23.4 GIBBS FREE ENERGY CHANGE

Learning outcomes

Candidates should be able to:

1. state and use the Gibbs equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
2. perform calculations using the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
3. state whether a reaction or process will be feasible by using the sign of ΔG
4. predict the effect of temperature change on the feasibility of a reaction, given standard enthalpy and entropy changes
5. Describe and explain qualitatively the trend in the thermal stability of the nitrates and carbonates, including the effect of ionic radius on the polarisation of the large anion

Introduction

The words *spontaneous* and *feasible* both mean 'likely to happen'. We use the word feasible for chemical reactions. The word spontaneous is a more general term and applies to physical processes such as diffusion and dissolving as well.

In determining whether a chemical reaction is likely to be spontaneous, we use the quantity Gibbs' free energy change ΔG. It is given by the relationship:

$$\Delta G^{\ominus} = -T.\Delta S^{\ominus}_{total}$$

Derivation

In a chemical reaction, we have to consider the entropy changes that occur both in the system (the reaction that is happening) and in the surroundings (which absorb or release heat). Many chemical reactions are exothermic, and the increase in entropy of the surroundings more than compensates for any decrease in entropy that may be occurring in the system.

We have:

$$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surroundings}$$

$$\Delta S^{\ominus}_{surroundings} = \frac{q}{T} = \frac{-\Delta H^{\ominus}}{T}$$

It is always possible to calculate the total entropy change from these two terms, but it is more convenient if they are combined together in a single function. This function is called the Gibbs free energy function.

It is a measure of the total entropy increase associated with the reaction and a measure of the driving force of that reaction. If the reaction has a decrease in free energy, it is feasible. We have:

$$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surroundings}$$

$$or, \quad \Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} - \frac{\Delta H^{\ominus}}{T}$$

$$or, \quad T.\Delta S^{\ominus}_{total} = T.\Delta S^{\ominus}_{system} - \Delta H^{\ominus}$$

$$or, \quad -T.\Delta S^{\ominus}_{total} = \Delta H^{\ominus} - T.\Delta S^{\ominus}_{system} \qquad [\Delta G^{\ominus} = -T.\Delta S^{\ominus}_{total}]$$

This equation can be written in the more familiar form:

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

Gibbs' Free Energy: the energy change that takes into account both the entropy change of a reaction and the enthalpy change. This is shown by the Gibbs equation above.

PHYSICAL MEANING of ΔG

−ΔG represents the maximum useful energy a reaction can supply to do work — power a muscle, drive a motor, push electrons round a circuit. It's the chemistry behind every battery and every meal you eat.

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

The entropy increase associated with a decrease in $\Delta G^{\ominus}$ can be given another interpretation. Whereas $-\Delta H^{\ominus}$ is a measure of the total heat energy q lost from the system, $-\Delta G^{\ominus}$ is the maximum amount of that total energy that is available to do work.

The unit of $\Delta G^{\ominus}$ is generally kJ mol^{-1}

In calculations involving the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus}_{system}$, don't forget to multiply the value of $\Delta H^{\ominus}$ by 1000 if $\Delta H^{\ominus}$ is in kJ. This is because the units of $\Delta S^{\ominus}$ are in joules per kelvin per mole.

Note that for any enthalpy change, e.g. enthalpy change of formation, or enthalpy change of reaction, you can get a corresponding Gibbs free energy change, e.g. $\Delta G^{\ominus}_{f}$ or $\Delta G^{\ominus}$ reaction. The Gibbs free energy change you will be using will usually be the Gibbs free energy change of formation.

If you are doing a calculation to find $\Delta G^{\ominus}$reaction, you do not have to draw an energy cycle unless asked. Just use **$\Sigma\Delta G^{\ominus}$reaction = $\Sigma\Delta G^{\ominus}$products − $\Sigma\Delta G^{\ominus}$ reactants**

Gibbs free energy changes equation calculations reaction feasibility, Extraction of Metals, cell emf GCE A level chemistry revision notes

Prediction of feasibility

We can use this ΔG *value* as follows:

» if ΔG is negative, the reaction is feasible

» if $\Delta G = 0$, the reaction is in equilibrium

» if ΔG is positive, the reaction will not go spontaneously to completion.

The Pluses and Minuses of Enthalpy, Entropy and Free Energy

Predicting the effect of temperature on the feasibility of a reaction

Since $\Delta G = \Delta H - T\Delta S$, the sign of ΔH and ΔS between them decide when (if ever) a reaction becomes feasible:

ΔH	ΔS	Feasible when…	Real examples
+	+	High T only (entropy-driven)	Melting, boiling, thermal decomposition, electrolysis
−	−	Low T only (enthalpy-driven)	Freezing, condensation, precipitation, addition reactions
−	+	All temperatures — always spontaneous	Combustion, explosions, ozone decomposition
+	−	Never spontaneous on its own	Photosynthesis (needs sunlight to drive it)

Bringing the table to life

- Decomposition of $CaCO_3$ ($\Delta H > 0$, $\Delta S > 0$): $\Delta G = +131$ kJ mol^{-1} at 298 K (not spontaneous) but $\Delta G = -64$ kJ mol^{-1} at 1500 K (spontaneous) — exactly why lime kilns must be so hot.
- Hydrogenation of ethene ($\Delta H < 0$, $\Delta S < 0$): feasible at room temperature, but less so as temperature rises.
- Ozone decomposition ($\Delta H < 0$, $\Delta S > 0$): spontaneous at every temperature — this is precisely why ozone is so unstable.
- Photosynthesis ($\Delta H > 0$, $\Delta S < 0$): ΔG is always positive, so plants must constantly feed in sunlight energy to force the reaction to occur.

Thermal stabilities of nitrates and carbonates

The carbonates and nitrates of Group 2 require increasingly higher temperatures before they break down. If we look at the general reactions

$MCO_3(s) \rightarrow MO(s) + CO_2(g)$

and

$M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + 1/2O_2(g)$

We can see that the entropy change for both reactions will be positive because one mole of each carbonate releases one mole of gas, and one mole of each nitrate releases two and half moles of gas.

Because the number of moles of gas evolved is the same for all the carbonates, their entropy change of decomposition should be similar; a similar argument applies to the entropy change of decomposition for all the nitrates.

This means that their enthalpy changes largely determine the ease of decomposition of the carbonates and nitrates. This is shown by the data in Tables 22.6 and 22.7.

	Mg	Ca	Sr	Ba
ΔH/kJ mol^{-1}	+100.3	+178.3	+234.6	+269.3
ΔG/kJ mol^{-1}	+ 48.3	+130.4	+184.1	+218.1
ΔS/J K−1 mol^{-1}	+174	+161	+168	+172

▲ **Table:** Values of ΔH, ΔG and ΔS for the decomposition of the Group 2 carbonates

ΔH/kJ mol^{-1}	+255.4	+369.7	+452.6	+505.0
ΔG/kJ mol^{-1}	+122.7	+241.8	+320.8	+374.2
ΔS/J K−1 mol^{-1}	+445	+429	+442	+439

▲ **Table:** Values of ΔH, ΔG and ΔS for the decomposition of anhydrous Group 2 nitrates.

Group 2 nitrates are usually obtained as hydrated salts, which will make the actual values different, but the general trend should remain the same.

At room temperature, ΔG for all the reactions is positive. If we assume that the values of ΔH and ΔS do not change much with temperature, ΔG will approach zero when $T\Delta S \approx \Delta H$. The temperature at which this occurs will be lowest when ΔH has the smallest positive value, that is, at the top of the group. This agrees with the observation that the carbonates and nitrates at the top of the group decompose at a lower temperature than those at the bottom.

The reason why ΔH becomes more positive as the proton number increases is that the size of the cation increases. During decomposition, the large carbonate and nitrate ions are converted into oxide ions at the same time as carbon dioxide or nitrogen dioxide and oxygen are being given off. The ease

with which this happens is affected by the cations that are next to the carbonate or nitrate ions. The two charges on the small magnesium cation create a much stronger electrostatic field than the two charges on the much larger barium cation. We say that the magnesium ion has a higher charge density.

This high charge density changes the shape of the anion, making it more like the shapes of the products (look at the following figure). This change in the shape of the anion is most marked when the anion is large, and its electrons are not so firmly attracted to the nucleus. We say that the carbonate and nitrate ions are easily polarised.

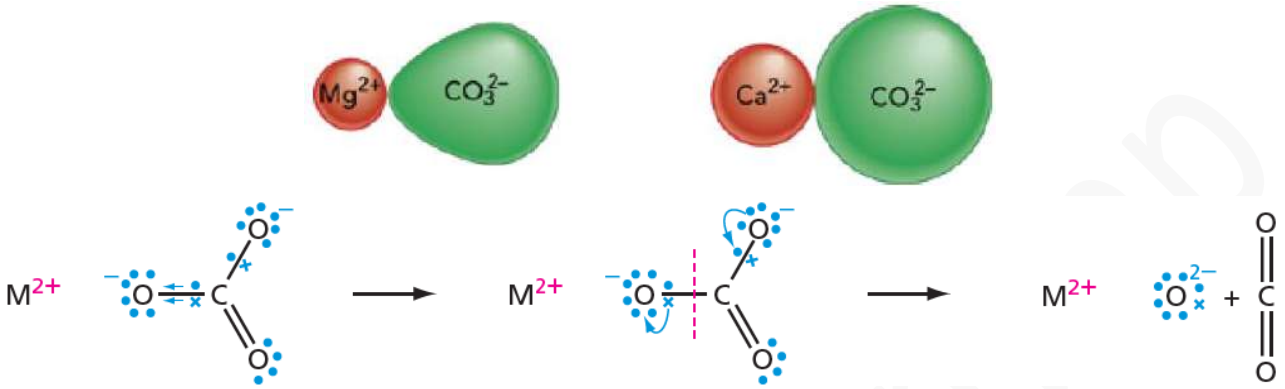

Figure: The small magnesium ion has a high charge density and changes the shape of the carbonate ion to a greater degree than does the much larger barium ion. A similar change in shape happens with the nitrate ion.

Why does the thermal stability of Group 2 metal carbonates increase down the group?

1. Describe the variation in the thermal stability of Group 2 carbonates. Explain your answer. [3]

Marking Scheme
M1 increases (down the group)
M2 (cation)ionic radius/ion size **increases** (down the group) **OR** charge density of M^{2+} **decreases**
M3 less polarisation/distortion of anion/carbonate ion / CO_3^{2-}

2. The carbonates and hydroxides of Group 2 elements show similar trends in thermal stability.
Suggest and explain the variation in the trend in the thermal stability of the Group 2 hydroxides. [3]

Marking Scheme
M1: increases down the group
M2: radius/size of (cat)ion / M^{2+} increases
M3: less polarisation / distortion of anion / hydroxide ion **/** hydroxide group / OH^- / OH

3. The lattice energy of the Group 2 carbonates, $\Delta H^\circ_{latt}(MCO_3)$, becomes less exothermic down the group.
The lattice energy of the Group 2 oxides, $\Delta H^\circ_{latt}(MO)$, also becomes less exothermic down the group.
$\Delta H^\circ_{latt}(MCO_3)$ and $\Delta H^\circ_{latt}(MO)$ change by different amounts going down the group.
Suggest how the standard enthalpy change of the decomposition reaction for Group 2 carbonates changes down the group.
Explain your reasoning in terms of the relative sizes of the anions and the relative changes in lattice energy down the group. [2]

Marking Scheme
- (ΔH_{decomp} / it) becomes more positive/less negative (down the group)
- size /(ionic) radii of oxide ion is smaller (than carbonate ion) ORA
- so ΔH_{latt} of oxides becomes ORA less exothermic, faster OR less negative, faster OR changes more]

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