Worksheet 6

February 8th, 2022

Collaborations are encouraged and students must report all collaborators on each assignment. All external sources (websites, books) must be cited. An *extra credit* (*EC*) problem will be available per assignment. Please submit a completed homework on-time to receive *EC* and no partial *EC* (all parts must be correct) will be given out. Additional problems are listed at the end of each assignment. This week's assignment is due *Tuesday, Feb 15th at 10:00am.*

1. (5 pts) **Direct Carbon Fuel Cell.** This technology uses a carbon rich material and converts the chemical energy in solid carbon to eletricity through fuel cell reactions and electrochemical oxidation. It has the following reactions

Anode: $C(s) + 2\ O^-(g) \rightarrow CO_2(g) + 4\ e^-$

Cathode: $4\ e^- + O_2(g) \rightarrow 2\ O^-(g)$

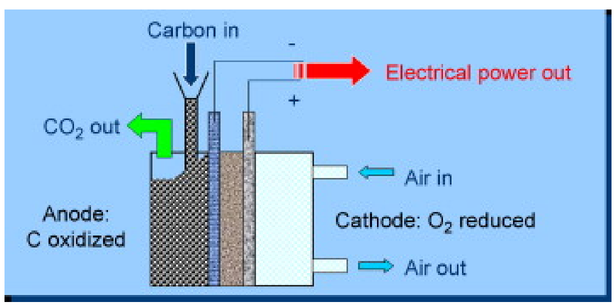


Figure 1: Illustration of direct carbon fuel cell

Report all values to 3 significant digits.

(a) What is the overall reaction?

(b) The standard enthalpy ($\Delta H°$) and standard Gibbs free energy ($\Delta G°$) are -393.5 kJ/mol and -394.5 kJ/mol, respectively. What is the entropy change?

(c) Assuming 100% efficiency, how much carbon (in kg) is needed to deliver 1 MWh of electricity?

2. (4 pts) **Equilibrium Constant** Calculate the equilibrium constant at 25°C for each of the following unbalanced reactions:

(a) the combustion of hydrogen: $H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O\,(g)$

(b) the oxidation of carbon monoxide: $CO\,(g) + O_2\,(g) \rightleftharpoons CO_2$

(c) the decomposition of limestone: $NO_2\,(g) + H_2O\,(l) \rightleftharpoons HNO_3\,(aq) + NO\,(g)$

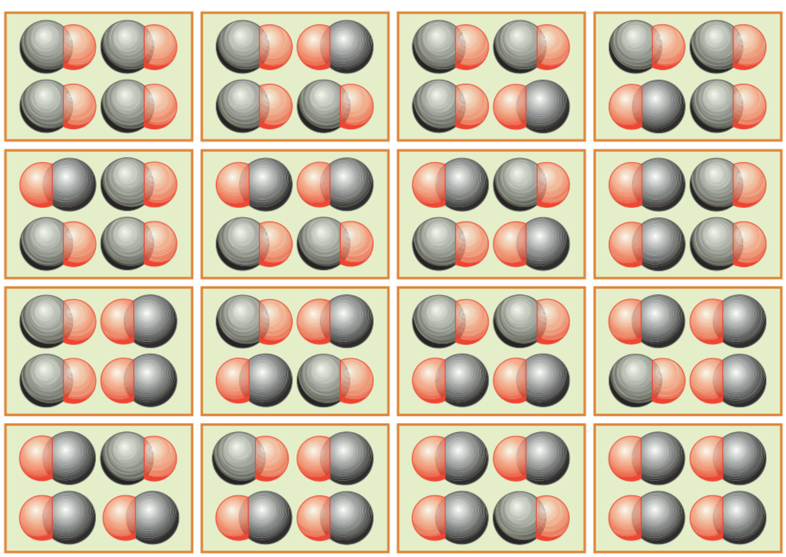
3. (2 pts) **Temperature dependence of K.** ATP is a compound that provides energy for biochemical reactions in the body when it undergoes hydrolysis. For the hydrolysis of ATP at 37°C (normal body temperature) $\Delta H_r^\circ = -20.$ and $\Delta S_r^\circ = +34\mathrm{J \cdot K/mol}$. Assuming that these quantities are independent of temperature, calculate the temperature at which the equilibrium constant for the hydrolysis of ATP becomes greater than 1. Report to 2 significant figures.

4. (4 pts) **Mixing Ideal Gases.** A container is divided into two equal compartments. One contains 3.0 mol CO_2 and the other contains 1.0 mol N_2 at 25°C. Assume ideal gas behavior. Calculate the Gibbs free energy of mixing when the partition is removed. Report to 2 significant figures.

5. Calculate the entropy (S) of a tiny solid made up of four diatomic molecules of a compound such as carbon monoxide, CO, at $T = 0$ when

(a) the four molecules have formed a perfectly ordered crystal in which all molecules are aligned with their C atoms on the left (top-left image illustrated below)

(b) the four molecules lie in random orientations (any images illustrated below)



Ozone Depletion

6. (6 pts) *Extra Credit:* Reactions between gases in the atmosphere are not at equilibrium, but for a thorough understanding of them we need to study both the rates at which they take place and their behavior under equilibrium conditions.

(a) Depletion of ozone (O_3(g)) in the stratosphere can be summarized by:

$$2\,O_3\,(g) \rightleftharpoons 3\,O_2\,(g)$$

Determine the standard Gibbs free energy, standard enthalpy and standard entropy for the reaction.

(b) In part (a), what is the equilibrium constant of the reaction at 25°C? What is the significance of your answer with regard to ozone depletion?

(c) At any given time, ozone molecules are constantly formed and destroyed. One of the reactions that depletes ozone is:

$$O_3\,(g) + O\,(g) \rightleftharpoons 2\,O_2\,(g)$$

Calculate the value of the equilibrium constant for this reaction at 25°C given that at that temperature the reaction is catalyzed by NO_2 molecules in a two-step process:

$$NO_2\,(g) + O\,(g) \rightleftharpoons NO\,(g) + O_2(g) \quad K = 7 \times 10^{103}$$
$$NO\,(g) + O_3\,(g) \rightleftharpoons NO_2\,(g) + O_2(g) \quad K = 5.8 \times 10^{-34}$$

(d) **No Laughing Matter.** Nitrous oxide (N_2O), known as laughing gas, has been the largest ozone-depleting substance and has a lifetime of 114 years in the atmosphere. N_2O decomposes into NO in the stratosphere:

$$N_2O(g) + O(g) + h\nu \rightarrow 2\ NO(g)$$

Based on the reaction, describe in words how N_2O is impacting ozone concentration. *Hint:* Look at the overall reactions in part (c). What role does NO and NO_2 play?

(e) The Van't Hoff equation describes the equilibrium constant K in term of temperature T, gas constant R, standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$):

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{1}$$

For the reaction $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$, will this reaction proceed further at very low temperatures of the stratosphere or high temperatures in an internal combustion engine? What implications do this suggest?

(f) An equimolar mixture of N_2(g) and O_2(g) with a total pressure of 4.00 bar was allowed to come to equilibrium in the reaction in part (e) at 1200. K. What will be the partial pressure of each reactant and product at equilibrium?

Optional Additional Problems: Ch. 18 - odd problems 69 - 81