Problem: Consider the reaction $2\,NO_2(g) <===> N_2O_4(g)$
Given:

	ΔH°_f (kJ/mol)	S° (J/K mol)
$NO_2(g)$	33.2	240.
$N_2O_4(g)$	9.2	304

Questions to answer:
a) What is ΔG° for the reaction? Is it spontaneous?
b) At what temperature does it change its spontaneity? (indicate > or < for spontaneity to be in effect)
c) What's its K_{eq}?

Solution:
a) Use the equation: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
where: $\Delta H^\circ = \sum\Delta H^\circ_f(prod) - \sum\Delta H^\circ_f(rxts) = (9.2\ kJ/mol) - 2\,(33.2\ kJ/mol) = -57.2\ kJ/mol$
$\Delta S^\circ = 304\ Jmol^{-1}K^{-1} - 2(240.) = -176\ J/molK$
$\Delta G^\circ = -57200\ J/mol - (298K)(-176)\ J/molK = -57200 + 52450 = \textbf{-4750 J/mol}$
spontaneous (ie product favored) since $\Delta G^\circ < 0$

b) For the temperature at which it changes its spontaneity, $\Delta G^\circ = 0$ and so...
So: $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ \implies T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{-57200\ J/mol}{-176\ J/molK} = 325\ K \implies (325-273)K = \textbf{52°C}$

So at 298 K , which is the same as 25°, it is spontaneous. Up to 52°C it is spontaneous.
We can tell because ΔH and ΔS are both negative and when that is the case the graph is:

spontaneous at temperatures below 52°C
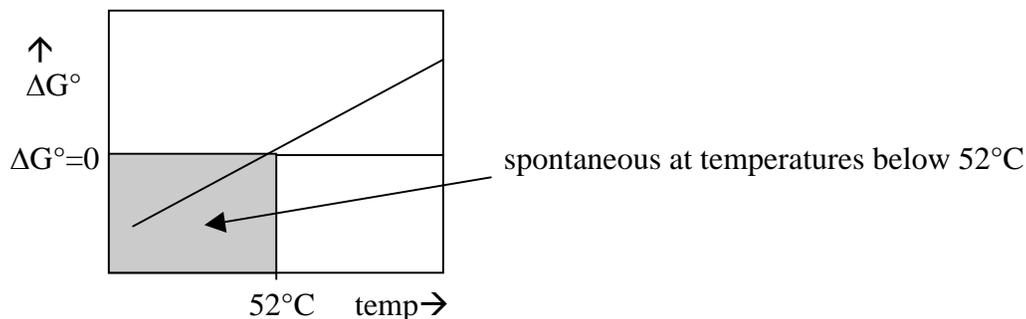
        at T < 52°C, product, N_2O_4 is favored.
 At T > 52°C, reactant, $NO_2(g)$ is favored.
(Note: how to actually draw the graph and how to decide whether it's spontaneous above or below the temperature you calculated)

c) The $\Delta G^\circ = -RT\ln K_{eq} \implies K_{eq} = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-4752\ J/mol)}{(8.314J/molK)(298K)}} = e^{+1.92} = \textbf{6.8}$
This is consistent with the idea that it is product favored (K>1) at 298K.

(To more deeply comprehend implications of (c) note: (i) the signs , (ii) the value of R, i.e. 8.314 J/mol K, (iii) that K>1 for spontaneous and thus product favored reactions).

Share-Pair Quiz2: Wednesday classroom demonstration (not yet graded)
One solution per pair: (have the same pairing as last time if possible)

In today's demonstration an aqueous supersaturated solution of sodium acetate ($NaCH_3CO_2$) was allowed to crystallize. Initially, we have a supersaturated solution which was obtained by heating 28 g of $NaCH_3CO_2*3H_2O$ crystals. We noted that upon reaching 54°C, the crystals dissolved into a liquid, dissolving into its own water of hydration! The solution was allowed to cool down to room temperature. This supersaturated solution was stable enough to bring to class, but upon being pored out of the test tube, it instantaneously crystallized. The thermometer initially read 24°C for the liquid solution, but when it instantaneously solidified, it read 54°C… and no higher.

From what you observed, write down the following:

1) The chemical equation for describing the process observed.

2) deduce the <u>signs</u> of ΔH, ΔG and ΔS for the process of crystallization just observed:
(just say if it's expected to be + or -)

3) Draw a sketch of the graph of ΔG vs T for this observed process.

4) Suppose that you can use the following magnitudes for process of crystallization of $NaCH_3CO_2$, what is the value of K_{eq}
  $| \Delta H° | = 25$ kJ/mol   ; $|\Delta S°| = 45.6$ J $mol^{-1}K^{-1}$

5) What is ΔG for the reaction if T = 500K, assuming that it's at equilibrium?

New Question:
6) What is $\Delta G°$ for the reaction at T =500K?

1) $NaCH_3CO_2(aq) \rightarrow NaCH_3CO_2*3H_2O$ (s)
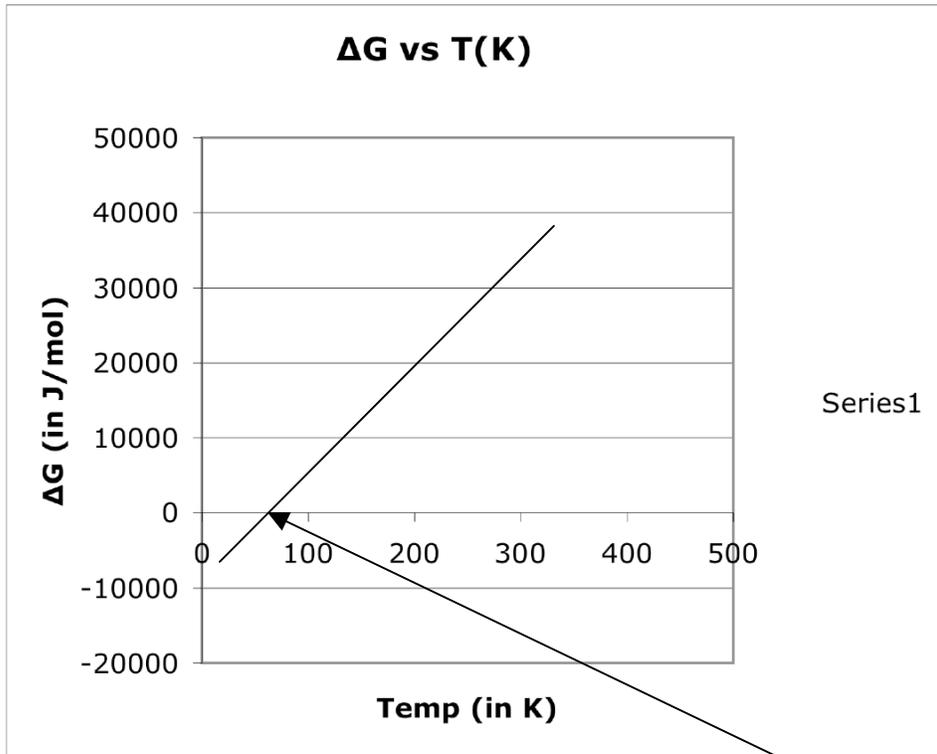2) ΔH is negative (exothermic since it got hotter to the touch),
ΔG is negative since it was quite spontaneous.
ΔS is negative since the process of converting from a liquid to a solid increases the order of the system and therefore $\Delta S = S_{final} - S_{initial} =$ negative since S_{final} is less than $S_{initial}$.

3) The ΔG vs T(K) graph looks like that below:

It is seen that the conversion of sodium acetate solution to sodium acetate crystals is spontaneous only below a certain temperature. That temperature is 54°C from our class data.

4) OK, ΔH°=-25000 J/mol, ΔS° = -45.6 J mol^{-1}K^{-1} (remember that the reaction was **exo**thermic and felt hot to the touch, and that the liquid crystallized into a solid).
so $\Delta G° = \Delta H° - T\Delta S° = -25000$ J/mol $-(298K)(-45.6$ J mol^{-1}K^{-1})
$= -25000$ J/mol $+13590$ J/mol $= -11,400$ J/mol $= -11.4$ kJ/mol
$$K = \exp(-\frac{\Delta G°}{RT}) = \exp(-\frac{-11400J/mol}{(8.314J/molK)(298)}) = 100$$
5) $\Delta G = 0$ (since it's at equilibrium).

6) $\Delta G° = \Delta H° - T\Delta S° = -25,000$ J/mol $-(500K)(-45.6$ J/molK) $= -2200$ J/mol $= -2.2$ kJ/mol.