Chem Factsheet

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How to Answer Questions Involving Entropy Changes and Free Energy Changes of Systems

This Chem Factsheet covers:

(a) entropy (S) as a "measure of disorder" of a substance or system,

(b) each term in the relationship $\Delta G = \Delta H - T\Delta S_{system}$ and

(c) the effects of varying the relative magnitudes of ΔH and $T\Delta S_{system}$ on ΔG and hence the feasibility of a reaction.

Note: the equation is usually written as just "$\Delta G = \Delta H - T\Delta S$", the; word "system" not being included.

Guidance is provided on answering questions plus an indication of careless slips that might be made. However this Factsheet is no substitute for taking time to understand the chemistry involved in your specification.

1. Entropy (S) is a Measure of the "Disorder" of a Substance

Several factors determine the entropy of a substance. These include:

(a) The Physical State / Phase

S (solid) < S (liquid) < S (solution) << S (gas).

e.g. various entropy values for sodium chloride in various phases at 298K.

$NaCl_{(state\ /\ phase)}$	$S/JK^{-1}mol^{-1}$	Comment
$Na^+Cl^-(s)$ (solid)	72	Regular array of vibrating ions: highest order → lowest entropy.
$Na^+(l) + Cl^-(l)$ (liquid)	95	Ions jostle randomly with limited movement: disorder increased → higher entropy than solid.
$Na^+(g) + Cl^-(g)$ (gas)	230	Ions move completely randomly: highest disorder → highest entropy.
$Na^+(aq) + Cl^-(aq)$ (aq)	116	Hydrated ions and water molecules move randomly but more slowly than in gas: intermediate disorder → entropy between liquid and gas.

Note S(s) < S(l) < S(aq) << S(g) is generally a good guide when comparing different substances provided the mole quantities, their M_r values and complexities are similar.

(b) The Temperature of the Phase / Physical State

At absolute zero (0 K) a perfect crystal has no disorder because motion ceases. Hence, the entropy is zero. As the temperature increases particles have more energy:

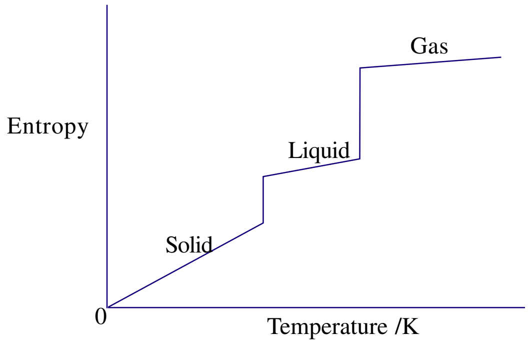
(i) in the solid state, particles vibrate more rapidly about a fixed point causing more disorder, and hence entropy to increase.

(ii) in the liquid state the random jostling and limited motion of the particles increases causing more disorder, and hence entropy to increase.

(iii) in the gaseous state the completely random linear motion of the particles increases causing more disorder, and hence entropy to increase.

(iv) at the melting and boiling point there is a very large increase in disorder, and hence a very large increase in entropy.

Entropy changes with physical state



(c) The Number of Moles of Particles

The greater the number of moles of particles / number of particles of a substance present in the system at a fixed temperature, the greater the disorder and hence the greater the entropy.

e.g. S for two moles NaCl(s) is 144 JK^{-1}.

2. How to Decide the Nature of Entropy Changes

What is needed is to be able to estimate whether the entropy change (ΔS) for any given physical or chemical change at constant temperature is positive, negative or negligible.

Look for a change in disorder, by looking at:

(i) changes in state / phase,

(ii) changes in moles / numbers of particles, to estimate the entropy change.

(a) Some Physical Changes

Physical change*	Melting	Evaporation / Boiling	Sublimation	Condensing	Freezing	Dissolving in water
Initial to final states	(s) to (l)	(l) to (g)	(s) to (g)	(g) to (l)	(l) to (s)	(s) + (l) to (aq)
Disorder	Increases: S(l) > S(s)	Large increase: S(g) >> S(l)	Large increase: S(g) >> S(s)	Large decrease: S(l) << S(g)	Decreases: S(g) < S(l)	Increases S(aq) > S(s) + S(l) especially if number particles increases by ion dissociation
Entropy change, ΔS	Positive	Very positive	Very positive	Very negative	Negative	Positive

(b) Some Chemical Changes

Chemical change	Example	Reason for change in disorder	Disorder	Entropy Change
Gas evolved	$CO_3^{2-}(s) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$	(s) / (aq) to (g)	Increase	Positive
Ionic precipitation	$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$	(aq) to (s) and less moles	Decrease	Negative
Fuel combustion	$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$	6 moles (g) to 3 moles (g)	Decrease	Negative
Fuel combustion	$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$	6 moles (g) to 7 moles (g)	Increase	Positive
Chelation	$[Cu(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow 6H_2O(l) + [CuEDTA]^{2-}(aq)$	2 to 7 moles	Increase	Positive

Note For chemical reactions the disorder of ALL particles need not be considered. Concentrate on the particles responsible for the MAJOR change in disorder. For example in fuel combustion, the disorder of **liquid** $4H_2O$ is not mentioned since it is much less than the disorder of 3 moles of CO_2 **gas**.

3. Gibbs Free Energy Change (ΔG) and Spontaneity of a Reaction

A reaction can be described as "spontaneous" if it will proceed without any outside energy input. It is often said to be "energetically feasible". It does not mean it will proceed quickly! It can be compared to a skier sliding *down* a slope, either quickly or slowly, depending on the gradient. However, a skier will not spontaneously slide *up* a slope – that would require an energy input!

(a) Enthalpy Change and Entropy Change Alone are Insufficient to Decide Spontaneity

Consider the following two reactions which occur immediately on mixing the reactants.

Reactants	Equation	$\Delta H / kJmol^{-1}$	$\Delta S / Jmol^{-1}K^{-1}$
(A) White phosphorus and oxygen	$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$	-2984	-837
(B) Sodium hydrogencarbonate + acid	$HCO_3^-(s) + H^+(aq) \rightarrow CO_2(g) + H_2O(l)$	+13	+192

For reaction (A), the negative ΔH alone must be insufficient to make it spontaneous because reaction (B) is spontaneous but has a positive ΔH.

For reaction (B), the positive ΔS alone must be insufficient to make it spontaneous because reaction (A) is spontaneous but has a negative ΔS.

Instead, the enthalpy change and entropy change are combined in a *single* energy term which will allow an unambiguous criterion for spontaneity. The is the Gibbs Free Energy change (ΔG).

The equation defining the Gibbs Free Energy change is: $\Delta G = \Delta H - T\Delta S$

The criterion for a spontaneous change is ΔG must be negative.

When ΔG is negative the *products are said to be thermodynamically stable relative to the reactants.*

In the example of combustion of graphite: $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta G = -393.5\ kJmol^{-1}$.

Thus carbon is thermodynamically *unstable* in air as ΔG is negative and carbon would be expected to convert spontaneously to carbon dioxide.

However, at room temperature there is no detectable reaction. The activation energy is very high (strong covalent bonds have to break) causing the spontaneous reaction to be so slow as to be undetectable. Carbon in air is said to be "kinetically stable".

A feasible / spontaneous change does not imply anything about the rate of reaction (kinetics). It is the activation energy that determines the rate of the reaction while ΔG determines spontaneity. Kinetic stability often *over-rides* energetic feasibility, especially at room temperature, leading to many reactions with a negative ΔG not being detectable.

(b) Deducing the Sign and Magnitude of the Gibbs Free Energy Change

There are four possible combinations of ΔH and ΔS that can produce a ΔG value.

	ΔH	ΔS	-TΔS	$\Delta G = \Delta H - T\Delta S$.
1	+ve	+ve	-ve	ΔG will only become negative when TΔS > ΔH. The reaction is spontaneous when the temperature is *high enough* as –TΔS becomes increasingly negative.
2	-ve	+ve	-ve	ΔG is always negative since ΔH and –TΔS are both negative. The reaction is spontaneous at all temperatures. As T increases ΔG becomes more negative and the reaction even more feasible.
3	-ve	-ve	+ve	ΔG will only become negative when TΔS < ΔH. The reaction is spontaneous when the temperature is *low enough* as –TΔS becomes increasingly less positive (i.e. more negative).
4	+ve	-ve	+ve	ΔG is always positive since ΔH and –TΔS are both positive. The reaction is never spontaneous at any temperature. As T increases ΔG becomes more positive.

Notes: Energetic feasibility is determined by a balance between enthalpy change, entropy change and temperature.

When ΔH and ΔS have *different signs*, a reaction will only be spontaneous (ΔG < 0) provided the temperature is suitable.

It is assumed that both ΔH and ΔS do not vary with temperature when determining the sign of ΔG. However, ΔH and ΔS will have different values if there is a change of state of a reactant or product.

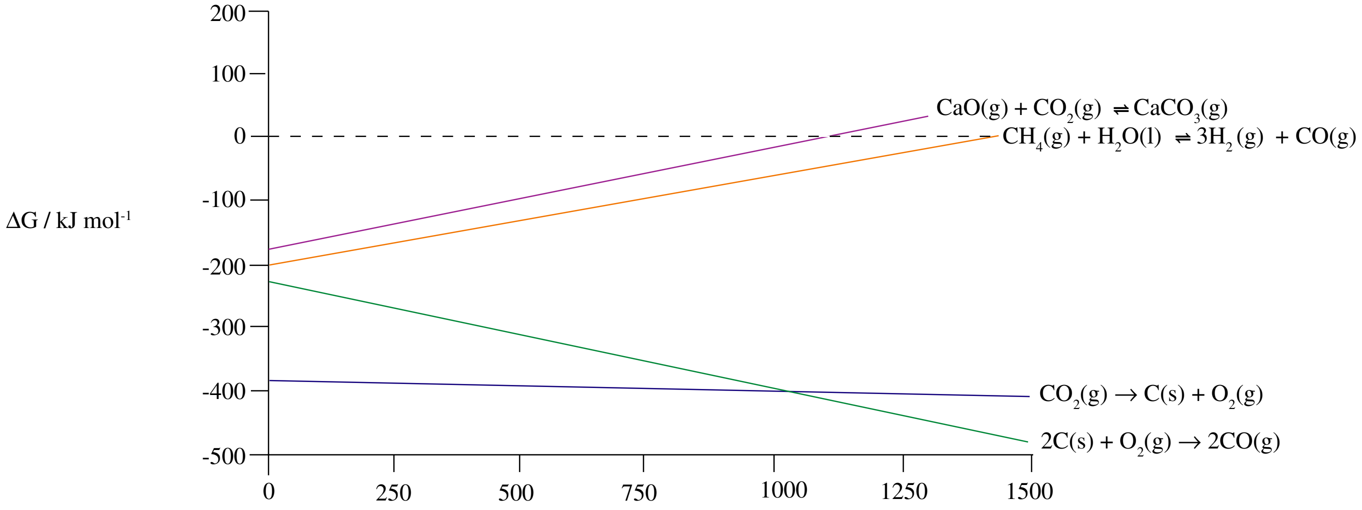
A system becomes *more* energetically stable when energy is lost to the surroundings (ΔH is negative).

A system becomes *more* energetically stable when it becomes more disordered (ΔS is positive).

Graphical Representation of the Variation of the ΔG with Temperature for Examples 1 to 4

	Example	ΔH / kJ mol^{-1}	ΔS / Jmol^{-1}K^{-1}
1	$CH_4(g) + H_2O(l) \rightleftharpoons 3H_2(g) + CO(g)$	+206	+213
2	$2C(s) + O_2(g) \rightarrow 2CO(g)$	–221	+179
3	$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$	-178	-161
4	$CO_2(g) \rightarrow C(s) + O_2(g)$	+393.5	-5.6

Variation of free energy change (ΔG) with temperature (Ellingham diagrams)



(c) Using Ellingham Diagrams to Determine ΔH, ΔS and T

ΔG = ΔH – TΔS can be written ΔG = –ΔST + ΔH and then compared to the general equation for a straight line, y = mx + c.

Hence for a Ellingham Diagram showing ΔG vs T, ΔH = y-intercept (c) and –ΔS = gradient (m).

Also, the temperature at which spontaneity "switches" is given by the x-value when ΔG = 0 (i.e. where the Ellingham Diagram crosses the dotted line i.e the x intercept).

(i) ΔH e.g. for: $CO_2(g) \rightarrow C(s) + O_2(g)$, ΔH ≈ –390 kJmol^{-1} for $2C(s) + O_2(g) \rightarrow 2CO(g)_,$ ΔH ≈ –220 kJmol^{-1}

(ii) ΔS e.g. for $2C(s) + O_2(g) \rightarrow 2CO(g)$, gradient ≈ -480 -(-220) /1500 = - 0.173 kJmol^{-1}K^{-1}. hence ΔS = +173 Jmol^{-1}K^{-1}.

(iii) T e.g. for: $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$ T ≈ 1100 K. So *below* 1100K, ΔG for with *forward* reaction is negative and feasible but, *above* 1100K, ΔG for with *backward* reaction is negative and feasible.

(d) Calculating ΔG by First Calculating ΔH and ΔS from Thermodynamic Data. (Units omitted.)

Substance	$\Delta H^\ominus_f$ / kJ mol^{-1}	$S^\ominus$ / J K^{-1} mol^{-1}	Substance	$\Delta H^\ominus_c$ / kJ mol^{-1}	$S^\ominus$/ J K^{-1} mol^{-1}	Substance	$S^\ominus$ / J K^{-1} mol^{-1}
$CaCO_3(s)$	-207	93	CO(g)	- 283	198	$CH_4(g)$	187.9
CaO(s)	- 635	40	$O_2(g)$	0	205	$H_2O(l)$	197.6
$CO_2(g)$	- 394	214	C(s)	- 394	6	$H_2(g)$	103.6
						CO(g)	188.7

Bond	Bond Enthalpy / kJ mol^{-1}
C-H	413
H-O	463
H-H	436
C≡O	1072

(i) Calculating $\Delta H^\ominus$ ΔH is usually calculated in one of three ways. From:

Enthalpy changes of formation	Enthalpy changes of combustion	Bond enthalpies (BE).
e.g. 1. $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$	e.g. 2. $2C(s) + O_2(g) \rightarrow 2CO(g)$	e.g. 3. $CH_4(g) + H_2O(l) \rightarrow 3H_2(g) + CO(g)$
ΔH $= \Sigma\Delta H_f\,(\text{products}) - \Sigma\Delta H_f\,(\text{reactants})$ $= -1207 - (-394 - 635)$ $= -178\ \text{kJmol}^{-1}$.	ΔH $= \Sigma\Delta H_c(\text{reactants}) - \Sigma\Delta H_c(\text{products})$ $= 2(-394) - 2(-283)$ $= -222\ \text{kJmol}^{-1}$.	ΔH $\approx \Sigma BE(\text{products}) - \Sigma BE(\text{reactants})$ $\approx 3(436) + 1072 - \{4(413) + 2(463)\}$ $\approx +236\ \text{kJmol}^{-1}$.

When doing these calculations, if the equations need to be written down, do not forget the Σ signs.
Also do not forget to include the number of moles and the correct units. By inspection, try to check that the sign of ΔH is correct.
e.g.1) Decomposition → ΔH +ve. e.g.2) Combustion → ΔH -ve. e.g.3) Not obvious.

The value of $\Delta H \approx +236\ \text{kJ mol}^{-1}$ is calculated using bond enthalpies which are mean values and only apply to the gaseous state and in the equation water is a liquid. The value of $+206\ \text{kJmol}^{-1}$ in the previous table was calculated using more reliable $\Delta H^\ominus_f$ values.

(ii) Calculating $\Delta S^\ominus$ e.g. $CH_4(g) + H_2O(l) \rightarrow 3H_2(g) + CO(g)$

$$\Delta S = \Sigma S(P) - \Sigma S(R) = \{3(130.6) + 197.6\} - (187.9 + 188.7) = +212.8\ \text{JK}^{-1}\text{mol}^{-1}.$$

Rem. Don't forget Σ and there are no Δ's on the RHS of this equation.

(iii) Calculating $\Delta G^\ominus$ e.g. $CH_4(g) + H_2O(l) \rightarrow 3H_2(g) + CO(g)$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = 206 - 298(212.8/\mathbf{1000}) = +143\ \text{kJmol}^{-1}.$$

Hence, this reaction is not feasible at 298K since $\Delta G^\ominus$ is positive.

(d) Calculating the Temperature at which a Reaction becomes Spontaneous

$\Delta G = \Delta H - T\Delta S$
When $\Delta G = 0$ dynamic equilibrium exists and the changeover from feasible to non-feasible occurs.
$\therefore \Delta H = T\Delta S$
$\therefore T = \Delta H/\Delta S = 206/0.2128 = 968\text{K}$.

Rem. In calculations c(iii) and d) remember to convert entropy units from $\text{Jmol}^{-1}\text{K}^{-1}$ to $\text{kJmol}^{-1}\text{K}^{-1}$.
Also, in c(iii) the temperature must be in Kelvin and in d) do not forget to include the units.
If a negative absolute temperature is obtained an error must have been made.
In d) type calculations, the reaction is more feasible *above* the calculated temperature for an endothermic reaction but *below* it for an exothermic reaction.
K and k cannot be cancelled when working out the units!

Practice Questions

1. Explain how endothermic reactions can take place spontaneously.
2. Explain how reactions that have a negative entropy change can take place spontaneously.
3. Calculate $\Delta G^\ominus$ for $\Delta H^\ominus_f[CuO(s)]$.
   $S^\ominus/\text{mol}^{-1}\text{K}^{-1}$: $Cu(s) = 33.2$, $O_2(g) = 205.1$, $CuO(s) = 42.6$; $\Delta H^\ominus_f[CuO(s)] = -157.3\ \text{kJmol}^{-1}$.
   What is the lowest temperature that the reaction is feasible?
   Suggest a reason when the temperature calculated is not the correct value.
4. Arrange the following in order of increasing ΔS beginning with the most –ve; state the sign of each entropy change
   (a) boiling of 1 mole of water, (b) $H_2(g) + ½O_2(g) \rightarrow H_2O(g)$,
   (c) $6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$, (d) freezing 1 mole of water
5. A process is endothermic and not feasible, which is true?
   (a) $\Delta S > 0$, (b) $\Delta S < 0$, (c) $\Delta H < 0$, (d) $\Delta G = 0$, (e) $\Delta G < 0$.
6. At equilibrium, which of the following is true?
   (a) $\Delta H < 0$, (b) $\Delta H = 0$, (c) $\Delta S = 0$, (d) $\Delta G = 0$, (e) $\Delta S < 0$.
7. Iodine is a solid at 298K. For the process at 25°C: $I_2(g) \rightarrow I_2(s)$, state and explain the signs of ΔH, ΔS and ΔG?
8. At what temperature would a reaction become feasible if $\Delta H = +100\ \text{kJ mol}^{-1}$ and $\Delta S = +200\ \text{Jmol}^{-1}\text{K}^{-1}$?

9. Calculate $\Delta G^{\ominus}$ for:
$2NH_4NO_3(s) + C(s) \rightarrow 2N_2(g) + CO_2(g) + 4H_2O(g)$ at 25^0C to three sig. figures.
$\Delta H^{\ominus}_f$ / $kJmol^{-1}$: $NH_4NO_3(s) = -365$, $CO_2(g) = -394$, $H_2O(g) = -242$.
S / $kJmol^{-1}K^{-1}$: $NH_4NO_3(s) = 260$, $C(s) = 5.6$, $N_2(g) = 192$, $CO_2(g) = 214$, $H_2O(g) = 119$.
Why would this reaction be slow at 25^0C?
Explain at what temperature (if any) this reaction will *not* be spontaneous.

10. Calculate $\Delta G^{\ominus}$ for $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ at 25°C.
$\Delta H^{\ominus}_f$ / $kJmol^{-1}$: $H_2O_2(l) = -187.8$, $H_2O(l) = -285.8$;
$S^{\ominus}$ / $Jmol^{-1}K^{-1}$: $H_2O_2(l) = 109.6$, $H_2O(l) = 69.6$, $O_2(g) = 205.1$.

11. Determine the boiling pt of mercury.
$\Delta H_{vaporisation}$ of Hg = 60.7 $kJmol^{-1}$;
Entropies: Hg(l) = 76, Hg(g) = 175 $Jmol^{-1}K^{-1}$.

12. Refer to the previous Ellingham Diagrams to answer the following questions.
(a) Estimate the entropy change for $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$
(b) Explain why the line for $CO_2(g) \rightarrow C(s) + O_2(g)$ is almost a straight line parallel to the x axis.
(c) At what temperatures is the reaction,
$CH_4(g) + H_2O(l) \rightarrow 3H_2(g) + CO(g)$ not feasible? Explain.

13. Write an equation, including state symbols, for the process that occurs when potassium chloride crystallizes from an aqueous solution. Explain why the entropy change for this process is negative.

14. Refer to the entropy variation with temperature and change of state "plot". At two temperatures the entropy increases while the temperatures remains constant. Explain why one increase is much greater than the other increase?

Answers

1. $\Delta G = \Delta H - T\Delta S$. ΔS must be +ve and the T high enough so that $T\Delta S > \Delta H$. $\therefore \Delta G$ is –ve so reaction is spontaneous.

2. $\Delta G = \Delta H - T\Delta S$. ΔH must be -ve and the T low enough so $T\Delta S < \Delta H$. $\therefore \Delta G$ is –ve so reaction is spontaneous.

3. $Cu(s) + ½O_2(g) \rightarrow CuO(s)$
$\Delta S = 42.6 - (33.2 + 205.1/2) = -93.15\ Jmol^{-1}K^{-1}$.
$\Delta G = -157.3 - 298(-0.09315) = -129.5\ kJmol^{-1}$.
$\Delta G = \Delta H - T\Delta S$, $\Delta G = 0$, $\Delta H = T\Delta S$.
$T = \Delta H/\Delta S = -157.3/-.093.15 = 1689K$.
Cu melts / ΔH or ΔS have different values with temperature.

4. (c) most negative, (b) negative, (d) least negative and (a) positive.

5 (b)

6 (d)

7. ΔH is –ve since VDW forces are formed between the molecules.
ΔS is –ve as order increases as a random gas becomes an ordered crystal.
ΔG is –ve as I_2 is a solid at 25°C.

8. $\Delta G = \Delta H - T\Delta S$.
When $\Delta G = 0$, $\Delta H = T\Delta S \rightarrow T = \Delta H/\Delta S = 100/0.2 = 500K$.
(Divide by 1000 for $Jmol^{-1}K^{-1}$ to $kJmol^{-1}K^{-1}$.)

9. $\Delta H = \{-394 + 4(-242)\} - 2(-365) = -632\ kJmol^{-1}$.
$\Delta S = \{2(192) + 214 + 4(119)\} - \{2(260) + 5.6\} = +548.4\ Jmol^{-1}K^{-1}$.
$\Delta G = \Delta H - T\Delta S = -632 - 298(0.5484) = -795\ kJmol^{-1}$.
Reaction is between two solids.
ΔH is –ve and ΔS is +ve so ΔG is always –ve and the reaction always spontaneous.

10. $\Delta H = 2(-285.8) - 2(-187.8) = -196.0\ kJmol^{-1}$.
$\Delta S = 2(69.6) + 205.1 - 2(109.6) = +125.1 Jmol^{-1}K^{-1}$.
$\Delta G = \Delta H - T\Delta S = -196 - 298(0.1251) = -233.3\ kJmol^{-1}$.

11. At equilibrium so $\Delta G = 0$ for $Hg_{(l)} \rightleftharpoons Hg_{(g)}$.
$\Delta H - T\Delta S = 0$.
$T = \Delta H / \Delta S$. $T = 60.7/(175 - 76)/1000 = 613\ K$.

12. (a) ΔS = gradient $\approx -180/1100 = -0.16\ kJmol^{-1}K^{-1}$.
(b) $\Delta S \approx 0$ / small since essentially 1 mole gas $\rightarrow$ 1 mole gas.
$\therefore \Delta G \approx \Delta H \approx -380\ kJ\ mol^{-1}$.
(c) above ≈ 1350K where $\Delta G > 0$.

13. $K^+(aq) + Cl^-(aq) \rightarrow KCl(s)$.
Two moles of randomly moving ions to one mole of a regular arrangement of ions in solid.
Order increased. ∴ entropy decreases. (Note. Do not say "molecules" for "ions".)

14. Smaller increase: disorder(liquid) > disorder(solid) so ΔS +ve as solid melts.
Larger increase: disorder(gas) >> disorder(liquid) so ΔS much more +ve as the liquid boils.

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