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 $\Delta S_{tot} > 0$, show that this implies $\Delta G < 0$. In terms of the available work resulting from a change, what is the significance of ΔG? (7)

Gibbs energy, G is defined as $H - TS$ (1)

For a feasible process, $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} > 0$ (1)

But for a process occurring at constant temperature, $\Delta S_{surr} = q_{rev}/T = -\Delta H/T$, where ΔH is ΔH_{sys} and T is assumed to be the same for the system and the surroundings. (1)

$\therefore\ \Delta S_{tot} = \Delta S_{sys} - \Delta H/T$ (1)

$\therefore T\Delta S_{tot} = T\Delta S_{sys} - \Delta H$

But if the temperature is constant $\Delta G = \Delta H - T\Delta S = -(T\Delta S - \Delta H)$, where all the terms refer to the system.

$\therefore\ \Delta G = -\ T\Delta S_{tot}$ (1)

$\therefore$ since $T > 0$, $\Delta G < 0$ if $\Delta S_{tot} > 0$

ΔG represents the maximum useful work that can be extracted from a change i.e. the work over and above that necessary for the system to expand against the external pressure. (1)

2) Write an equation for the thermal decomposition of magnesium carbonate. (11)

$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ (1)

Look up and tabulate the values of standard entropy and standard enthalpy of formation for carbon dioxide, magnesium oxide and magnesium carbonate at 25°C, and use them to calculate the following:

Substance	$\Delta H_f^{\ominus}$	$S^{\ominus}$
CO_2	-393.5	213.6
MgO	-601.60	26.95
$MgCO_3$	-1112.9	65.7

(1)

a) The standard entropy and enthalpy changes for the decomposition of magnesium carbonate at 25°C.

$\Delta H^{\ominus}_r = (-393.5) + (-601.6) - (-1112.9) = \underline{117.8\ \text{kJ mol}^{-1}\ (1)}$

$\Delta S^{\ominus}_r = 213 + 26.95 - 65.7 = \underline{174.3\ \text{J mol}^{-1}\text{K}^{-1}\ (1)}$

b) The value of $\Delta G^{\ominus}$ for the decomposition at 25°C.

$\therefore \Delta G^{\ominus} = \Delta H^{\ominus}_r - T\Delta S^{\ominus}_r = 117.8\ \text{kJ mol}^{-1} - (25 + 273) \times 174.3\ \text{J mol}^{-1}\text{K}^{-1} = 117.8 - 51.93\ \text{kJ mol}^{-1} = \underline{65.87\ \text{kJ mol}^{-1}\ (1)}$

In addition:

c) *Estimate* the value of $\Delta G^{\ominus}$ at 1000°C. Make clear what assumptions are necessary to perform this calculation.

Assuming that the values of $\Delta H^{\ominus}_r$ and $\Delta S^{\ominus}_r$ are constant over the range of temperature considered[1], (1)

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[1] Although values are calculated to 4 significant figures, because $\Delta H^{\ominus}_r$ and $\Delta S^{\ominus}_r$ are not constant, the results at higher temperatures are unlikely to be correct to more than 2 significant figures.

$\Delta G^{\ominus} = \Delta H^{\ominus}_r - T\Delta S^{\ominus}_r = 117.8\ \text{kJ mol}^{-1} - (1000 + 273) \times 174.3\ \text{J mol}^{-1}\text{K}^{-1} = -104.1\ \text{kJ mol}^{-1}$ = -100 to 2 sig. figs (1)

d) *Estimate* the temperature at which the system is at equilibrium under standard conditions.

At equlilbrium, $\Delta G = 0$. In this case we can interpret this as $\Delta G^{\ominus}_r = 0$. (1)

Since $\Delta G = \Delta H - T\Delta S$ we have here $\Delta G^{\ominus}_r = \Delta H^{\ominus}_r - T\Delta S^{\ominus}_r = 0$

$\therefore \Delta H^{\ominus}_r = T\Delta S^{\ominus}_r$

$\therefore T = \Delta H^{\ominus}_r / \Delta S^{\ominus}_r = 117.8\ \text{kJ mol}^{-1} / 174.3\ \text{J mol}^{-1}\text{K}^{-1} = 675.8\ \text{K}$ = 680 K to 2 sig. figs.(1)

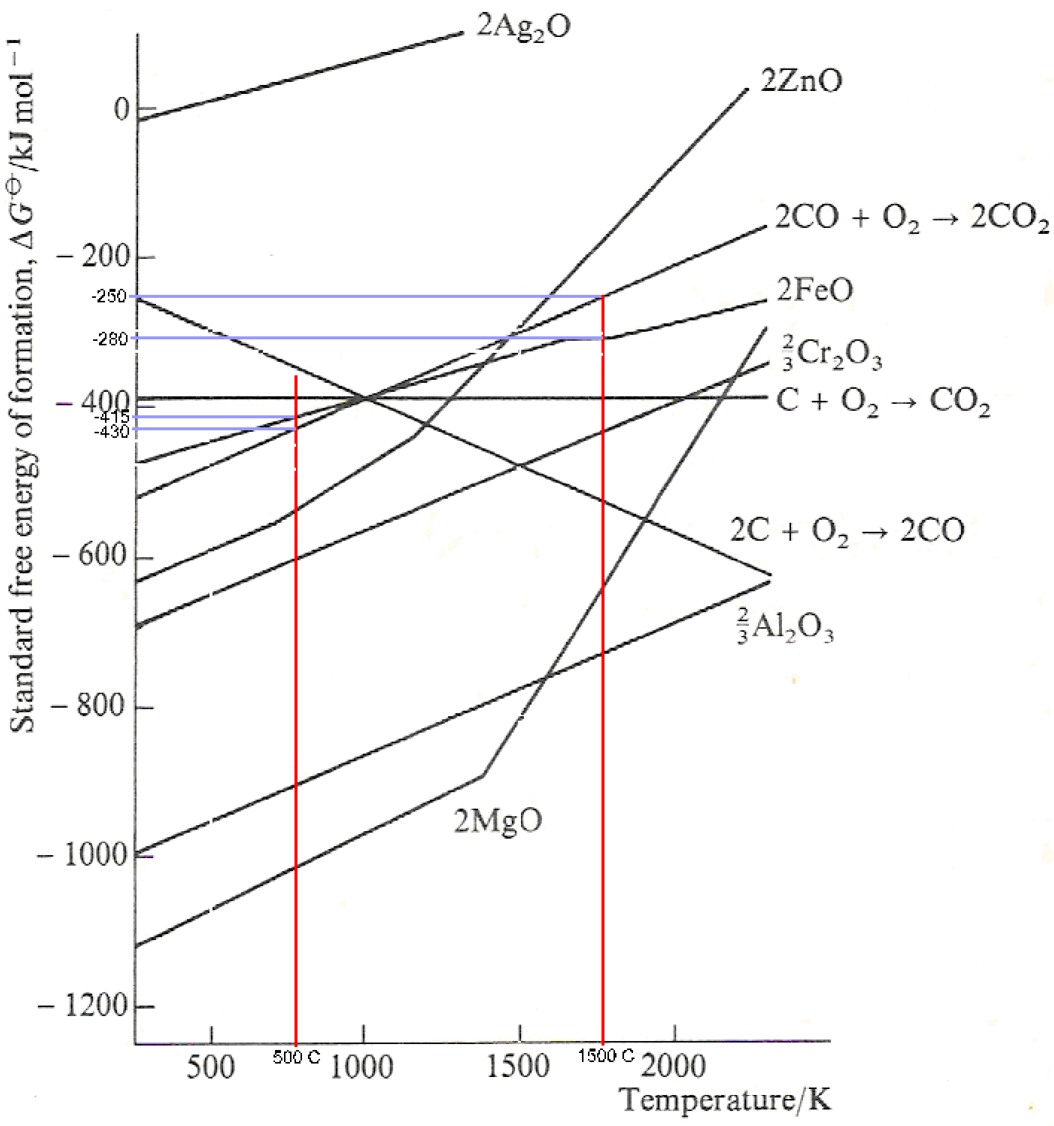
e) Write down the expression for the equilibrium constant and determine its value. (No calculation is required; the answer follows from the definitions.)

$K = (P_{CO2})$ (1)

Since the reaction is under standard conditions, $P_{CO2} = 1$ atm.

Hence K = 1 (1)

3) The following diagram is known as an *Ellingham* diagram, after its creator. (21)



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_2 is involved so as to produce the stated amount of product, rather than the formation of 1 mol of the product.)

a) Estimate the values of $\Delta G^{\ominus}$ for the reactions (i) $2CO + O_2 \rightarrow 2CO_2$ and (ii) $2Fe + O_2 \rightarrow 2FeO$ at both 500°C and 1500°C, and use these values to calculate $\Delta G^{\ominus}$ for $2FeO + 2CO \rightarrow 2Fe + 2CO_2$ at the two temperatures. What can you conclude from these figures?

From the graph,

#	Reaction	$\Delta G^{\ominus}$ @ 500°C / kJ mol^{-1}	$\Delta G^{\ominus}$ @ 1500°C / kJ mol^{-1}
(i)	$2CO + O_2 \rightarrow 2CO_2$	-430	-250
(ii)	$2Fe + O_2 \rightarrow 2FeO$	-415	-280

(4)

We note that eqn. (i) – eqn. (ii) = $2FeO + 2CO \rightarrow 2Fe + 2CO_2$ and so $\Delta G^{\ominus}$ for this reaction is given by $\Delta G^{\ominus}(i) - \Delta G^{\ominus}(ii)$. (1)

At 500°C this gives us (-430) – (-415) = -15 kJ mol^{-1}.(1)

At 1500°C this gives us (-250) – (-280) = +30 kJ mol^{-1}. (1)

These figures tell us that carbon monoxide can reduce iron(II) oxide to iron at 500°C but not at 1500°C. (1)

b) Suggest why the graphs are essentially straight lines.

The graphs are straight lines because they are graphs of $\Delta G = \Delta H - T\Delta S$, which has the form of a straight line with intercept ΔH and slope $(-\Delta S)$ if their values remain constant over the range of temperature considered. (2)

c) Look up and tabulate the melting and boiling points of Mg, MgO, and O_2, and hence suggest why the line labelled 2MgO consists of two straight line portions.

Substance	Mg	MgO	O_2
m. p. / °C, K	650 / 923	2900 / 3173	-219 / 54
b. p. / °C, K	1117 / 1390	3600 / 3873	-183 / 90

(1)

The line labelled 2MgO consists of two straight line portions because it has a sharp corner (i.e. change of slope) in it at about 1400°C. Since this is very close to the boiling point of Mg it suggests that the change of state of magnesium alters ΔS for the reaction substantially (as well as ΔH). (2)

d) Suggest why the line labelled $2C + O_2 \rightarrow 2CO$ has negative slope and why most of the lines have positive slope.

The line for $2C + O_2 \rightarrow 2CO$ has negative slope because ΔS is positive, since it involves a decrease in the number of moles of gas, and the slope is given by $(-\Delta S)$. Most of the lines have positive slope because ΔS is negative (3)

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. (6)

Look up the standard reduction potentials for

$$Fe^{3+}(aq) + e^{-} \rightarrow F^{2+}(aq) \text{ and}$$
$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

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

$$Fe^{3+}(aq) + Ag(s) \rightarrow F^{2+}(aq) + Ag(s)$$

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

$\Delta G^{\ominus} = -nFE$ (1) and $\Delta G^{\ominus} = -RT\ln K$ (1)

For $Fe^{3+}(aq) + e^{-} \rightarrow F^{2+}(aq)$, $E^{\ominus} = 0.77$ v and for $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$, $E^{\ominus} = +0.80$ v

This means that $E^{\ominus}_{cell}$ for $Fe^{3+}(aq) + Ag(s) \rightarrow F^{2+}(aq) + Ag(s) = E^{\ominus}_{red} - E^{\ominus}_{ox} = 0.77 - 0.80 = -0.03$ v. (1)

$\therefore \Delta G^{\ominus} = -nFE^{\ominus} = -1 \times 96500 \times (-0.03) = 2895 \text{ J mol}^{-1}$ (1)

But $\Delta G^{\ominus} = 2895 = -RT\ln K = -8.31 \times 298 \times \ln K$

$\therefore \ln K = -(2895) / (8.31 \times 298) = -1.169$

$\therefore$ K = 0.3 @ 25°C (2)

5) Write down the defining equations for G, H and the work of expansion, w_{exp}, for a reversible process occurring at constant temperature and pressure. Recognising that work can be split into two categories, w_{exp} (work of expansion against an external pressure) and w_n (work which is not due to expansion), show that for such a process, ΔG represents the amount of non-expansion work involved. (8)

$G = H - TS$ (1), $H = U + PV$ (1), and $w_{exp} = -P_{ex}\Delta V$ (1) (where P_{ex} refers to the external pressure)

At constant temperature and pressure,

$\Delta G = \Delta H - T\Delta S$ (1) and $\Delta H = \Delta U + P\Delta V$ (1) and so substituting for ΔH, we have

$\Delta G = \Delta U + P\Delta V - T\Delta S$ (1)

For a reversible process, $P_{ex} = P$ (pressure of the system) and so $w_{exp} = -P\Delta V$ (1)

$\therefore \Delta G = \Delta U + -w_{exp} - T\Delta S$

Now $\Delta S = q_{rev} / T$

$\therefore \Delta G = \Delta U + -w_{exp} - (Tq_{rev} / T) = \Delta U - w_{exp} - q_{rev}$

But $\Delta U = q + w = q_{rev} + w_{rev}$ (specifically) since the process is reversible.

$\therefore \Delta G = q_{rev} + w_{rev} - w_{exp} - q_{rev}$

$\therefore \Delta G = w_{rev} - w_{exp}$ (1)

Since w_{rev} is the maximum amount of work possible, and w_{exp} is the (minimum) work of expansion, their difference represents the maximum amount of non-expansion work involved, w_n

Hence $\Delta G = w_n$

(Note. This means that ΔG represents the *increase* in G brought about by work done *on* the system, hence w_n is positive when ΔG is positive. Often we are interested in the available work that can be done *by* the system, which is $-w_n$ and $(-w_n)$ is, of course, $(-\Delta G)$. Hence a spontaneous process (one with ΔG negative) is one from which useful work can be extracted.)