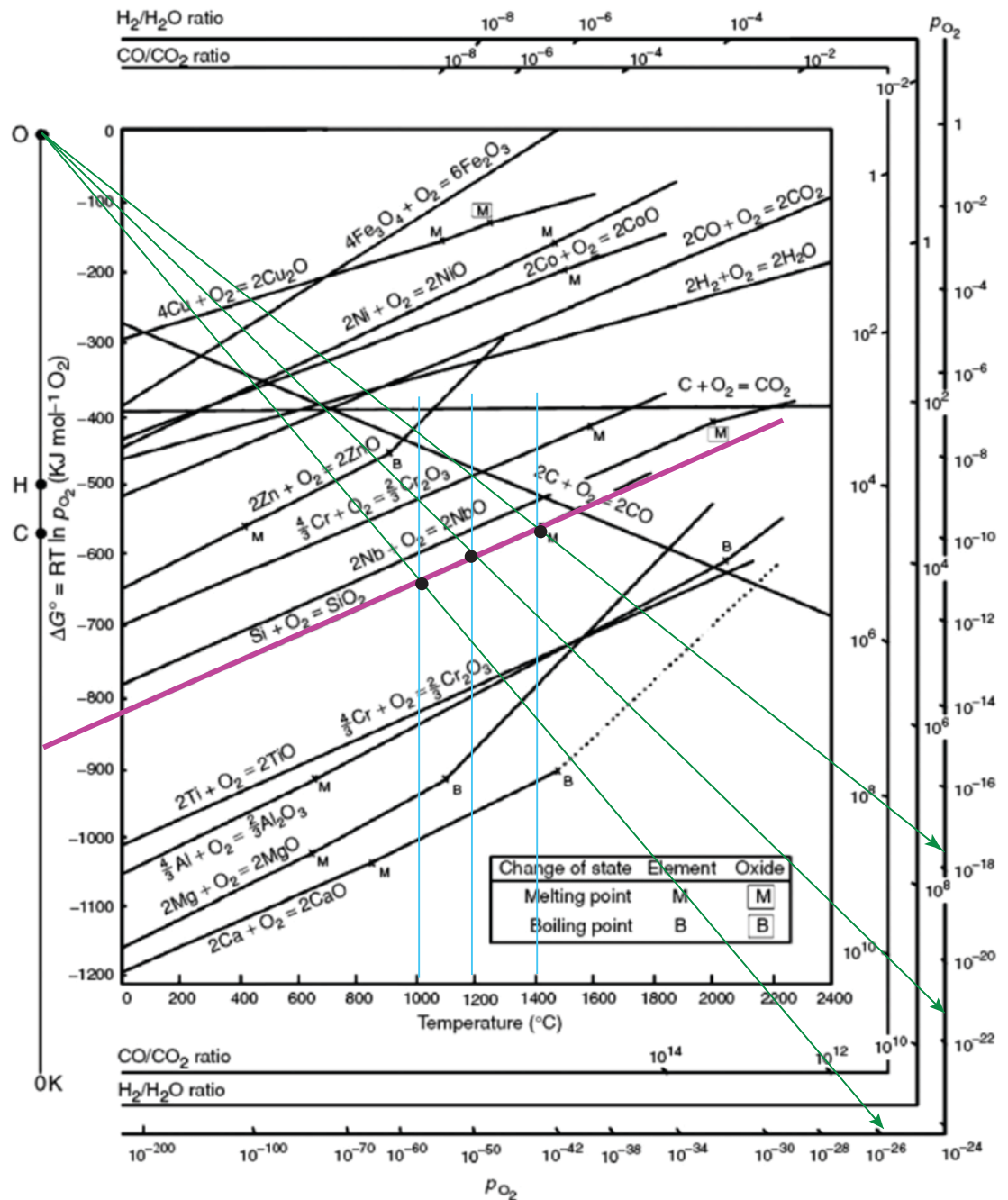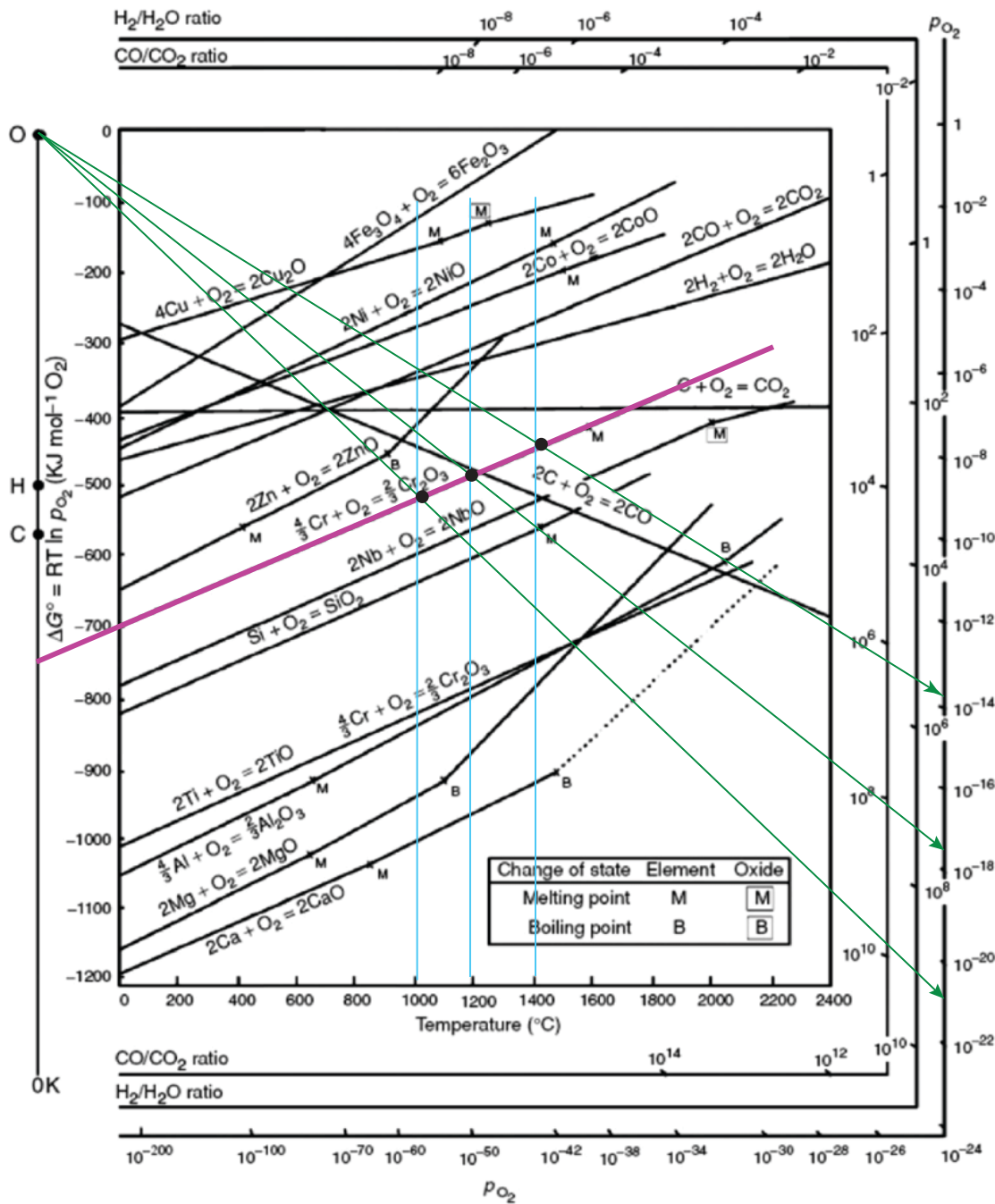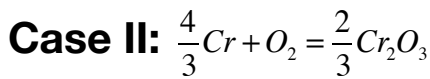
3x10⁻¹⁸ at 1400 ºC

10⁻²¹ at 1200 ºC

and,

10⁻²⁶ at 1000 ºC

and so on for other temperatures.

•Note the extremely small values of these vapor pressures and you may ask if they are meaningful. Actually they are; THE BEHAVIOR CAN CHANGE EVEN AT THESE VERY LOW VAPOR PRESSURES.

Case II: $\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$

Note that the vapor pressures of oxygen for the same temperatures as for silica, are higher than for Case I.

Case III: 4Cu + O₂ = 2Cu₂O

The JANAF line for this reaction lies above those for silica and chromium oxide. Therefore the vapor pressures will be even higher than for chromium oxide.

Questions:

(i) If a reaction is performed between Cu_2O and Cr (metal) say at 1200 °C, what to do you expect to happen. Will Cr reduce the cuprous oxide or not?

(ii) What will be the redox reaction between Cu_2O and Si?