Chem Factsheet

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Examiner's Approach : Spontaneous Change, Gibb's Free Energy and Entropy

This FactSheet is broken down into 2 sections:
1. Key Note Understanding with Examiner's Cautions
2. Synoptic Application and Exemplar Questions

Understanding
For so many years throughout Chemistry lessons we observe chemical reactions; instinct gives us ideas about why they happen but rarely do we sit back and consider all the factors that contribute to making them happen.

Gibb's free energy (G) is the true measure of whether a reaction will happen or not; or as is explained in many textbooks whether the reaction is spontaneous or not.

- If the change in Gibb's Free Energy (ΔG) is zero or negative the reaction will happen; the reaction is spontaneous (i.e. energetically feasible).

What determines whether or not the change in Gibb's free energy is zero or negative? It is the relationship between:
1. The change in ENTHALPY ΔH (the heat energy change of a reaction; is it endothermic or exothermic?)
2. The TEMPERATURE T of the reaction; and
3. The change in ENTROPY ΔS (the measure of disorder of particles in the reaction).

Their relationship is linked by the equation: $\Delta G = \Delta H - T\Delta S$

Exam Hint:- *Examiners will test a candidate's understanding of units when calculating all aspects of this equation: Check ΔH is in $Jmol^{-1}$ by multiplying $kJmol^{-1}$ values by 1000 as the units for ΔS will always be in $JK^{-1}mol^{-1}$. Alternatively, convert ΔS to $kJK^{-1}mol^{-1}$ by dividing by 1000.*

So what are ΔH, T and ΔS?

ΔH: This is the heat energy change of a reaction measured at constant pressure; the reaction may be endothermic (overall it takes in heat energy) or it may be exothermic (overall it gives out heat energy). Units can be usually $kJmol^{-1}$ but may be $Jmol^{-1}$.

Exam Hint:- *A reaction can be spontaneous if the heat energy change is exothermic or endothermic; remember ΔH is only a contributing part of determining whether a reaction is spontaneous or not.*

T: This is the temperature at which the reaction is taking place. Units are in Kelvin.

Exam Hint:- *If the temperature is in °C add 273 to convert it into Kelvin.*

ΔS: This is the change in entropy; the change in the disorder as reactants are converted into products. Remember entropy increases if a state change takes place from a solid to a liquid or a gas or if the number of moles of products is greater than the number of moles of a reactant. Units of entropy are usually $JK^{-1}mol^{-1}$ but may be $kJK^{-1}mol^{-1}$

Exam Hint:- *When substituting values for ΔH into the Gibb's Free Energy equation ($\Delta G = \Delta H - T\Delta S$) make sure the units are consistent – both ΔH and ΔS in terms of J or both in terms of kJ (see above).*

How do we apply this theory? You may be asked to:

1. Calculate the entropy change for a chemical reaction given the standard molar entropy ($S^\ominus$ which measures amount of disorder) of each reactant and each product. If the products have greater entropy than the reactants then clearly the overall entropy of the reaction increases and ΔS is positive.

Exam Hint:- *Do not be fooled; just because there may be an increase in entropy (ΔS is positive) does not necessarily mean that the reaction is spontaneous (if ΔH was very positive and ΔS was only a small positive value, assuming that there was no change in T, ΔG would be positive; therefore the reaction would not be spontaneous / energetically feasible. The key to being able to apply this knowledge is the understanding of the relationship between the different variables in the ΔG equation.*

In Summary:
- A reaction is spontaneous if ΔG is less than or equal to 0.
- If $\Delta H > 0$ and $\Delta S < 0$, the reaction is not spontaneous at any T since ΔG will always be positive.
- If $\Delta H < 0$ and $\Delta S < 0$, the reaction is more likely to be spontaneous at lower T because ΔH can outweigh $T\Delta S$ and ΔG will be negative.
- If $\Delta H > 0$ and $\Delta S > 0$, the reaction is more likely to be spontaneous at higher T because $T\Delta S$ can outweigh ΔH and ΔG will be negative.

2. To calculate the temperature at which a reaction starts to happen; i.e the temperature at which it becomes energetically feasible:

Worked example: For the reaction which accompanies the enthalpy of formation of ammonia at what temperature would the reaction become feasible?

An essential fact has to be remembered: The reaction will become feasible when $\Delta G = 0$.

The equation: $0.5N_2(g) + 1.5\ H_2(g) \rightarrow NH_3(g)$
The data for S: $S\ (JK^{-1}mol^{-1})$: $N_2(g) = 191.6$, $H_2(g) = 130.6$, $NH_3(g) = 192.3$
The data for ΔH: $-46 kJmol^{-1}$

The answer: From the equation: $\Delta G = \Delta H - T\Delta S$
When $\Delta G = 0$, $T = \Delta H / \Delta S$

Now we need to calculate ΔS from the sum of S(products) - sum of S(reactants)
Therefore ΔS $= 192.3 - (191.6 + (1.5 \times 130.6) = -99.4\ JK^{-1}mol^{-1}$
and ΔH $= -46\ kJmol^{-1} = -46 \times 1000\ Jmol^{-1} = -46000\ Jmol^{-1}$
Therefore the temperature at which the reaction becomes feasible is calculated as: $T = -46000\ Jmol^{-1} / -99.4\ JK^{-1}mol^{-1} = 463K$ (3 sf)

Since the reaction is exothermic, the forward reaction is favoured by lower temperatures. This means energetic feasibility is in the range $T \leq 463K$.

This question includes all key areas for focus:

1. The understanding that the highest (most positive) value that ΔG can be for a reaction to become feasible is 0.
2. Ensuring that the units of ΔH match up with the units of ΔS.

Synoptic Application and Exemplar Questions

Synoptic Application; can you?

1. Identify from an equation whether the entropy is likely to increase or decrease.
2. Calculate the change in entropy for a reaction
3. Calculate the temperature at which a reaction or state change becomes feasible.
4. Apply these ideas to transition metal chemistry where a multidentate ligand substitutes a unidenate ligand resulting in an increase in entropy of the system.
5. Apply these ideas to a more challenging scenario, when ΔH needs to be calculated using Hess's Law:

Exemplar Question 1

Sulphur dioxide reacts with oxygen to form sulphur trioxide according to the equation: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

The enthalpy of formation data and entropy data for the different components of the reaction are as follows:

Substance	SO_3	SO_2	O_2
$\Delta H^\ominus_f$ / kJ mol^{-1}	-396	-297	0
$S^\ominus_f$ / J K^{-1} mol^{-1}	257	248	204

From this data and equation at 298K:

(a) Identify whether there is an increase or decrease in entropy in the forward direction.
(b) Calculate the standard enthalpy change for the reaction.
(c) Calculate the standard entropy change for the reaction.
(d) Calculate the standard free energy change for the reaction.
(e) State the point at which the reaction becomes feasible.
(f) Calculate the temperature at which the reaction becomes feasible 12 marks

Exemplar Question 2:

For the following ligand substitution reaction explain what would happen to the entropy of the system as EDTA^{4-} substitutes the water.

$[Co(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [Co(EDTA)]^{2-} + 6H_2O$ 3 marks

Exemplar Question 3:

Using the data below for the following industrial equilibrium reactions, calculate the temperatures at which the free energy change for each reaction is equal to zero.

Reaction 1 $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
Reaction 2 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Substance	$CH_4(g)$	$H_2O(g)$	$CO(g)$	$H_2(g)$	$N_2(g)$	$NH_3(g)$
$\Delta H^\ominus_f$/kJ mol^{-1}	-74.8	-241.8	-110.5	0	0	-46.1
$S^\ominus$ /J K^{-1}mol^{-1}	186.2	188.7	197.6	130.6	191.6	192.3

10 marks

Exemplar Question 4

Iron (II) oxide can be reduced to iron both by carbon, which is oxidised to carbon monoxide, and by carbon monoxide, which is oxidised to carbon dioxide, as shown in the equations below.

$FeO(s) + C(s) \rightarrow Fe(s) + CO(g)$
$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$

(a) Use the data below to deduce the free energy change, $\Delta G^\ominus$, measured at 450 K, for each of these reduction processes; assume that the enthalpy change and entropy change in each of these reactions remains the same if the temperature is raised from 298K to 450K.

10 marks

Substance	FeO(s)	Fe(s)	C(s)	CO(g)	CO_2 (g)
$\Delta H^\ominus_f$/kJ mol^{-1}	-271.9	0	0	-110.5	-393.5
$S^\ominus$/J K^{-1}mol^{-1}	58.5	27.3	5.7	197.6	213.6

(b) Deduce how an increase in temperature will affect the feasibility of each of the processes in which iron (II) oxide is reduced to iron

5 marks

Answer to Exemplar Question 1
(a) There is a decrease in entropy as three moles of gas form 2 moles of gas. (1)
(b) $\Delta H = \Sigma\Delta H_f$ (products) - $\Delta\Sigma H_f$ (reactants) (1)
$= (2 \times -396) - (2 \times -297) = -198$ KJmol^{-1} (1).
(c) ΔS = S (products) - S (reactants) (1)
$= ((2 \times 257) - 204) - (2 \times 248)$ (1) $= -186$ JK^{-1}mol^{-1} (1).
(d) $\Delta G = \Delta H - T\Delta S$ (1)
$= -198 - (298 (-186/1000))$ (1) $= -143$ KJmol^{-1} (1).
(e) When $\Delta G = 0$ (1)
(f) $T = \Delta H/\Delta S$ when $\Delta G = O$ (1)
$\rightarrow T = -198 \times 1000 / -186 = 1065K$ (1)

Answer to Exemplar Question 2
Due to the increase in number of particles on the right hand side of the equation (1),
the entropy of this system would increase (1)
because 2 moles of reactants produce 7 moles of products. (1)

Note: ΔH is approximately 0 because 6 coordinate bonds are replaced by 6 similar bonds. As a result $\Delta G \approx -T\Delta S$. This means the reaction is spontaneous at all temperatures

Answer to Exemplar Question 3
Reaction 1: $\Delta H = \Sigma\, \Delta H_f$ products – $\Sigma\, \Delta H_f$ reactants (1);
$= (\Delta H\, CO + 3\Delta H\, H_2) - (\Delta H\, CH_4 + \Delta H\, H_2O)$
$= (-110.5 + 3[0])_{-1} - (-74.8 - 241.8)$
$= +206.1$ kJ mol (1)
$\Delta S = \Sigma S$ products – ΣS reactants (1)
$= (197.6 + [3 \times 130.6]) - (186.2 + 188.7) = 213.5$ J K^{-1}mol^{-1} (1)
$\Delta G = \Delta H - T\Delta S$ (1)
$0 = +\, 206.1 - T \times 214.5/1000$ (1)
$T = (206.1 \times 1000)/214.5 = 964.9K$ (1)

Reaction 2: $\Delta H = 2\Delta H_f\, NH_3$
$= -92.2$ (kJ mol^{-1}) (1)
$\Delta S = (2 \times 192.3) - (191.6 + [3 \times 130.6])$
$= -198.8$ J K^{-1}mol^{-1} (1)
$\Delta G = 0 = -92.2 + T \times 198.8/1000$
$T = -92.2 \times 1000/-198.8 = 463.8$ K (1)

Answer to Exemplar Question 4
(a) Reaction 1:
$\Delta H = \Sigma H_f$ (products) – ΣH_f (reactants) (1)
$= (-110.5) - (-271.9)$
$= +161.4$ kJ mol^{-1} (1)
$\Delta S = \Sigma S$ (products) – ΣS (reactants) (1)
$= (27.3 + 197.6) - (58.5 + 5.7)$
$= +160.7$ J mol^{-1} K^{-1}(1)
$\Delta G = \Delta H - T\Delta S$ (1)
$\Delta G = +161.4 - 450 \times 160.7/1000$ (1)
$= +\, 89.1$ kJ mol^{-1}. (1)
Reaction 2:
$\Delta H = (-393.5) - (-271.9 - 110.5)$
$= -11.1$ kJ mol^{-1}. (1)
$\Delta S = (213.6 + 27.3) - (58.5 + 197.6)$
$= -15.2$ J mo1^{-1} K^{-1}. (1)
$\Delta G = -11.1 + 450 \times -15.2/1000$
$= -4.26$ kJ mol^{-1}. (1)

(b) Feasible when $\Delta G = 0$ or ΔG is negative (1);
Process 1 is more feasible as temperature is increased (1)
as ΔS is positive or $-T\Delta S$ is negative or $T\Delta S$ is positive (1)
Process 2 is less feasible as temperature is increased (1)
As ΔS is negative or $-T\Delta S$ is positive or $T\Delta S$ is negative (1)

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