Chemical equilibrium (Examples)

By

Assist. Prof.

Dr. Kadhum Muttar

Example (1)

Calculate the equilibrium constant and equilibrium partial pressure of oxygen for the reaction: $ZrO_2 \rightarrow Zr + O_2$

$$\Delta G^\circ = 259{,}940 + 4.33\,T \log T - 59.12\,T \text{ cal}$$

at 1727 °C. Also, predict the possibility of decomposing a pure zirconi a crucible under a vacuum of 10^{-5} mm Hg at that temperature.

Example (2)

Calculate the equilibrium constant for the reaction

$$<NiO> + (H_2) = <Ni> + (H_2O)$$

at 750°C *(1,023 K)* from the following data:

$<Ni> + 1/2(O_2) = <NiO>$; $\Delta G^\circ = -58{,}450 + 23.55\,T$ cal

$(H_2) + 1/2(O_2) = (H_2O)$; $\Delta G^\circ = -58{,}900 + 13.1\,T$ cal

Could pure nickel sheet be annealed at 750°C *(1,023 K)* in an atmosphere containing 95% H_2O and 5% H_2 by volume without oxidation?

Example (3)

A gas mixture of the following composition by volume:

CO: 30%, CO_2: 10%, H_2: 10%, and N_2: 50%

is fed into a heat-treating furnace at 927°C *(1200 K).* Calculate the equilibrium composition of the gas mixture, assuming the total pressure in the furnace to be 1 atm, from the following data:

$$<C> + \tfrac{1}{2}(O_2) = (CO); \quad \Delta G^\circ = -26{,}700 - 21.0\,T \text{ cal}$$

$$<C> + (O_2) = (CO_2); \quad \Delta G^\circ = -94{,}200 - 0.2\,T \text{ cal}$$

$$(H_2) + \tfrac{1}{2}(O_2) = (H_2O); \quad \Delta G^\circ = -58{,}900 + 13.0\,T \text{ cal}$$

Assume that all the gases behave ideally.

Van't Hoff Equation

The Gibbs-Helmholtz equation at constant pressure is represented as

$$\frac{d(\Delta G^{o}/T)}{d(1/T)} = \Delta H^{o}.$$

Substituting the value of ΔG°

$$\frac{d(\ln K)}{d(1/T)} = \frac{-\Delta H^{o}}{R},$$

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^{o}}{RT^{2}}.$$

The above equation is commonly called the Van't Hoff equation

Example (4)

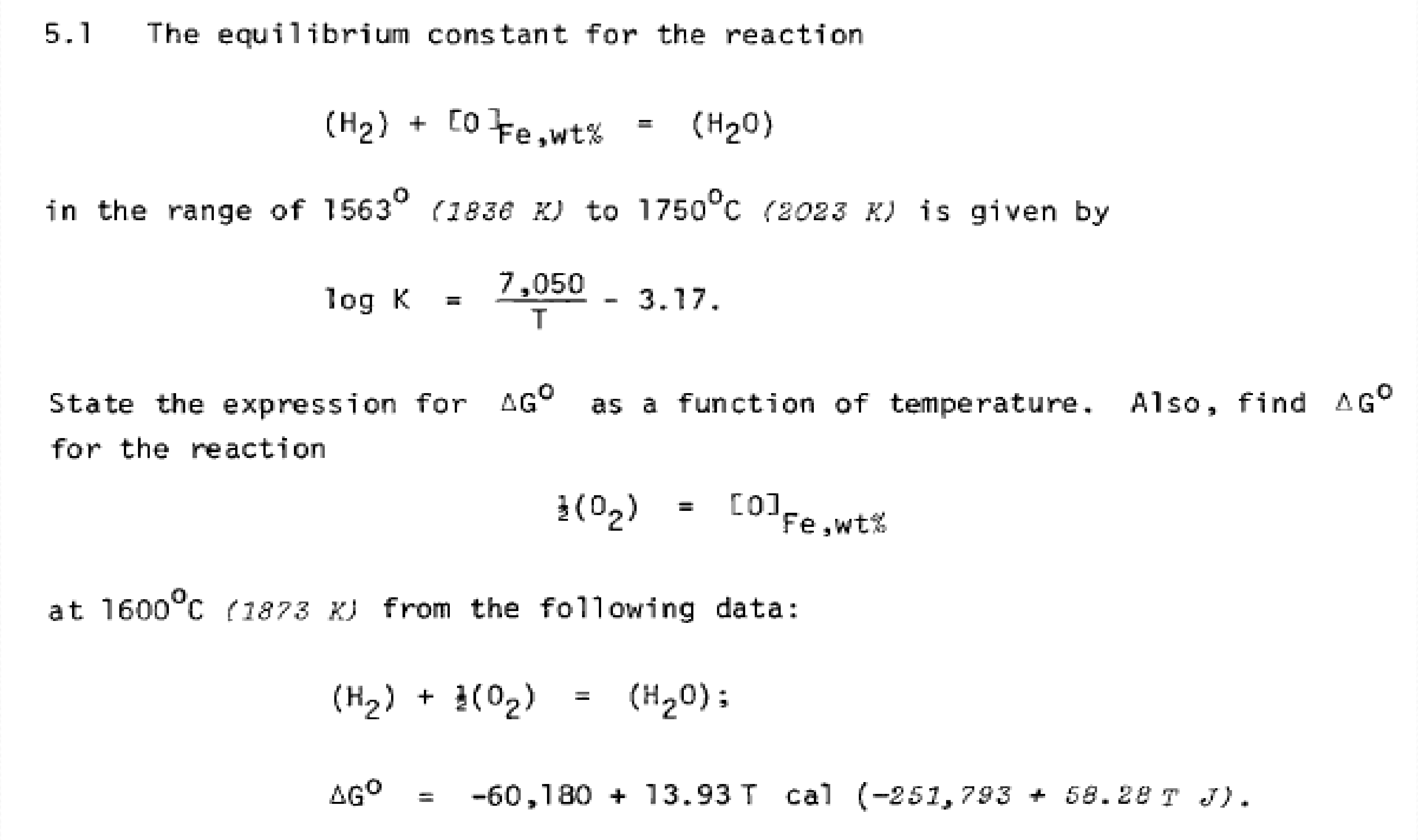
The equilibrium constants for the decomposition of nickel oxide

$$\mathbf{NiO = Ni + 1/2O_2}$$

are 1.514 x 10^{-11} and 2.355 x 10^{-8} at 527° and 727°C respectively. Calculate the value of the equilibrium constant at 627°C from the following data:

	Cp (cal/deg.mol)
NiO(s)	$11.18 + 2.02\times10^{-3}\, T$
O_2 (g)	$7.16 + 1\times10^{-3}\, T - 0.4\times10^{5}\, T^{-2}$
Ni (s)	$7.1 + 1\times10^{-3}\, T - 2.23\times10^{5}\, T^{-2}$

Exercises



5.1 The equilibrium constant for the reaction

$$(H_2) + [O]_{Fe,wt\%} = (H_2O)$$

in the range of 1563° *(1836 K)* to 1750°C *(2023 K)* is given by

$$\log K = \frac{7,050}{T} - 3.17.$$

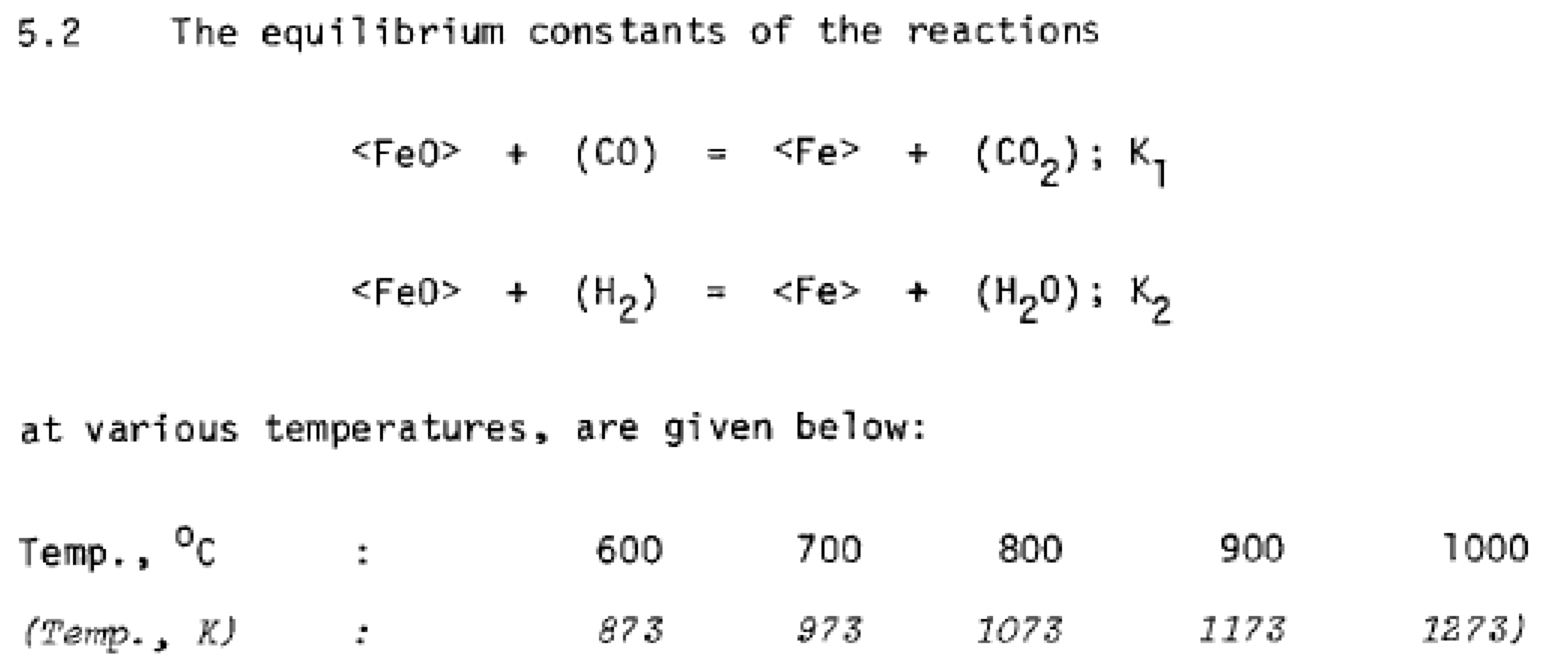
State the expression for ΔG^o as a function of temperature. Also, find ΔG^o for the reaction

$$\tfrac{1}{2}(O_2) = [O]_{Fe,wt\%}$$

at 1600°C *(1873 K)* from the following data:

$$(H_2) + \tfrac{1}{2}(O_2) = (H_2O);$$

$$\Delta G^o = -60,180 + 13.93\,T \text{ cal } (-251,793 + 58.28\,T \text{ J}).$$



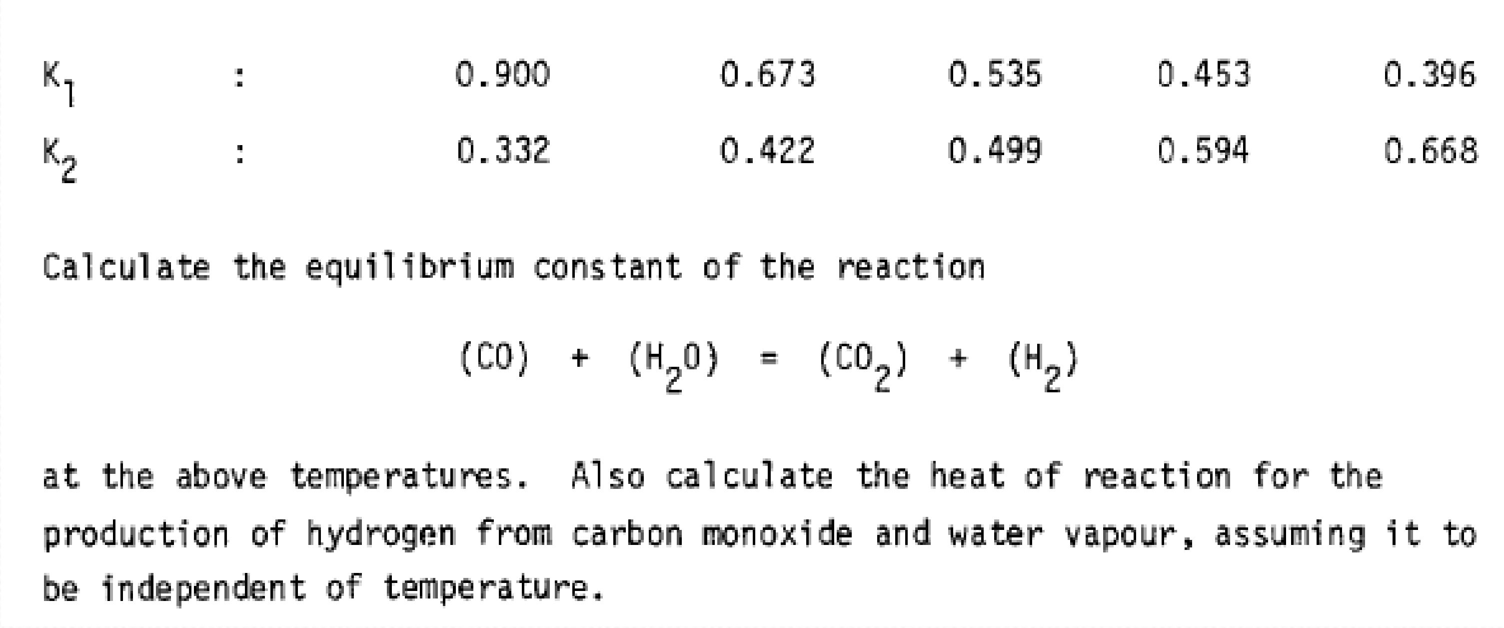
5.2 The equilibrium constants of the reactions

$$\langle FeO\rangle + (CO) = \langle Fe\rangle + (CO_2);\ K_1$$

$$\langle FeO\rangle + (H_2) = \langle Fe\rangle + (H_2O);\ K_2$$

at various temperatures, are given below:

Temp., °C	:	600	700	800	900	1000
(Temp., K)	:	*873*	*973*	*1073*	*1173*	*1273)*



K_1	:	0.900	0.673	0.535	0.453	0.396
K_2	:	0.332	0.422	0.499	0.594	0.668

Calculate the equilibrium constant of the reaction

$$(CO) + (H_2O) = (CO_2) + (H_2)$$

at the above temperatures. Also calculate the heat of reaction for the production of hydrogen from carbon monoxide and water vapour, assuming it to be independent of temperature.

5.3 The complete reduction of αWO_3 takes place in four successive stages, according to the following reactions:

$$10\,\alpha WO_3 + H_2 = 10\,WO_{2.9} + H_2O\,;\ K_1.$$

$$\log K_1 = \frac{-3{,}792}{T} + 4.8268.$$

$$\frac{50}{9}WO_{2.9} + H_2 = \frac{50}{9}WO_{2.72} + H_2O\,;\ K_2.$$

$$\log K_2 = \frac{-1{,}442.5}{T} + 1.684.$$

$$\frac{50}{36}WO_{2.72} + H_2 = \frac{50}{36}WO_2 + H_2O\,;\ K_3.$$

$$\log K_3 = \frac{-801.7}{T} + 0.8615.$$

$$\tfrac{1}{2}WO_2 + H_2 = \tfrac{1}{2}W + H_2O\,;\ K_4.$$

$$\log K_4 = \frac{-2{,}219}{T} + 1.5809.$$

Find an expression for the standard free energy change for the complete reduction of αWO_3, i.e.

$$\alpha WO_3 + 3\,H_2 = W + 3\,H_2O$$

as a function of temperature and, hence, calculate its value at 800°C *(1073 K)*.

5.4 Calculate the vacuum needed for obtaining molybdenum metal according to the reaction

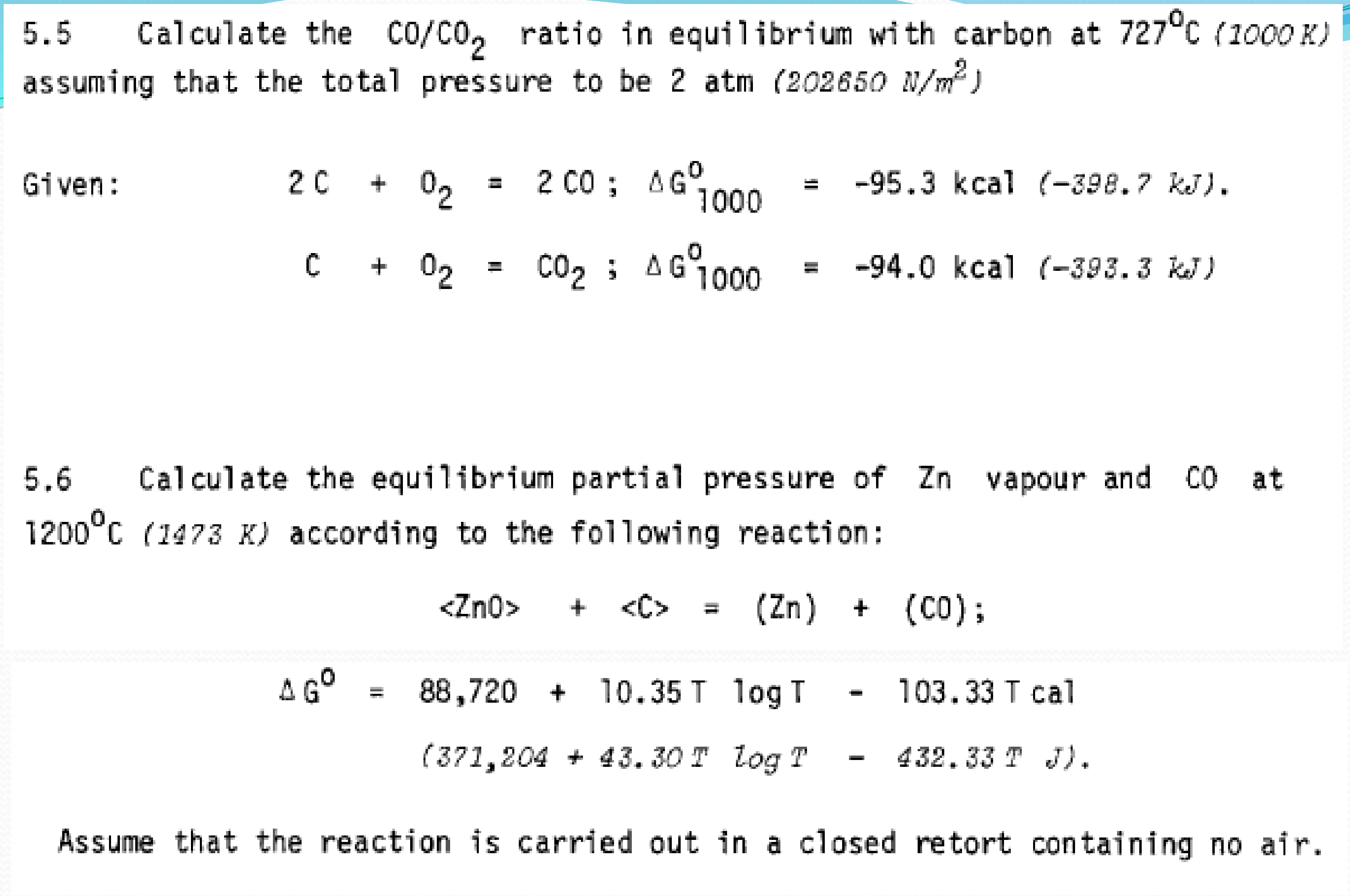
$$MoS_2 = Mo + S_2$$

at 800°C *(1073 K)* and 1000°C *(1273 K)*.

Given: $MoS_2 + 2\,H_2 = Mo + 2\,H_2S\,;\ K_1.$

$2\,H_2S = 2\,H_2 + S_2\,;\ K_2.$

Temp., °C	:	800	1000
(Temp., K	*:*	*1073*	*1273)*
K_1	:	7.311×10^{-6}	1.439×10^{-3}
K_2	:	2.2×10^{-4}	5.6×10^{-3}



5.5 Calculate the CO/CO_2 ratio in equilibrium with carbon at 727°C *(1000 K)* assuming that the total pressure to be 2 atm *(202650 N/m²)*

Given:

$$2\,C + O_2 = 2\,CO\ ;\ \Delta G^o_{1000} = -95.3\ \text{kcal}\ (-398.7\ kJ).$$

$$C + O_2 = CO_2\ ;\ \Delta G^o_{1000} = -94.0\ \text{kcal}\ (-393.3\ kJ)$$

5.6 Calculate the equilibrium partial pressure of Zn vapour and CO at 1200°C *(1473 K)* according to the following reaction:

$$\langle ZnO \rangle + \langle C \rangle = (Zn) + (CO);$$

$$\Delta G^o = 88{,}720 + 10.35\,T\,\log T - 103.33\,T\ \text{cal}$$

$$(371{,}204 + 43.30\,T\,\log T - 432.33\,T\ J).$$

Assume that the reaction is carried out in a closed retort containing no air.

5.7 Evaluate the partial pressure of Mg vapour at 1200°C *(1473 K)* for the following reaction:

$$2\langle MgO\rangle + 2\langle CaO\rangle + \langle Si\rangle = 2(Mg) + \langle 2\,CaO\cdot SiO_2\rangle.$$

Given: $2\langle MgO\rangle + \langle Si\rangle = 2(Mg) + \langle SiO_2\rangle;$

$$\Delta G^o = 152{,}600 + 11.37\,T\log T - 99.18\,T\text{ cal}$$
$$(638{,}478 + 47.57\,T\log T - 414.97\,T\text{ J}).$$

$$2\langle CaO\rangle + \langle SiO_2\rangle = \langle 2\,CaO\cdot SiO_2\rangle;$$

$$\Delta G^o = -30{,}200 - 1.2\,T\text{ cal }(-126{,}357 - 5.02\,T\text{ J}).$$

5.8 In a copper converter, the following reaction is believed to occur in the latter stages:

$$\{Cu_2S\} + 2\{Cu_2O\} = 6\{Cu\} + (SO_2)\,;$$

$$\Delta G^o = -87 - 5.13\,T\text{ cal }(-364 - 21.46\,T\text{ J}).$$

Calculate the equilibrium partial pressure of SO_2 at 1250°C *(1523 K)*. Assume that both Cu_2S and Cu_2O exist as pure melts.

5.9 Will a magnesia crucible decompose at 1000°C *(1273 K)* in a vacuum of 0.01 atm *(1013 N/m^2)* ?

Given:

$$\langle MgO \rangle = \{Mg\} + \tfrac{1}{2}(O_2);$$

$$\Delta G^o = 145{,}350 + 0.24\,T \log T - 26.95\,T \text{ cal}$$

$$(608{,}144 + 1.0\,T \log T - 112.75\,T \text{ J}).$$

5.10 Will a blast furnace gas analyzing 28% CO, 13% CO_2 and 59% N_2 reduce wustite (FeO) at 727°C *(1000 K)* ?

Given:

$$\langle Fe \rangle + \tfrac{1}{2}(O_2) = \langle FeO \rangle;$$

$$\Delta G^o = -62{,}050 + 14.95\,T \text{ cal } (-259{,}617 + 62.55\,T \text{ J}).$$

$$(CO) + \tfrac{1}{2}(O_2) = (CO_2);$$

$$\Delta G^o = -67{,}500 + 20.75\,T \text{ cal } (-282{,}420 + 86.82\,T \text{ J}).$$