Chem Factsheet

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Introduction

The energetic feasibility (also called spontaneity) of a chemical reaction was originally assessed using the enthalpy change (ΔH) of the reaction.

Note: "Energetic feasibility" should not be confused with "kinetic feasibility" which refers to how fast a reaction can happen, rather than whether it can happen at all. Kinetic stability is controlled by the activation energy (E_a) of the reaction – the reactants are more kinetically stable with respect to the products as the activation energy for the reaction increases.

Exothermic (ΔH negative) reactions were considered more likely to be energetically feasible because this would involve a decrease in energy content and so achieve a more stable state on proceeding from reactants to products.

The converse applied to endothermic reactions. However, many reactions were noticed to occur very easily at room temperature, even though they were endothermic $(\Delta H$ positive)!

e.g.1 $H_2O(s) \to H_2O(l)$; $\Delta H = +6$ kJ mol⁻¹ e.g.2 $\text{HCO}_3(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$; $\Delta \text{H} = +73 \text{ kJ} \text{mol}^{-1}$

It was noticed that, apart from being endothermic, these reactions all showed an increase in disorder (chaos) on proceeding from reactants to products.

In example 1, an ordered lattice of water molecules in ice becomes the more disordered liquid water where the molecules are relatively free to move around.

In example 2, a solution containing relatively disordered free moving ions becomes a gas where the molecules are totally free moving and even more random.

It seemed that this increase in disorder was the "driving force" behind these endothermic reactions. It seemed to be able to "overcome" the fact that these reactions need to absorb energy.

The "degree of disorder" of a single substance (X) is quantified by its standard molar entropy (S^{Θ}_{X}) and measured in J K⁻¹ mole⁻¹. Each substance is assigned a S^o value (usually tabulated at 298K) by measuring the area under an experimental graph of C_p/T against T [C_p = specific heat capacity of the substance in $J K^{-1}$ mole⁻¹ as shown in figure 1.

Q1 The entropy, and hence disorder, of the particles in a substance clearly increase as the temperature increases and the number of moles of the substance increases. The data shown in table 1 also show that

- (a) the transition from solid to liquid to gas involves **DECREASING / INCREASING** entropy / disorder.
- (b) the transition from a less complex to a more complex molecule involves **DECREASING / INCREASING** entropy / disorder.
- Q2 As alluded to earlier, it is the **entropy change** of a reaction (represented by ΔS) that influences the energetic feasibility of a reaction. A reaction is more likely to be energetically feasible if its entropy change is **POSITIVE / NEGATIVE**.

Estimating ΔS **Qualitatively**

Given a balanced equation for a reaction, the nature of its entropy change can be assessed as positive, negative or negligible by looking for any changes in states of matter and/or numbers of moles.

- e.g. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ should show a **negative** ΔS because, states of matter being constant, there is a decrease in the total number of moles from 4 on the left to 2 on the right.
- e.g. $CaCO₃(s)$ \rightarrow $CaO(s)$ + $CO₂(g)$ should show a **positive** ΔS because, with one mole of solid on each side of the equation, there is an increase in the number of moles of gas (very disordered) from 0 on the left to 1 on the right.
- Q3 Using the same ideas, estimate ΔS as positive, negative or negligible for reactions / processes (a) (e).

Estimating ΔS **Quantitatively**

A value for DS can be calculated by summing (Σ) the standard molar entropies (SΘ) of all the **products** of the reaction and subtracting the total molar entropies of the **reactants**.

Note: This is negative which agrees with the qualitative estimate made earlier.

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Note: This is positive which agrees with the qualitative estimate made earlier.

Note: Remember to show the **sign and units** of ΔS.

Where do Δh Values Come From?

ΔH can be measured directly by calorimetry or, more usually by calculation from tabulated ΔH^Θ data, especially standard enthalpies of formation, ΔH_f^{Θ} . The latter is used in a similar way to S^{Θ} data for the calculation of ΔS^{Θ} .

i.e. $\Delta H = \Sigma(\Delta H_f^{\Theta} \text{ all products}) - \Sigma(\Delta H_f^{\Theta} \text{ all reactants})$

Note: As before, remember to show the **sign and units** of ΔH.

Q5 Practice this calculation technique for each of the following reactions:

The Gibbs Free Energy Change

In 1875, Josiah Willard Gibbs introduced a new thermodynamic quantity which combines the enthalpy (ΔH) and entropy (ΔS) changes of the reaction into a single value called the **Gibbs Free Energy Change (**ΔG**)** for the reaction. This gets round the problems involved in using ΔH as a predictor and allows the energetic feasibility of any reaction to be predicted and also, the effects of temperature changes on that energetic feasibility.

Possibly the most important equation in chemistry, the value of ΔG is given by $\Lambda G = \Lambda H - T\Lambda S$ where T is the temperature in Kelvin.

Note: ΔG is almost always stated in kJ mole⁻¹. This is consistent with the units of ΔH but, since the usual units of ΔS are J K⁻¹ mole⁻¹, any value for ΔS **must** to be converted to kJ K⁻¹ mole⁻¹ by dividing by 1000 before substituting into $\Delta G = \Delta H - T\Delta S$.

Having calculated a value of ΔG , the energetic feasibility of a reaction is predicted using:

A reaction **is** energetically feasible if ΔG < 0 (i.e. negative). A reaction **is not** energetically feasible if $\Delta G > 0$ (i.e. positive).

Note: If ΔG = 0, the reaction is at the point of transition between feasible and not feasible. It is at equilibrium. Furthermore, how to change temperature to push the reaction towards feasibility can be predicted (see later).

The ΔG equation will be illustrated using the previous examples where ΔS and ΔH were calculated.

e.g.1 $N_2(g)$ (g) $+$ 3H₂ (g) \rightarrow 2NH₃(g) $\Delta S = -199.3 \text{ J K}^{-1} \text{ mole}^{-1}$ $\Delta H = -92.2 \text{ kJ mole}^{-1}$ $\rightarrow \Delta S = -0.1993$ kJ K⁻¹ mole⁻¹ At 298K, $\Delta G = \Delta H - T \Delta S = (-92.2) - 298(-0.1993) = -32.8 \text{ kJ mole}^{-1}$ At $400K$, $\Delta G = \Delta H - T\Delta S = (-92.2) - 400(-0.1993) = -12.5 \text{ kJ mole}^{-1}$ At $600K$, $\Delta G = \Delta H - T\Delta S = (-92.2) - 600(-0.1993) = +27.4 \text{ kJ mole}^{-1}$

- **Note:** This shows the production of ammonia is energetically feasible at both 298K and 400K but not at 600K. The transition temperature for energetic feasibility is in the range 400-600K.
- Q6 In general, this also shows that, as temperature increases, the energetic feasibility of the reaction is **DECREASING / INCREASING** because ΔG is becoming **LESS / MORE** negative. This is consistent with Le Chatelier's Principle which predicts that when temperature is increased, the equilibrium position will shift in the **ENDOTHERMIC / EXOTHERMIC** direction. In this case, towards the **REACTANTS / PRODUCTS**.
	- e.g.2 $CaCO₃(s)$ (s) \rightarrow CaO(s) + CO₂ $CO_a(g)$ $\Delta S = +160.4 \text{ J K}^{-1} \text{ mole}^{-1}$ $\Delta H = +178.3 \text{ kJ mole}^{-1}$ $\rightarrow \Delta S = +0.1604 \text{ kJ K}^{-1} \text{ mole}^{-1}$ At 298K, $\Delta G = \Delta H - T \Delta S = (+178.3) - 298(+0.1604) = +130.5 \text{ kJ mole}^{-1}$ At $400K$, $\Delta G = \Delta H - T\Delta S = (+178.3) - 400(+0.1604) = +114.1 \text{ kJ mole}^{-1}$ At $600K$, $\Delta G = \Delta H - T\Delta S = (+178.3) - 600(+0.1604) = +82.1 \text{ kJ mole}^{-1}$
- **Note:** This shows the decomposition of calcium carbonate is not energetically feasible at any of these temperature. The transition temperature for energetic feasibility must be above 600K.

- Q7 In general, this also shows that, as temperature increases, the energetic feasibility of the reaction is **DECREASING / INCREASING** because ΔG is becoming **LESS / MORE** negative. This is consistent with Le Chatelier's Principle which predicts that when temperature is increased, the equilibrium position will shift in the **ENDOTHERMIC / EXOTHERMIC** direction. In this case, towards the **REACTANTS / PRODUCTS**.
- Q8 Practice this calculation technique for each of the reactions considered earlier:

(a) $N_2O_4(g) \to 2NO_2(g)$

As temperature increases, the energetic feasibility of this reaction **DECREASES / INCREASES** because ΔG is becoming **LESS / MORE** negative.

(b) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(l)$

As temperature increases, the energetic feasibility of this reaction **DECREASES / INCREASES** because ΔG is becoming **LESS / MORE** negative.

(c) $2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$ $\Delta S = +876.4 \text{ J K}^{-1} \text{ mole}^{-1}$ $\Delta H = +602 \text{ kJ mole}^{-1}$ $\rightarrow \Delta S = kJ K^{-1} \text{ mole}^{-1}$ At 298K, $\Delta G =$ At 400K, $\Delta G =$ At 600K, $\Delta G =$

As temperature increases, the energetic feasibility of this reaction **DECREASES / INCREASES** because ΔG is becoming **LESS / MORE** negative.

Note: These calculations assume that ΔS and ΔH values do not vary with temperature. Percentage wise is usually a reasonable assumption for ΔH values but not for ΔS if a change of state occurs amongst the reactants and / or products as a result of the temperature change.

How to Find the Transition Temperature From Non-Feasible to Feasible

This occurs when $\Delta G = 0$ $\rightarrow \Delta H - T \Delta S = 0$

\rightarrow T = Δ H/ Δ S

Again, make sure both ΔH and ΔS are both in terms of kJ!

Note: This falls within the range 400-600K noticed earlier.

This reaction is energetically feasible **ABOVE / BELOW** _________.

Note: In order to give a meaningful transition temperature, since T values can only be positive, then ΔH and ΔS must both be positive (see e.g.2) or **both** negative (see e.g.1).

Consider: $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$; $\Delta H = -98.8$ kJ mole⁻¹; $\Delta S = +125.6$ J K⁻¹ mole⁻¹

Here, using $T = \Delta H / \Delta S$ would give -787K. This is impossible. The interpretation of this is that there is no transition temperature! Hydrogen peroxide is energetically unstable with respect to water and oxygen at all temperatures and this reaction is energetically feasible at all temperatures.

Another way of looking at this is to use $\Delta G = \Delta H - T\Delta S$ directly. ΔH is negative and "-T ΔS " is always negative. Hence ΔG is always negative making the reaction always energetically feasible.

This means hydrogen peroxide only exists because its kinetic stability over-rides its energetic instability!

Qualitative Use Of The Gibbs Equation

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

How ΔG, and hence energetic feasibility, varies as T varies for various combinations of ΔH and ΔS can be predicted as follows:

- Q12 For a reaction with a POSITIVE ΔH and a POSITIVE ΔS, the "-TΔS" term will be **POSITIVE / NEGATIVE**. As T increases "-TΔS" will become more **POSITIVE / NEGATIVE** and hence, the value of ΔG will become more **POSITIVE / NEGATIVE** and the reaction therefore **LESS / MORE** energetically feasible.
- Q13 For a reaction with a NEGATIVE ΔH and a NEGATIVE ΔS, the "-TΔS" term will be **POSITIVE / NEGATIVE**. As T increases "-TΔS" will become more **POSITIVE / NEGATIVE** and hence, the value of ΔG will become more **POSITIVE / NEGATIVE** and the reaction therefore **LESS / MORE** energetically feasible.

- Q14 For a reaction with a NEGATIVE ΔH and a POSITIVE ΔS, the "-TΔS" term will *always* be **POSITIVE / NEGATIVE**. Hence, the value of ΔG will be **POSITIVE / NEGATIVE** for all temperatures making the reaction **ALWAYS FEASIBLE / NEVER FEASIBLE**.
- Q15 For a reaction with a POSITIVE ΔH and a NEGATIVE ΔS, the "-TΔS" term will *always* be **POSITIVE / NEGATIVE**. Hence, the value of ΔG will be **POSITIVE / NEGATIVE** for all temperatures making the reaction **ALWAYS FEASIBLE / NEVER FEASIBLE**.

Ellingham Diagrams

These are graphs of ΔG against T first formulated by Harold Ellingham in 1944.

Gibbs equation can be rearranged to give $\Delta G = -\Delta ST + \Delta H$.

This can be compared with the standard equation for a straight line, $y = mx + c$ where "m" is the gradient and "c" is the y-intercept.

- Q16 Comparing these two equations, if ΔG is plotted against T, a straight line graph should result with (a) gradient equal to **ΔG / ΔS / -ΔS / T / ΔH** and (b) y-intercept equal to **ΔG / ΔS / -ΔS / T / ΔH**.
- **Note:** this assumes ΔS and ΔH do not change with temperature. See earlier comments.

Figure 2 shows some Ellingham diagrams for four different reactions, A-D. Examine these and, using the answers to Q16, answer the questions that follow.

- Q17 Reaction A's graph has a **POSITIVE / NEGATIVE** y-intercept. It is therefore **EXOTHERMIC / ENDOTHERMIC**. Also, its gradient is **POSITIVE / NEGATIVE**. It therefore has a **POSITIVE / NEGATIVE** ΔS. Finally, since its ΔG values are always **POSITIVE / NEGATIVE**, this reaction is energetically **FEASIBLE / NOT FEASIBLE** at any temperature.
- Q18 Reaction B's graph has a **POSITIVE / NEGATIVE** y-intercept. It is therefore **EXOTHERMIC / ENDOTHERMIC**. Also, its gradient is **POSITIVE / NEGATIVE**. It therefore has a **POSITIVE / NEGATIVE** ΔS. Finally, its ΔG values are negative at temperatures **ABOVE** / **BELOW** T_1 , meaning this reaction is energetically feasible **ABOVE** / **BELOW** T_1 .
- Q19 Reaction C's graph has a **POSITIVE / NEGATIVE** y-intercept. It is therefore **EXOTHERMIC / ENDOTHERMIC**. Also, its gradient is **POSITIVE / NEGATIVE**. It therefore has a **POSITIVE / NEGATIVE** ΔS. Finally, its ΔG values are negative at temperatures **ABOVE** / **BELOW** T_2 , meaning this reaction is energetically feasible **ABOVE** / **BELOW** T_2 .
- Q20 Reaction D's graph has a **POSITIVE / NEGATIVE** y-intercept. It is therefore **EXOTHERMIC / ENDOTHERMIC**. Also, its gradient is **POSITIVE / NEGATIVE**. It therefore has a **POSITIVE / NEGATIVE** ΔS. Finally, since its ΔG values are always **POSITIVE / NEGATIVE**, this reaction is energetically **FEASIBLE / NOT FEASIBLE** at any temperature.

Answers to Questions

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Q1 (a) -- INCREASING entropy / disorder.
       (b) -- INCREASING entropy / disorder.
Q2 -- entropy change is POSITIVE.
Q3 (a) negative (b) negligible (c) negative (d) negative (e) positive
O4 (a) \Delta S = +175.8 J K<sup>-1</sup> mole<sup>-1</sup>
       (b) \Delta S = -510.0 J K<sup>-1</sup> mole<sup>-1</sup>
       (c) \Delta S = +876.4 J K<sup>-1</sup> mole<sup>-1</sup>
Q5 (a) \Delta H = +57.2 kJ mole<sup>-1</sup>
       (b) \Delta H = -288.4 \text{ kJ} \text{ mole}^{-1}(c) \Delta H = +602 kJ mole<sup>-1</sup>
Q6 -- DECREASING -- LESS -- ENDOTHERMIC -- REACTANTS.
Q7 -- INCREASING – MORE – ENDOTHERMIC -- PRODUCTS.
Q8 (a) At 298K, \Delta G = +4.81 kJ mole<sup>-1</sup>
                   At 400K, \Delta G = -13.1 \text{ kJ mole}^{-1}At 600K, \Delta G = -48.3 kJ mole<sup>-1</sup>
       -- energetic feasibility INCREASES -- ΔG MORE negative.
       (b) At 298K, \Delta G = -136.4 \text{ kJ mole}^{-1}At 400K, \Delta G = -84.4 kJ mole<sup>-1</sup>
                   At 600K, \Delta G = +17.6 kJ mole<sup>-1</sup>
       -- energetic feasibility DECREASES -- ΔG LESS negative.
       (c) At 298K, \Delta G = +340.8 \text{ kJ mole}^{-1}At 400K, \Delta G = +251.4 kJ mole<sup>-1</sup>
                   At 600K, \Delta G = +76.2 kJ mole<sup>-1</sup>
       -- energetic feasibility INCREASES -- ΔG MORE negative.
Q9 -- LOWER -- BELOW 463K.
Q10 -- HIGHER -- ABOVE 1112K.
Q11 (a) Transition T = 325K. -- feasible ABOVE 325K.
       (b) Transition T = 565K. -- feasible BELOW 565K.
       (c) Transition T = 687K. -- feasible ABOVE 687K.
Q12 NEGATIVE. -- NEGATIVE -- NEGATIVE -- MORE energetically feasible.
Q13 POSITIVE. -- POSITIVE -- POSITIVE -- LESS energetically feasible.
Q14 NEGATIVE. -- NEGATIVE -- ALWAYS FEASIBLE.
Q15 POSITIVE. -- POSITIVE -- NEVER FEASIBLE.
Q16 (a) gradient equal to -\Delta S and (b) y-intercept equal to \Delta H.
Q17 -- POSITIVE y-intercept. -- ENDOTHERMIC. -- gradient is POSITIVE. -- a NEGATIVE ΔS. -- ΔG values are always POSITIVE, -- 
       energetically NOT FEASIBLE at any temperature.
Q18 -- NEGATIVE y-intercept. -- EXOTHERMIC. -- gradient is POSITIVE. -- a NEGATIVE \Delta S. -- at temperatures BELOW T<sub>1</sub>, --
        energetically feasible BELOW T_{1}.
Q19 -- POSITIVE y-intercept. -- ENDOTHERMIC. -- gradient is NEGATIVE. -- a POSITIVE \Delta S. -- at temperatures ABOVE T<sub>2</sub>, --
        energetically feasible ABOVE T_2.
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Acknowledgements:

Q20 -- NEGATIVE y-intercept. -- EXOTHERMIC. -- gradient is NEGATIVE. -- a POSITIVE ΔS. -- ΔG values are always NEGATIVE, -- energetically FEASIBLE at any temperature.

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