What makes it go?

Introduction

This problem could be used immediately before students meet Gibbs free energy to demonstrate the inadequacy of the possible explanations. Repeating the problem once students become familiar with the concept demonstrates its utility. Students should use a qualitative approach. However, worked numerical examples are given which could be used as homework for consolidation.

Teachers who have not used the problems before should read the section Using the problems before starting.

Prior knowledge

Discussion can be at one of two levels, depending on whether students are familiar with the Gibbs equation:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

For the third experiment, knowledge of lattice enthalpies/entropies and hydration enthalpies/entropies could form the basis of extension material.

Resources

Data books and textbooks (physical and inorganic) should be available for reference.

The following is also required:

- for the first experiment, magnesium ribbon;
- for the second experiment (after 10–20 minutes), citric acid and sodium
- hydrogencarbonate along with small (100 cm^3) beakers;
- for the third experiment, ammonium nitrate and more small beakers;
- for the second and third experiments, thermometers (–10 to 110 °C).

Group size

3.

Risk assessment

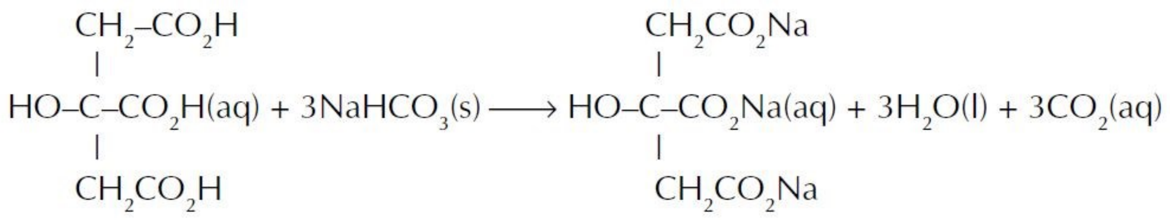
A risk assessment must be carried out for this problem.

Special safety requirements

Students should not look directly at burning magnesium.

Equations

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$



$$\begin{array}{c}\mathrm{CH_2{-}CO_2H}\\ | \\ \mathrm{HO{-}C{-}CO_2H(aq)}\\ | \\ \mathrm{CH_2CO_2H}\end{array} + 3\mathrm{NaHCO_3(s)} \longrightarrow \begin{array}{c}\mathrm{CH_2CO_2Na}\\ | \\ \mathrm{HO{-}C{-}CO_2Na(aq)}\\ | \\ \mathrm{CH_2CO_2Na}\end{array} + 3\mathrm{H_2O(l)} + 3\mathrm{CO_2(aq)}$$

$$NH_4NO_3(s) \longrightarrow NH_4NO_3(aq)$$

The first reaction is exothermic, the other two are endothermic.

Possible answers

a. From students who are unfamiliar the Gibbs equation

Most reactions are exothermic and are seen by students as ‘running down energy hills’ analogous to an object falling under gravity to a position of minimum potential energy. The most useful discussion can take place when they try to interpret the endothermic reactions and to look for the unusual in them in order to try to devise alternative explanations.

Burning magnesium

This is identified as an exothermic reaction, one moving to a position of minimum energy. The heat supplied is the activation energy needed to start the reaction.

Reaction between citric acid and sodium hydrogencarbonate

What is unusual here? The evolution of copious quantities of gas. Could this be the driving force?

Dissolving ammonium nitrate in water

There is nothing unusual here. Dissolving involves breaking the lattice and hydration of the ions. Clearly, the lattice energy has a larger absolute value than the ion hydration energies, but this does not explain why the reaction takes place.

b. From students who are familiar with the Gibbs equation

$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$

Burning magnesium

ΔH^θ is large and negative (favourable)

ΔS^θ is negative because of the gas being used up (unfavourable)

ΔH^θ is the larger of the two factors at the temperature concerned and makes ΔG^θ negative.

Reaction between citric acid and sodium hydrogencarbonate

ΔH° is positive (unfavourable)

ΔS° is positive because of the evolution of gas (favourable)

$T\Delta S^\circ$ is the larger of the two factors at room temperature and makes ΔG° negative.

Dissolving ammonium nitrate in water

ΔH° is positive (unfavourable)

ΔS° must be positive for the reaction to go

$T\Delta S^\circ$ is the controlling factor, and makes ΔG° negative.

There is more order in the lattice than there is in the solution of the hydrated ions. Some salts dissolve endothermically as in this case, some dissolve exothermically, and others are thermally neutral, such as sodium chloride.

Suggested approach

During trialling the following instructions were given to students and proved to be extremely effective:

1. Working as a group, carry out the first experiment.
2. As a group, discuss the change. What is the driving force that makes it go? Such discussion can play a vital part in working out solutions to problems like these. Several minds working on a problem together can stimulate ideas that one on its own could not manage.
3. Write up in note form what your group decided. Say what the driving force is and explain it with reference to this change.
4. Repeat steps 1 to 3 for the second experiment.
5. Repeat steps 1 to 3 for the last experiment.
6. Working as a group, prepare a short (ca 5-minutes maximum) presentation to give to the rest of the class. If possible, all group members should take part: any method of presentation (such as a blackboard, overhead projector, etc) can be used.

Outline the problem and describe what you did. Details of the practical work are not needed, but explain what you decided was the driving force for each change. After the presentation, be prepared to accept and answer questions and to discuss what you did with the rest of the class.

Background information

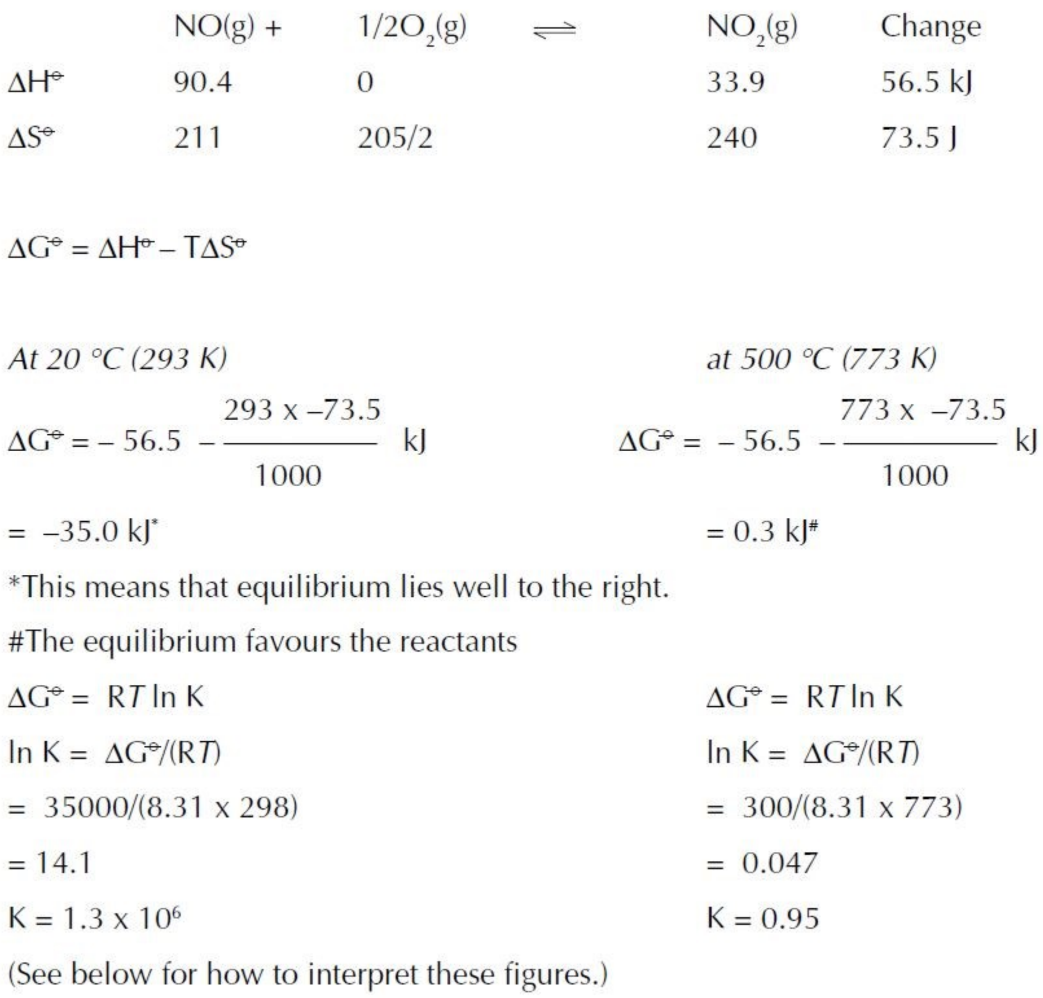
The following ‘thought experiments’ can reinforce the ideas discussed above. One approach is to give the students one or more of these problems to think about in advance, perhaps asking for calculations to be done, and then discussing what the driving force is in each case.
This can help to develop an understanding of the concept of ‘feasibility’.

1. $2NO(g) + O_2(g)\ 2NO_2(g)$

a. NO combines spontaneously with oxygen in air at room temperature to give NO^2.
ΔS^{θ} is negative (more gas moles on LHS – unfavourable)
ΔG^{θ} is negative (favourable)
ΔH^{θ} must be negative, and the reaction is enthalpy driven.
ΔH^{θ} is the larger of the two factors at room temperature and drives the reaction by making ΔG^{θ} negative.

b. However, at 500°C ΔG^{θ} is positive and the equilibrium constant <1, because of the increased effect of the T in the $T\Delta S^{\theta}$ term. This can lead to useful discussion.

Students can look up the figures in a data book and calculate ΔG^{θ} at the two temperatures (see below), and then use the figures to consider what is meant by saying that the reaction is ‘feasible’ or ‘not feasible’.



	$NO(g)$ +	$1/2O_2(g)$	$\rightleftharpoons$	$NO_2(g)$	Change
$\Delta H^{\ominus}$	90.4	0		33.9	56.5 kJ
$\Delta S^{\ominus}$	211	205/2		240	73.5 J

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

At 20 °C (293 K)

$$\Delta G^{\ominus} = -56.5 - \frac{293 \times -73.5}{1000} \text{ kJ}$$

$= -35.0$ kJ*

at 500 °C (773 K)

$$\Delta G^{\ominus} = -56.5 - \frac{773 \times -73.5}{1000} \text{ kJ}$$

$= 0.3$ kJ#

*This means that equilibrium lies well to the right.

#The equilibrium favours the reactants

$\Delta G^{\ominus} = RT \ln K$

$\ln K = \Delta G^{\ominus}/(RT)$

$= 35000/(8.31 \times 298)$

$= 14.1$

$K = 1.3 \times 10^6$

$\Delta G^{\ominus} = RT \ln K$

$\ln K = \Delta G^{\ominus}/(RT)$

$= 300/(8.31 \times 773)$

$= 0.047$

$K = 0.95$

(See below for how to interpret these figures.)

2. Discuss how solid carbon dioxide changes to a gas at –78 °C. (ΔG^{θ} is negative, ΔH^{θ} positive and ΔS^{θ} positive (solid → gas), so the reaction is entropy driven.)

At this temperature the solid and the gas co-exist because the vapour pressure of the solid is one atmosphere. This is similar to water and water vapour co-existing at 100°C because the vapour pressure of the liquid is one atmosphere.

In both cases, students should consider what difference it makes if the changes occur in a closed vessel that is initially evacuated, or in the open.

3. Discuss why the reaction

carbon dioxide + water → starch + oxygen

takes place in living plants, while the reverse occurs in animals.

4. A discussion of the difference between water evaporating at room temperature and boiling at 100°C can provide further insight.

	$H_2O(l)$	$\rightleftharpoons$	$H_2O(g)$	Change
$\Delta H^\ominus$	–285.8		–241.8	44.0 kJ
$\Delta S^\ominus$	69.9		188.7	118.8 J

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

At 20 °C (293 K)

$$\Delta G^\ominus = 44.0 - \frac{293 \times 118.8}{1000}\ \text{kJ}$$

$$= 9.2\ \text{kJ}$$

$$\Delta G^\ominus = -RT \ln K$$

$$\ln K = \Delta G^\ominus / RT$$

$$= \frac{-9200}{8.31 \times 293}$$

$$= -3.78$$

$$K = 0.023$$

at 100 °C (373 K)

$$\Delta G^\ominus = 44.0 - \frac{373 \times 118.8}{1000}\ \text{kJ}$$

$$= -0.30\ \text{kJ}$$

$$\Delta G^\ominus = -RT \ln K$$

$$\ln K = \Delta G^\ominus / RT$$

$$= \frac{300}{8.31 \times 373}$$

$$= 0.097$$

$K = 1.1$ (but see below)

Interpreting the numbers

a. Consider the change $H_2O(l) \rightarrow H_2O(g)$ at 20 °C and one atmosphere pressure; $\Delta G^\theta = 9.2$ kJ and K = 0.023.

The fact that the change is not feasible simply means that at this temperature liquid water is not in equilibrium with water vapour at one atmosphere pressure. Liquid water is converted to vapour but the vapour pressure is less than one atmosphere:

K = activity of $H_2O(g)$ divided by the activity of $H_2O(l)$
= vapour pressure of $H_2O(g)$ divided by unity

Thus vapour pressure of water vapour is 0.023 atmosphere, or 17.5 mm mercury.

The equilibrium favours liquid water.

In a closed system, liquid water does not change completely to vapour as ΔG^θ is positive. Vapour will be in equilibrium with the liquid at below atmospheric pressure.

In the open, the vapour will diffuse away and eventually all the liquid will change to vapour. This is not an equilibrium situation. Similar principles apply to the vaporisation of solid carbon dioxide.

Thus ΔG^{θ} does not have to be negative for a change to take place. ΔG^{θ} only indicates the final position of equilibrium, but where the product is being continually removed as in an open system, there is no equilibrium. The Haber process is another good example of this.

b. Consider the same change but at 100°C

$H_2O(l) \rightarrow H_2O(g)$ at 100°C and one atmosphere pressure;
$\Delta G^{\theta} = 0.09$ kJ and $K = 1$.

In a closed vessel, water will be in equilibrium with vapour at one atmosphere pressure. In an open system, for example when a kettle boils, the vapour is removed and again there is no equilibrium.

NB The value of ΔGθ calculated above for the vaporisation of water → vapour at 100°C and one atmosphere pressure is –0.3 kJ. It should be exactly zero, becoming negative above 100°C. The discrepancy arises from the fact that ΔH^{θ} and ΔS^{θ} are measured at 298 K, and they vary slightly with temperature. When this variation is taken into account ΔG^{θ} is precisely zero and K = 1. The calculation is included below for reference.

Calculation of DG$^{\ominus}{}_{373}$ for water to water vapour

In this problem, the more familiar unit of atmospheres has been used in place of bar.

$H_2O(l) \rightleftharpoons H_2O(g)$

	$\Delta H^{\ominus}{}_{373}$	$C_p^{\ominus}$ (J K^{-1} mol^{-1})	$S^{\ominus}{}_{298}$ (J K^{-1}mol^{-1})
$H_2O(l)$	–258.8	75.29	69.91
$H_2O(g)$	–241.8	33.58	188.83
change	44.0	–41.71	–

Data from P. W. Atkins, *Physical Chemistry*, 4th ed, Oxford: Oxford University Press, 1990.

$H_2O(l) \longrightarrow H_2O(g)$

$\Delta G^{\ominus}{}_{373} = \Delta H^{\ominus} - T\Delta S^{\ominus}{}_{373}$ ($T = 373$ K)

$\Delta H^{\ominus}{}_{373} = \Delta H^{\ominus}{}_{298} + (\Delta C_p^{\ominus} \times \Delta T)/1000$

$= \Delta H^{\ominus}{}_{298} + \{(41.71) \times 75/1000\} = 44.0 - 3.1$

$= 40.9$ kJ

$S^{\ominus}{}_{373}$ for $H_2O(l) = S^{\ominus}{}_{298} + \int_{273}^{373} C_p \, dT/T$

$= 69.91 + 75.29 \ln (373/298)$
$= 69.91 + 16.90$
$= 86.81$ J mol^{-1} K^{-1}

Similarly

$S^{\ominus}_{373}$ for $H_2O(g) = 188.83 + 33.58 \ln(373/298) = 188.83 + 7.54$

$= 196.37\ \text{J mol}^{-1}\ \text{K}^{-1}$

Thus
$\Delta S^{\ominus}_{373} = S^{\ominus}_{373}$ for $H_2O(g) - S^{\ominus}_{373}$ for $H_2O(l)$

$= 196.37 - 86.81\ \text{J mol}^{-1}\ \text{K}^{-1}$
$= 109.56\ \text{J mol}^{-1}\ \text{K}^{-1}$

Hence $\Delta G^{\ominus}_{373} = \Delta H^{\ominus}_{373} - T\Delta S^{\ominus}_{373}$ $(T = 373\ \text{K})$

$= 40.9 - 373 \times 109.56/1000 = 40.9 - 40.9$
$= 0.0\ \text{kJ}$

$$\text{Thus } K = \frac{a(H_2O,\ g)}{a(H_2O,l)} = 1 \text{ exactly } (a = \text{activity})$$

Water vapour at one atmosphere pressure is in equilibrium with liquid water at this temperature.

Notes

1. D. Druce, School Science Review, 1983, **65**, 329.
2. There is a fine dividing line between over-simplifying the thermodynamics and offering explanations that are too complex for the age group concerned. In particular, the difference between ΔG^{θ} and ΔG, although of fundamental Importance, should not be dealt with here. However, the importance of standard state has been emphasised at appropriate points.
3. One bar is defined as a pressure of exactly $1 \times 10^5\ \text{N m}^{-2}$. One atmosphere is a pressure of $1.01325 \times 10^5\ \text{N m}^{-2}$. This means that water will boil at slightly under 100°C at a pressure of one bar.

What makes it go?

The following experiments should be carried out in this order.

(i) Burn a 5 cm length of magnesium ribbon.
(ii) React citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) and sodium hydrogencarbonate (one level teaspoon of each) in 20 cm^3 water.
(iii) Dissolve ammonium nitrate (one level teaspoon) in 20 cm^3 water.

Then without doing any calculations, explain what the driving force of the reaction is in each case – ie qualitatively rather than quantitatively.

You should refer to any sources of information that you think might help such as your notebooks, textbooks and data books. Ask for assistance if you get stuck.

Safety

Normal safety procedures when handling chemicals should be adhered to and eye protection worn. Do not look directly at burning magnesium.
You must get your method checked for safety before starting on the practical work.