Chem Factsheet

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How to Answer Questions Involving Entropy, Entropy Changes and Total Entropy Changes

This Factsheet initially covers entropy in a qualitative manner and the factors that affect the entropy (S) of a substance.

Secondly calculations of ΔS_{system} from entropy data, $\Delta S_{surroundings}$ from enthalpy data and ΔS_{total} from equilibrium constants and from ΔS_{system} plus $\Delta S_{surroundings}$ are provided. Also, why some reactions are spontaneous and others are non-spontaneous in terms of ΔS_{total} and the variation of ΔS_{total} with temperature are considered. Guidance is also provided on answering related questions plus an indication of careless slips that might be made.

Qualitatively the entropy of a substance is related to the random arrangement of the particles of that substance and also the random arrangement of the energy quanta between the particles. The greater the number of ways the particles and the energy quanta can be arranged the greater the entropy.

1. Factors that Determine the Entropy (S) of a Substance

(a) The Temperature (T) and the Physical State

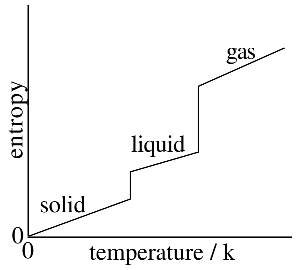
At absolute zero a perfect crystal has no entropy. As T increases S increases. The particles have more energy quanta. More ways exist of arranging these quanta between increasing numbers of available energy levels.

Increasing the temperature also increases the movement of the particles.

Solid The particles vibrate more rapidly about a fixed point.

Liquid The random jostling of particles increases.

Gas The completely random linear motion of the particles increases.
In all states, as the temperature increases, disorder is increasing and so is the entropy.



The graph also shows that entropy (solid) < entropy (liquid) << entropy (gas). This is also shown by the actual values for sodium chloride at 298K with the value for an aqueous solution also included.

NaCl (state/phase)	$S/JK^{-1}mol^{-1}$	Comment about the random motion of the ions
$Na^+Cl^-(s)$	72	Regular array of vibrating ions: highest order: lowest entropy.
$Na^+(l) + Cl^-(l)$	95	Ions jostle randomly: disorder increased: higher entropy than solid.
$Na^+(g) + Cl^-(g)$	230	Ions move completely randomly: highest disorder: highest entropy.
$Na^+(aq) + Cl^-(aq)$	116	Hydrated ions and water molecules move randomly. Entropy more than liquid.

For NaCl: entropy (solid) < entropy (liquid) < entropy (aq. solution) << entropy (gas). This order is also a good guide when comparing different substances especially of similar complexities.

(b) The Complexity of a Substance

Entropy increases as molecules become more complex. In a homologous series such as primary alcohols the molar mass is increasing. The more atoms in a molecule, the more ways the molecule can change its shape by vibrating so the more ways the energy can be distributed among the molecules.

	Primary alcohols: increasing complexity and M_r				Substances: increasing complexity but similar M_r		
Molecular formula	$CH_3OH(l)$	$C_2H_5OH(l)$	$C_3H_7OH(l)$	$C_4H_9OH(l)$	$CO(g)$	$C_2H_4(g)$	$B_2H_6(g)$
$S/JK^{-1}mol^{-1}$	127	160	192	226	198	220	232
Molar mass/g mol^{-1}	32	46	60	74	28	28	27.6
Number of atoms	6	9	12	15	2	6	8

(c) The Number of Moles / Particles

The greater the number of moles / particles present in the system, the greater the disorder and hence the greater the entropy. e.g. S for two moles liquid methanol is $2 \times 127 = 254\ JK^{-1}$.

2. Qualitative Estimation of an Entropy Change for a System (ΔS_{system}) at Constant Temperature

(a) Physical Changes Use: $S(s) < S(l) < S(aq) << S(g)$

Physical change	Melting	Evaporation/Boiling	Sublimination	Dissolving: s or l in water	Dissolving a gas in water
Initial to final states/phases	(s) to (l)	(l) to (g)	(s) to (g)	(s) / (l) to (aq)	(g) to (aq)
Disorder	Increases: $S(l) > S(s)$	Big increase: $S(g) >> S(l)$	Big increase: $S(g) >> S(s)$	Increase: $S(s)/(l) < S(aq)$	Decrease: $S(g) > S(aq)$
Entropy change, ΔS_{system}	Positive	Very positive	Very positive	Positive	Negative

Note The entropy changes for the *reverse* change.is equal in magnitude but of opposite sign.

(b) Chemical Changes

Look for a change in disorder caused by either
(i) change in phase and / or
(ii) change in the number of moles and /or iii) a change in complexity.

Type	Example	ΔS_{system}	Reason for S change of the system
Gas evolved	$CO_3^{2-}(s) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$	Increase	(s) / (aq) to (g): more disorder
Precipitation	$Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$	Decrease	(aq) to (s) & less particles: less disorder
Combustion	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	Decrease	3 moles (g) to 1 mole (g): less disorder
Combustion	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	Increase	Moles & states same but increase in complexity
Synthesis of a binary solid compound	$Mg(s) + ½O_2(g) \rightarrow MgO(s)$ $Al(s) + 1½Br_2(l) \rightarrow AlBr_3(s)$ $K(s) + ½I_2(s) \rightarrow KI(s)$	Decrease	Gaseous reactant: solid product / less moles Liquid reactant: solid product / less moles Less moles of product than reactants
Chelation	$[Cu(H_2O)_6]^{2+} + 3en \rightarrow 6H_2O + [Cu(en)_3]^{2+}$	Increase	4 to 7 moles: more disorder
Very endothermic	$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + 10H_2O(l) + BaCl_2(s)$	Big Increase	13 moles formed including 2 moles gas and 10 moles liquid from 3 moles solid.

Note "en" is 1,2-diaminoethane. $[Cu(en)_3]^{2+}$ is $[Cu(H_2NCH_2CH_2NH_2)_3]^{2+}$ - high complexity.

3. Qualitative Estimation of the Entropy Change for the Surroundings, ($\Delta S_{surroundings}$)

$\Delta S_{surroundings}$ is positive when the reaction is exothermic. Heat energy has been given to the surroundings so there are now more energy quanta to distribute between its particles.
$\Delta S_{surroundings}$ is negative when the reaction is endothermic. Heat energy has been taken from the surroundings so there are now less energy quanta to distribute between its particles.

4. Qualitative Estimation of the Total Entropy Change (ΔS_{total})

ΔS_{system}	$\Delta S_{surroundings} = -\Delta H/T$	When is ΔS_{total} positive and the reaction therefore spontaneous?
(a) positive	positive ($\Delta H < 0$)	ΔS_{total} is always positive as it is the sum of two positive numbers.
(b) negative	negative ($\Delta H > 0$)	ΔS_{total} is never positive as it is the sum of two negative numbers.
(c) positive	negative ($\Delta H > 0$)	If +ve ΔS_{system} outweighs the –ve $\Delta S_{surroundings}$. Favoured by a high temperature since the –ve $\Delta S_{surroundings}$ becomes less significant.
(d) negative	positive ($\Delta H < 0$)	If +ve $\Delta S_{surroundings}$ outweighs the –ve ΔS_{system}. Favoured by a low temperature since the +ve $\Delta S_{surroundings}$ becomes more significant.

(a) ΔS_{system} and $\Delta S_{surroundings}$ are both positive e.g. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

ΔS_{system} is positive because 6 gas moles/molecules of reactants produce 7 gas moles/molecules of products.
Combustion of a fuel is exothermic so ΔH is negative. $\Delta S_{surr} = -\Delta H/T$ and so ΔS_{surr} is positive.

Note There are **not** "more atoms" or "more substances". Use the correct particle term in answers to any questions.

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ is therefore always positive. The reactants, $C_3H_{8\,(g)}$ and $O_{2\,(g)}$, are thermodynamically unstable with respect to the products, CO_2 (g) & H_2O (g). However, the reaction rate is very slow at 298K. The reactants are said to be "kinetically stable". This is because the reaction has high activation energy. Most importantly, ΔS_{total} and rate of reaction are *not* related and kinetic stability can override energetic instability if the temperature is low enough.

(b) ΔS_{sys} and ΔS_{surr} are both negative e.g. $3CO_2(g) + 4H_2O(g) \rightarrow C_3H_8(g) + 5O_2(g)$; the reverse of the example used in a).

ΔS_{total} is always negative so no reaction is possible and the $CO_2(g)$ and $H_2O(g)$ have thermodynamic stability.

(c) ΔS_{system} is positive and $\Delta S_{surroundings}$ is negative e.g. $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$.

ΔS_{system} is positive because a solid produces a gas and gases have much higher entropies than solids. Also, all decompositions are endothermic so ΔH is positive. $\Delta S_{surr} = -\Delta H/T$ and so ΔS_{surr} is negative.

$\Delta S_{system} + \Delta S_{surr} = \Delta S_{total} = 0$ defines the point at which the reaction switches from not energetically feasible to energetically feasible. i.e. when $\Delta S_{system} = -\Delta S_{surr} = \Delta H/T$ which means $T = \Delta H/\Delta S_{system}$
At *higher* temperatures $\Delta S_{total} > 0$ and the reaction becomes more and more energetically feasible.

(d) ΔS_{system} is negative and $\Delta S_{surroundings}$ is positive. e.g. $Mg_{(s)} + ½O_{2(g)} \rightarrow MgO_{(s)}$
ΔS_{system} is negative because a solid is produced from a gas and solids have much lower entropies than gases.
Also, magnesium burns exothermically so ΔH is negtive. $\Delta S_{surr} = -\Delta H/T$ and so ΔS_{surr} is positive.

Again, $\Delta S_{system} + \Delta S_{surr} = \Delta S_{total} = 0$ defines the point at which the reaction switches from not energetically feasible to energetically feasible. i.e. when $\Delta S_{system} = -\Delta S_{surr} = \Delta H/T$ which means $T = \Delta H/\Delta S_{system}$.
At *lower* temperatures $\Delta S_{total} > 0$ and the reaction becomes more and more energetically feasible.

5. Calculations

The calculations in (a) and (b) are for the reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

(a) ΔS_{total}

Method 1. $\Delta S_{total} = R\ln K$ (or $\Delta S_{total} = 2.3R\log K$). K is the equilibrium constant and R the ideal gas constant.

Method 2. $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = \{\mathbf{\Sigma}S(\text{Products}) - \mathbf{\Sigma}S(\text{Reactants})\} - \Delta H/T$.

Q1. Calculate ΔS_{total} by method 1: $K = 1.5 \times 10^{90}\ mol^{-1}\ dm^{-3}$; $R = 8.314\ Jmol^{-1}K^{-1}$ at 298K and by method 2 using $\Delta H = -556\ kJmol^{-1}$ and S values / $Jmol^{-1}K^{-1}$: $O_2(g) = 204$, $CO(g) = 198$, $CO_2(g) = +214$.

Method 1 $\Delta S_{total} = R\ln K = 8.314 \ln 1.5 \times 10^{90} = +1700\ J\ mol^{-1}\ K^{-1}$. (+1726)

Method 2

Calculating $\Delta S_{surroundings}$	Calculating ΔS_{system}	Calculating ΔS_{total}
$\Delta S_{surr} = \frac{-\Delta H}{T} = \frac{+556}{298}\ \frac{kJmol^{-1}}{K}$	$\Delta S_{system} = \mathbf{\Sigma}S(P) - \mathbf{\Sigma}S(R)$ - - - (**A**)	$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
	$\Delta S_{sys} = (\mathbf{2}\times 214) - (\mathbf{2}\times 198 + 204)$	$\Delta S_{total} = -172 + (1.87 \times 1000)$
$\Delta S_{surr} = +1.87\ kJmol^{-1}K^{-1}$	$\Delta S_{sys} = -172\ Jmol^{-1}K^{-1}$	$\Delta S_{total} = +1700\ Jmol^{-1}K^{-1}$ (+1698)

Note Make sure ΔS_{sys} and ΔS_{surr} are in the same entropy units before adding to obtain ΔS_{total}.
1kJ = 1000 J. Don't be careless when writing units. $J\ mol^{-1}\ K^{-}$ or $J\ mol^{-}\ K^{-1}$ are all wrong!

Note ΔH_r values can be calculated from ΔH_f, ΔH_c or estimated from bond enthalpies (BE), using:
(i) $\Delta H_r = \mathbf{\Sigma}\Delta H_f(P) - \mathbf{\Sigma}\Delta H_f(R)$,
(ii) $\Delta H_r = \mathbf{\Sigma}\Delta H_c(R) - \mathbf{\Sigma}\Delta H_c(P)$
or (iii) $\Delta H_r \approx \mathbf{\Sigma}BE(P) - \mathbf{\Sigma}BE(R)$ as appropriate.

Note When ΔS_{system} (or ΔH) is being calculated don't confuse R and P and include the number of moles of each R and each P.
Don't confuse S with ΔS in equation (**A**) and include the $\mathbf{\Sigma}$ signs if the equation is written.

Note ΔS_{system} (like ΔH) depends upon the initial and final states of the system and not on the reaction route.

(b) The Temperature at which ΔS_{total} is Zero

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ and $\Delta S_{surroundings} = -\Delta H/T \quad \therefore \Delta S_{total} = \Delta S_{system} - \Delta H/T$

$\therefore 0 = -172 + \frac{556 \times 1000}{T} \qquad \therefore T = \frac{556 \times 1000}{172} = 3290$ K. (Don't forget the units of T.)

(c) ΔS_{total} at a Different Temperature (Assume that ΔS_{sys} and ΔH do not change with temperature.)

Q2. Calculate ΔS_{total} at 40°C for $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$ if $\Delta S_{total} = +9040$ and $\Delta S_{sys} = -960\ Jmol^{-1}K^{-1}$ at 298K.

At 298K, $\Delta S_{total} = \Delta S_{system} - \Delta H/T \quad \therefore 9040 = -960 - (\Delta H/298) \therefore \Delta H = -2980000\ Jmol^{-1}$

$\therefore$ At 3.13K, $\Delta S_{total} = -960 + 2980000/313 \therefore \quad \Delta S_{total} = +8561\ J\ K^{-1}\ mol^{-1}$ (Rem. $^0C + 273 = K$)

Practice Questions

Assume that ΔH and ΔS_{system} do not vary with temperature unless a change of state is given.

1. Explain, in terms of entropy changes, why ammonium nitrate dissolves in water. The temperature of the solution formed is lower than the temperature of the water.

2. Explain, in terms of entropy changes, why the exothermic reaction (i) is spontaneous at all temperature, but the exothermic reaction (ii) is spontaneous only if the temperature is sufficiently low. (Assume no changes of states occur.)
   (i) $Al(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 1\frac{1}{2}H_2(g)$
   (ii) $Al(s) + 3HCl(g) \rightarrow AlCl_3(s) + 1\frac{1}{2}H_2(g)$

3. Explain briefly which one in each of the following pairs has the higher molar entropy at 298K.
   (a) $CuSO_4(s)$, $CuSO_4 5H_2O(s)$;
   (b) $^{20}Ne(g)$, $^{14}N^2H_3(g)$;
   (c) $[Cu(H_2O)_6]^{2+}(aq)$, $[CuEDTA]^{2-}$;
   (d) $C_2H_4(g)$, $C_2H_6(g)$.

4. Explain in terms of entropy how endothermic reactions can take place spontaneously.

5. Calculate the entropy change of the system when 4 moles of ammonia condense at its boiling point of -33.4^0C. The heat of vaporization of NH_3 is + 23.4 $kJmol^{-1}$.

6. Calculate ΔS_{total} for $CS_2(l) + 2O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$ at 298K. $\Delta H = -1075.0\ kJmol^{-1}$.
   S values / $CS_2(l)$ 238.0, $O_2(g)$ 205.2, $CO_2(g)$ 213.4, $SO_2(g)$ 248.2 $Jmol^{-1}K^{-1}$

7. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ - - (1) $\Delta S^{\ominus}_{total} = +768\ kJmol^{-1}$
   and $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ - - (2) $\Delta S^{\ominus}_{total} = +795\ kJmol^{-1}$.
   Explain the differences in ΔS_{system} and $\Delta S_{surroundings}$ and hence in ΔS_{total} for the two reactions.

8. Calculate ΔS_{total} for $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$ at 404K. ΔS_{total} at 298K = - 119 $Jmol^{-1}K^{-1}$.
   Entropies at 298K are: $NaHCO_3(s)$ = 102; $Na_2CO_{3(s)}$ =135; $CO_2(g)$ = 214; $H_2O(g)$ = 189 $Jmol^{-1}K^{-1}$. (Give your answer to the nearest integer.)
   What is the significance of your answer?

9. Calculate $\Delta S^{\ominus}$ for $2NH_4NO_3(s) + C(s) \rightarrow 2N_2(g) + CO_2(g) + 4H_2O(g)$ at 25^oC to three s.f.
   $\Delta H^{\ominus}_f$ / $kJmol^{-1}$: $NH_4NO_3(s)$ = - 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^oC?
   Explain at what temperature (if any) this reaction will be spontaneous.

10. Methanol is mixed with ethanol to make methylated spirits. Describe and explain what happens to the entropy of the system when mixing occurs, compared with the separate compounds.

Answers

(Make sure the number of sig figs in your answer is appropriate)

1. ΔS_{system} is +ve as disorder increases (more particles of P than R).
   Temp change → dissolving is endothermic
   so ΔS_{surr} is –ve ($\Delta S_{surr} = -\Delta H/T$).
   The ΔS_{system} increase must be greater than the $\Delta S_{surr.}$ decrease to make ΔS_{total} +ve and dissolving feasible.

2. (i) ΔS_{surr} is =+ ve since the reaction is exothermic (ÄS_{surr} = - ÄH/T).
   ΔS_{system} is +ve (gas produced which is more disordered than (s) / (aq) reactants).
   $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ is +ve and the reaction is therefore spontaneous.

   (ii) Here ΔS_{system} is - ve (less moles of gas so less disorder).
   $\Delta S_{surroundings}$ will only be more + ve than ΔS_{system} is -ve if the temperature is sufficiently low.
   Only then will ΔS_{total} be +ve and the reaction spontaneous.

3. (a) $CuSO_4 5H_2O(s)$; (b) $^{14}N^2H_3(g)$; (c) $[CuEDTA]^{2-}$; (d) $C_2H_6(g)$.
   They are all more complex.

4. ΔS_{system} must be more positive than $\Delta H/T$, ($\Delta S_{surr} = -\Delta H/T$).
   $\therefore \Delta S_{total} > 0$. $\therefore$ Spontaneous.

5. $\Delta S_{sys} = -\Delta H/T$ per mole $= -(+23.4)/(273 - 33.4) = -0.0977\ kJmol^{-1}K^{-1}$.
   Ans to Q = $-0.0977 \times 4 = -0.391\ kJK^{-1}$

6. $\Delta S_{sys} = 213.4 + 2(248.2) - \{238 + 2(205.2)\} = +61.4$.
   $\Delta S_{surr} = 1075 \times 1000/298 = +3607.4$.
   $\therefore \Delta S_{tot} = +3668.4\ Jmol^{-1}K^{-1}$

7. ΔS_{system} for (2) is more negative than (1) since $S_{H2O}(l) < S_{H2O}(g)$. (This makes ΔS_{total} less positive.)
   ΔH for (2) is more exothermic since when $H_2O(g)$ condenses energy is released because hydrogen bonds form. So ΔS_{surr} is more positive for (2).
   The increase in ΔS_{surr} exceeds the decrease in ΔS_{system} by 27 $Jmol^{-1}K^{-1}$ so ΔS_{total} is more positive for (2).

8. $\Delta S_{system} = (135 + 189 + 214) - 2(102) = +334\ Jmol^{-1}K^{-1}$.
   At 298K $\Delta S_{total} = \Delta S_{system} - \Delta H/T$ $\therefore -119.1 = 334 - (\Delta H/298)$
   $\therefore \Delta H = +135023.8\ Jmol^{-1}$
   $\therefore \Delta S_{total}$ at 404K $= 334 - 134994/404$ $\therefore \Delta S_{total} = 0\ JK^{-1}\ mol^{-1}$
   The reaction just becomes feasible at404K.

9. $\Delta H = \{-394 + 4(-242)\} - 2(-365) = -632\ kJmol^{-1}$.
   $\Delta S_{sys} = 2(192) + 214 + 4(119) - \{2(260) + 5.6\} = +548.4\ Jmol^{-1}K^{-1}$.
   $\Delta S_{tot} = 548.4 + 632 \times 1000/298 = +2669\ Jmol^{-1}K^{-1}$.
   Reaction is between two solids.
   ΔH is –ve and ΔS_{system} is +ve so ΔS_{total} is always +ve.
   The reaction is spontaneous at all temperatures.

10. Entropy increases. More ways of arranging the molecules when the liquids are mixed than in the separate liquids.

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