Chem Factsheet

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The Gibb's Free Energy Change and Spontaneity

Before studying this Factsheet you need to understand:
1. Enthalpy changes of reaction, ΔH
2. Entropy (S) and entropy changes of reaction, ΔS.

After studying this Factsheet you should be confident about deciding if a chemical reaction or a physical change is spontaneous or non-spontaneous.

The word "spontaneous" means "energetically possible" or "feasible without the input of energy". "Spontaneous" **does not** mean quick or immediate; in fact no statement can be made about the rate of the reaction since there is no relationship between activation energy, which controls rate, and spontaneity.

A spontaneous chemical reaction may be defined in terms of the Standard Gibbs free energy change, ΔG.

Under standard conditions, ΔG is related to the enthalpy change, ΔH, the temperature, T and the entropy change, ΔS, by:

> **$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$**
> **A reaction is spontaneous if, and only if, $\Delta G^\ominus < o$**

Note : $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$ refer to those changes for the **reacting system** and are sometimes written as $\Delta H^\ominus_{sys}$, $\Delta S^\ominus_{sys}$ and $\Delta G^\ominus_{sys}$. In particular, this aims to differentiate $\Delta S^\ominus_{sys}$ and $\Delta S^\ominus_{surr}$ where $\Delta S^\ominus_{surr}$ is the entropy change occurring in the **surrounds** of a reacting system and ***caused*** by the reacting system.

We will consider four possible combinations of ΔH and ΔS (excluding ΔH or ΔS being zero).

	$\Delta H^\ominus$	$\Delta S^\ominus$	$-T\Delta S^\ominus$	$\Delta G^\ominus = \Delta H^\ominus + (-T\Delta S^\ominus)$
1	- ve (exothermic)	+ ve	- ve	**ΔG = (-ve) + (-ve)** ΔG is - ve at all temperatures. Such reactions are always spontaneous. **Increasing** the temperature makes ΔG even more negative because $-T\Delta S$ gets more negative.
	e.g. $CH_4(g) + 1\frac{1}{2}O_2(g) \rightarrow CO(g) + 2H_2O(g)$			
2	- ve (exothermic)	- ve	+ ve	**ΔG = (-ve) + (+ve)** ΔG is - ve providing ΔH is more negative than $-T\Delta S$ is positive. **Decreasing** the temperature makes $-T\Delta S$ less positive and this favours ΔG being negative.
	e.g. $Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)$			
3	+ ve (endothermic)	- ve	+ ve	**ΔG = (+ve) + (+ve)** ΔG is + ve at all temperatures. These reactions can **never** be spontaneous. No change of T or P can cause ΔG to become negative!
	e.g. $CO(g) + 2H_2O(g) \rightarrow CH_4(g) + 1\frac{1}{2}O_2(g)$			
4	+ ve (endothermic)	+ ve	- ve	**ΔG = (+ve) + (-ve)** ΔG is - ve providing $-T\Delta S$ is more negative than ΔH is positive. **Increasing** the temperature makes $-T\Delta S$ more negative and this favours ΔG being negative.
	e.g. $H_2O(l) \rightarrow H_2O(g)$ at a temperature of 100^0C or greater.			

Note 1. The statements about changing the temperature assume that ΔH and ΔS remain constant as temperature changes.

Note 2. For a reaction involving gases, increasing the pressure favours the reaction where there is a decrease in the number of moles of gas since the **entropy decrease is less** when the molecules are more closely packed together.

Note 3. Using standard enthalpy changes and standard entropies gives a value of the standard Gibb's free energy change. If this is negative but the reaction actually fails to be spontaneous it may be because the conditions are **non-standard** and the wrong values of ΔH and S have been used.

Note 4. If ΔG is clearly negative but the reaction is not seen to occur, it may be that the reaction has a high activation energy causing it to be so slow that it occurs at a negligible rate. This is described as "kinetic control" or "kinetic stability".

Note 5. Look at cases 2 and 4 and note the relationship to Le Chatelier's Principle which predicts, but does not explain, that higher temperatures cause a shift in the endothermic direction in an equilibrium reaction, whereas lower temperatures favour the exothermic direction.

Deciding the +ve or –ve nature of the enthalpy change for the reaction, ΔH

1. May be provided in the question as an actual value.
2. May be indicated in the question by a written statement. e.g. "the test-tube became hot" suggests an exothermic reaction.
3. May be calculated via an enthalpy cycle using Hess's Law.
4. May be estimated via a calculation using mean bond enthalpies.
5. May be calculated if the entropy change for the **surroundings** is given since $\Delta H = -T\Delta S_{Surr} / 1000$
6. May be indicated by the type of reaction. e.g. combustions are all exothermic; decompositions are endothermic with very few exceptions; neutralisations are exothermic.
7. May be deduced from combinations of information about spontaneity of the reaction and the nature of ΔS. e.g. if the question says "the reaction **occurs** and the entropy change for the system is **negative**", ΔH must be negative and more negative than -TΔS is positive, so ΔG is –ve.

Deciding the +ve or –ve nature of the entropy change of the system, ΔS

1. May be provided in the question as an actual value.
2. May be calculated from the entropies of the reactants and products if they are provided using :
   $\Delta S = \Sigma S(\text{Products}) - \Sigma S(\text{Reactants})$.
3. May be deduced by considering the equation and looking for such factors as changes in the numbers of moles and changes in state.

   e.g. 1. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
   ΔS is –ve since the moles of **gases** decreases, 6 to 3.

   e.g. 2. $[Cu(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [Cu(EDTA)]^{2-}(aq) + 6H_2O(l)$
   ΔS is + ve because of an increase in the number of particles in solution, 2 to 7.

   e.g. 3. $KCl(s) + (aq) \rightarrow K^+(aq) + Cl^-(aq)$
   ΔS is + ve since the ions move randomly in solution and vibrate about a fixed point in the solid state.

> Note. Deciding whether the entropy change is positive or negative when a substance dissolves in water is not straight forward since some of the water molecules are attracted to and ordered around the ions. The higher the charges on the ions the greater their hydration numbers and hence the lower the sum of the entropies of the products.

4. May be deduced from combinations of information about spontaneity of the reaction and the nature of ΔH. e.g. if the question says "a reaction **occurs** and is **endothermic**", ΔS must be + ve so that -TΔS is –ve enough to outweigh the +ve ΔH, giving a –ve ΔG.

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Practice Questions

1. Consider the reaction: $2Na(s) + \frac{1}{2}O_2(g) \rightarrow Na_2O(s)$

   (a) Explain why this reaction is spontaneous at 298K even though the entropy change for the system is negative.

   (b) Assuming no changes in ΔH and ΔS, explain how the temperature should be changed to favour the decomposition of sodium oxide?

2. When titanium is manufactured by the Kroll process the two reactions are:

   $TiO_2(s) + 2Cl_2(g) + 2C(s) \rightarrow TiCl_4(g) + 2CO(g)$ - - - - (1)

   and $TiCl_4(g) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(l)$ - - - - (2)

   (a) For which reaction will the entropy change of the system be negative? Explain your answer.

   (b) For which reaction will increasing the temperature make ΔG more negative? Explain your answer and state any assumptions made?

3. Predict and explain the signs of the (a) enthalpy change, (b) entropy of the system change, (c) Gibb's free energy change for the following reaction. If any of the predictions cannot be made explain why.
   $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$

4. Consider the following reaction:
   $3KClO_4(s) + KCl(s) \rightarrow 4KClO_3(s) \quad \Delta H^\ominus = -16.8\ kJ\ mol^{-1}$.

   The standard molar entropy, $S^\ominus$, (in units of $JK^{-1}mol^{-1}$) for each substance is: KCl(s) 83, $KClO_3(s)$ 112, $KClO_4(s)$ 134.

   (a) Why does potassium chlorate(VII) have the highest entropy?

   (b) Calculate the standard entropy change for the reaction.

   (c) Calculate the standard free energy change at 298K for the above reaction.

   (d) In terms of the standard free energy change explain if the above reaction is spontaneous at 298K.

   (e) Explain why no noticeable reaction occurs at 298 K.

   (f) Assuming that ΔH and ΔS do not vary with temperature calculate the temperature at which the reaction will fail to be feasible.

Answers. (One ✓ is one mark)

1. (a) The reaction must be exothermic ✓. ΔH must be more negative than -TΔS is positive, thus making ΔG < 0. ✓
   (b) Increase the temperature. ✓ To make -TΔS more negative than ΔH is positive, so eventually making ΔG < 0. ✓

2. (a) Reaction 2. ✓ Explanation: There is a decrease in the number of moles of gas. ✓
   (b) Reaction 1. ✓ Explanation: -TΔS becomes more –ve ✓ so ΔG also becomes more –ve. ✓
   Assumptions: ΔH and ΔS remain constant. ✓

3. (a) Positive. ✓ because 6 bonds to copper are broken, only 4 are formed ✓
   (b) Positive. ✓ because 5 particles change to 7 ✓
   (c) It cannot be decided if $- T\Delta S^\ominus_{Sys}$ is more or less negative than $\Delta H^\ominus$ is positive. ✓
   So the sign of $\Delta G^\ominus$ cannot be decided as $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus_{Sys.}$ ✓

4. (a) Highest molar mass. ✓
   (b) $\Delta S = \Sigma S(Products) - \Sigma S(Reactants)$ ✓ $\therefore \Delta S = 4\,(112) - \{3\,(134) + 83\} = -37\ JK^{-1}mol^{-1}$ ✓
   (c) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus_{Sys}$ ✓ $\therefore \Delta G^\ominus = -16.8 - 298\,(-37/1000)$ ✓ $= -5.8\ kJ\ mol^{-1}$. ✓
   (d) The reaction is spontaneous since $\Delta G^\ominus$ is < 0. ✓
   (e) The reaction is between solids ✓(so no collisions will be occurring) so the rate of the reaction will be low ✓ / zero. (No particles will have energies = ✓ the activation energy as it is too high. ✓)
   (f) $0 = \Delta H - T\Delta S$. ✓ $\therefore T = \Delta H/\Delta S = -16.8 \times 1000 / -37 = 454$ K. ✓ Answer. **Below** 454 K ✓