

# Chemistry 240 Semester 01-2009

## Homework for Submission #5

Answer the following questions and submit them for marking on or before 25th March 2009. If any answers show evidence of copying, the whole exercise will attract zero marks.

1) State the definition of the Gibbs energy,  $G$ . Given that the criterion for a feasible (spontaneous) process is that  $\Delta S_{\text{tot}} > 0$ , show that this implies  $\Delta G < 0$ . In terms of the available work resulting from a change, what is the significance of  $\Delta G$ ?

2) Write an equation for the thermal decomposition of magnesium carbonate.

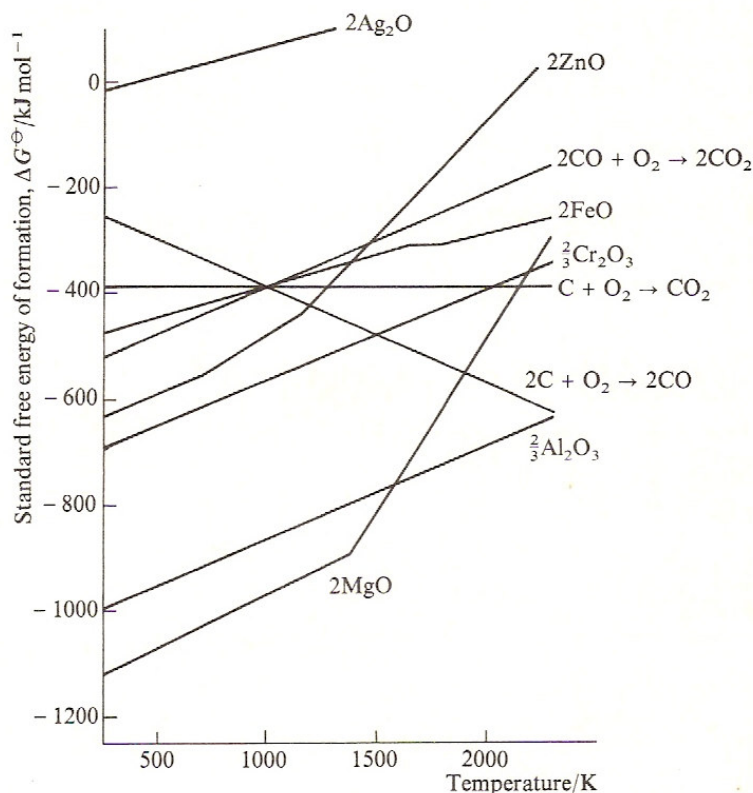
Look up and tabulate the values of standard entropy and standard enthalpy of formation for carbon dioxide, magnesium oxide and magnesium carbonate at  $25^\circ\text{C}$ , and use them to calculate the following:

- The standard entropy and enthalpy changes for the decomposition of magnesium carbonate at  $25^\circ\text{C}$ .
- The value of  $\Delta G^\ominus$  for the decomposition at  $25^\circ\text{C}$ .

In addition:

- Estimate the value of  $\Delta G^\ominus$  at  $1000^\circ\text{C}$ . Make clear what assumptions are necessary to perform this calculation.
- Estimate the temperature at which the system is at equilibrium under standard conditions.
- Write down the expression for the equilibrium constant and determine its value. (No calculation is required; the answer follows from the definitions.)

3) The following diagram is known as an *Ellingham* diagram, after its creator.



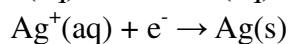
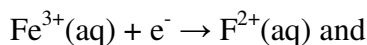
Use the diagram to answer the following questions. (Note that the description *standard free energy of*

*formation* does not strictly apply here. The equations and formulae refer to processes in which 1 mol of O<sub>2</sub> is involved so as to produce the stated amount of product, rather than the formation of 1 mol of the product.)

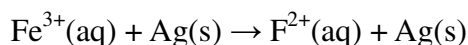
- Estimate the values of  $\Delta G^\ominus$  for the reactions (i)  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  and (ii)  $2\text{Fe} + \text{O}_2 \rightarrow 2\text{FeO}$  at both 500°C and 1500°C, and use these values to calculate  $\Delta G^\ominus$  for  $2\text{FeO} + 2\text{CO} \rightarrow 2\text{Fe} + 2\text{CO}_2$  at the two temperatures. What can you conclude from these figures?
- Suggest why the graphs are essentially straight lines.
- Look up and tabulate the melting and boiling points of Mg, MgO, and O<sub>2</sub>, and hence suggest why the line labelled 2MgO consists of two straight line portions.
- Suggest why the line labelled  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$  has negative slope and why most of the lines have positive slope.

- 4) Write down the relationship between  $\Delta G^\ominus$  and the standard reduction potential,  $E^\ominus$ , as well the relationship between  $\Delta G^\ominus$  and the equilibrium constant.

Look up the standard reduction potentials for



Use these values to find  $\Delta G^\ominus$  for the reaction:



And hence the equilibrium constant for the reaction. At what temperature do your values apply?

- 5) Write down the defining equations for G, H and the work of expansion,  $w_{\text{exp}}$ , for a reversible process occurring at constant temperature and pressure. Recognising that work can be split into two categories,  $w_{\text{exp}}$  (work of expansion against an external pressure) and  $w_{\text{n}}$  (work which is not due to expansion), show that for such a process,  $\Delta G$  represents the amount of non-expansion work involved.