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Tutorials for IB Chemistry

Topic 15
Energetics HL

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Born-Haber cycles

Born-Haber cycles

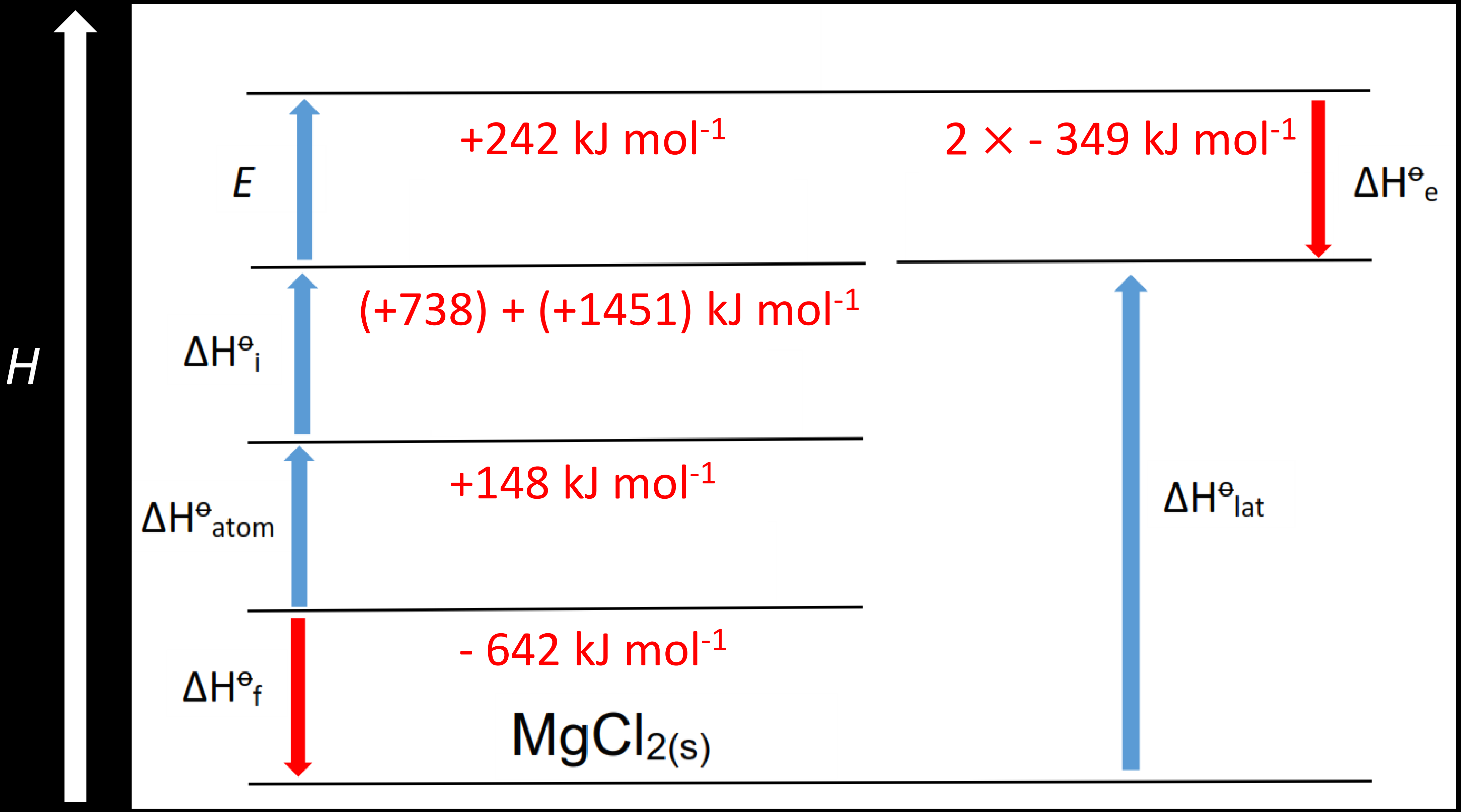
A Born-Haber cycle is an energy cycle for the formation of an ionic compound ($\Delta H^\ominus_f$).

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

The lattice enthalpy ($\Delta H^\ominus_{lat}$) is the enthalpy change when one mole of solid ionic compound is broken down into gaseous ions under standard conditions.

$$MgCl_{2(s)} \rightarrow Mg^{2+}_{(g)} + 2Cl^{-}_{(g)}$$

Born-Haber cycles



H

E

+242 kJ mol^{-1}

2 × - 349 kJ mol^{-1}

$\Delta H^{\ominus}_{e}$

$\Delta H^{\ominus}_{i}$

(+738) + (+1451) kJ mol^{-1}

$\Delta H^{\ominus}_{atom}$

+148 kJ mol^{-1}

$\Delta H^{\ominus}_{lat}$

$\Delta H^{\ominus}_{f}$

- 642 kJ mol^{-1}

$MgCl_{2(s)}$

Born-Haber cycles

$$\Delta H^{\ominus}_{f} = \Delta H^{\ominus}_{atom} + \Delta H^{\ominus}_{i} + E + \Delta H^{\ominus}_{e} - \Delta H^{\ominus}_{lat}$$

$$\Delta H^{\ominus}_{lat} = \Delta H^{\ominus}_{atom} + \Delta H^{\ominus}_{i} + E + \Delta H^{\ominus}_{e} - \Delta H^{\ominus}_{f}$$

$$\Delta H^{\ominus}_{lat} = 148 + (738 + 1451) + 242 + (2 \times - 349) - (- 642)$$

$$\Delta H^{\ominus}_{lat} = +2523 \text{ kJmol}^{-1}$$

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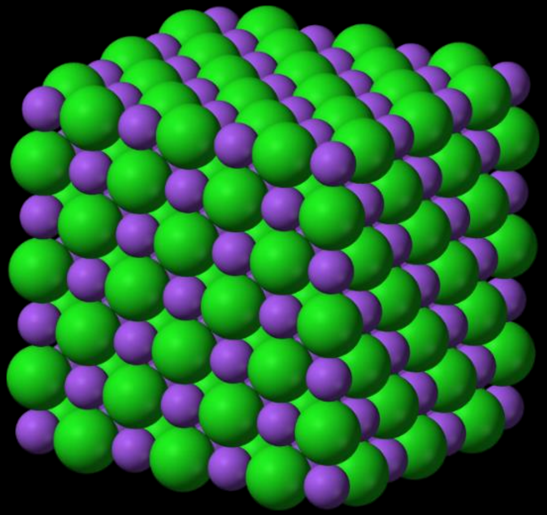
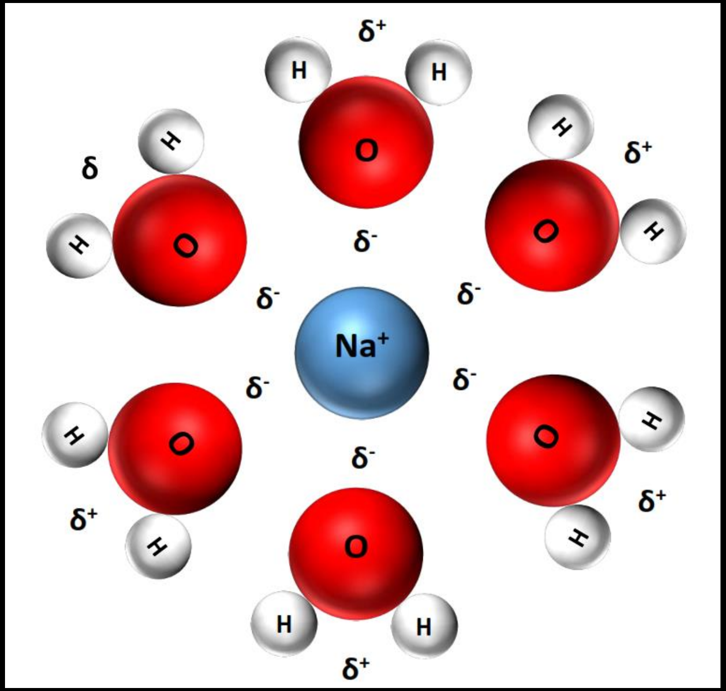
Enthalpy change of solution, ΔH_{sol}

Enthalpy of solution ($\Delta H^{\ominus}_{sol}$)



The solid ionic compound is broken down into gaseous ions ($\Delta H^{\ominus}_{lat}$).

The gaseous ions are hydrated by water molecules ($\Delta H^{\ominus}_{hyd}$).


δ+
H
H
O
δ
H
H
O
δ+
H
O
H
δ-
δ-
δ-
Na+
δ-
δ-
H
O
O
H
δ-
δ+
H
O
H
δ+
H
H
δ+

Enthalpy of solution ($\Delta H^\ominus_{sol}$)

The enthalpy change of solution ($\Delta H^\ominus_{sol}$) is the enthalpy change when one mole of an ionic substance dissolves in water to give a solution of infinite dilution.

$$\boxed{NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}}$$

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Enthalpy of hydration (ΔH°_{hyd})

The enthalpy of hydration (ΔH°_{hyd}) is the enthalpy change when one mole of gaseous ions dissolve in water to give a solution of infinite dilution.

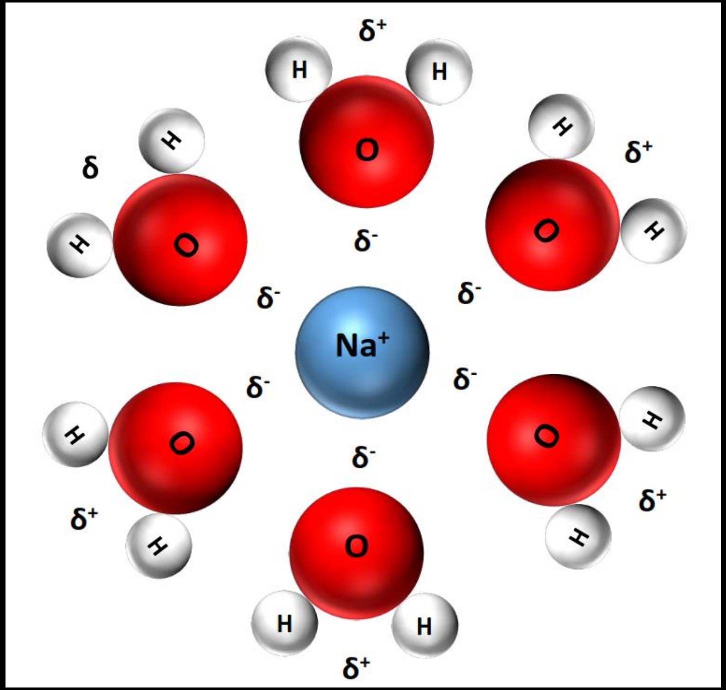
Enthalpies of hydration are always negative (exothermic).

$$Na^{+}_{(g)} \rightarrow Na^{+}_{(aq)}$$

$$Cl^{-}_{(g)} \rightarrow Cl^{-}_{(aq)}$$

Enthalpy of hydration ($\Delta H^{\ominus}_{hyd}$)

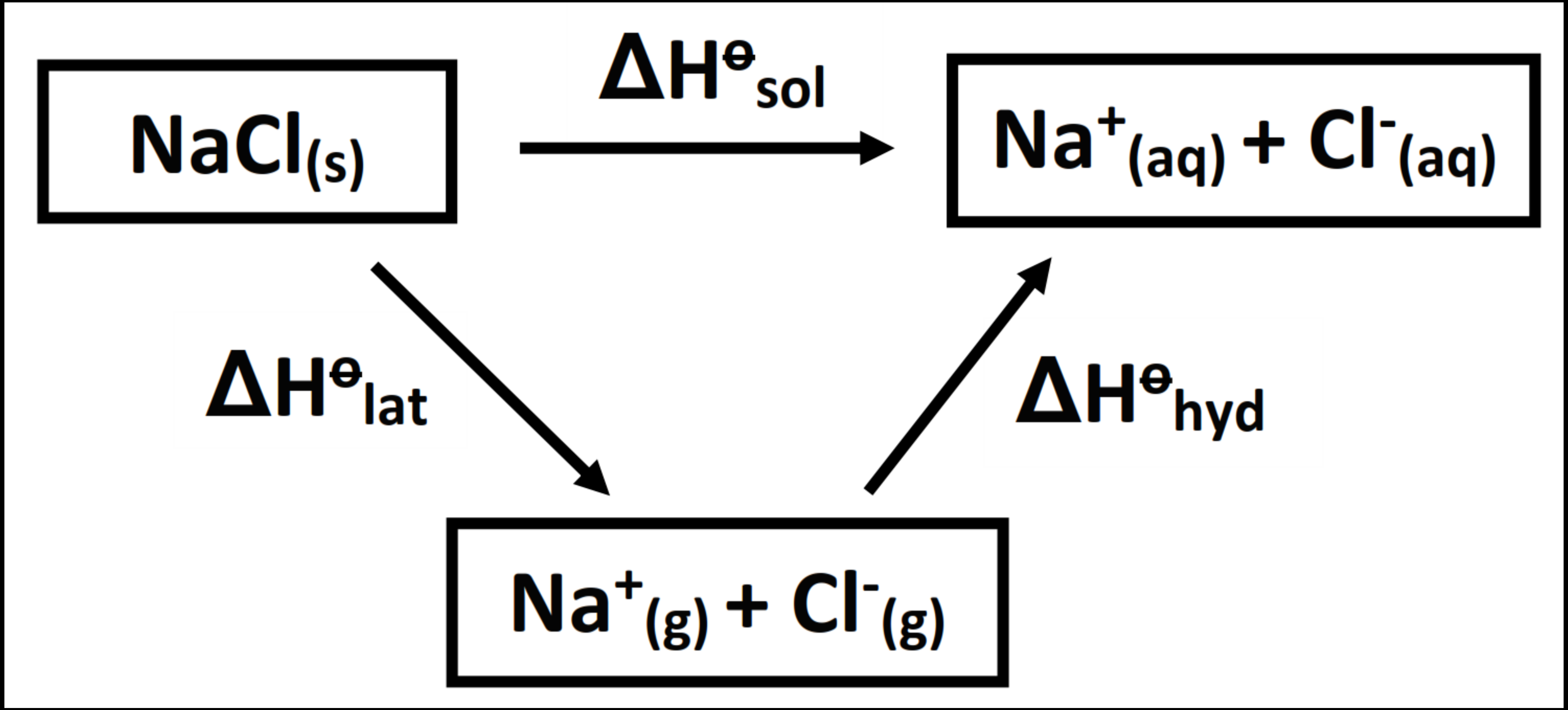
When a gaseous ion is hydrated, ion-dipole forces occur between the gaseous ion and the dipoles of the water molecule.



The formation of ion-dipole forces releases energy so ΔH_{hyd} values are always negative.

The higher the charge on the ion and the smaller the ionic radius, the more exothermic the value of the ΔH_{hyd} .

Enthalpy of solution ($\Delta H^\ominus_{sol}$)


$NaCl_{(s)}$
$\Delta H^\ominus_{sol}$
$Na^+_{(aq)} + Cl^-_{(aq)}$
$\Delta H^\ominus_{lat}$
$\Delta H^\ominus_{hyd}$
$Na^+_{(g)} + Cl^-_{(g)}$

$$\Delta H^\ominus_{sol} = \Delta H^\ominus_{lat} + \Delta H^\ominus_{hyd}$$

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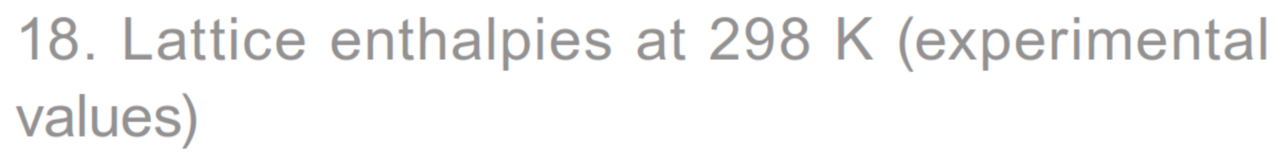
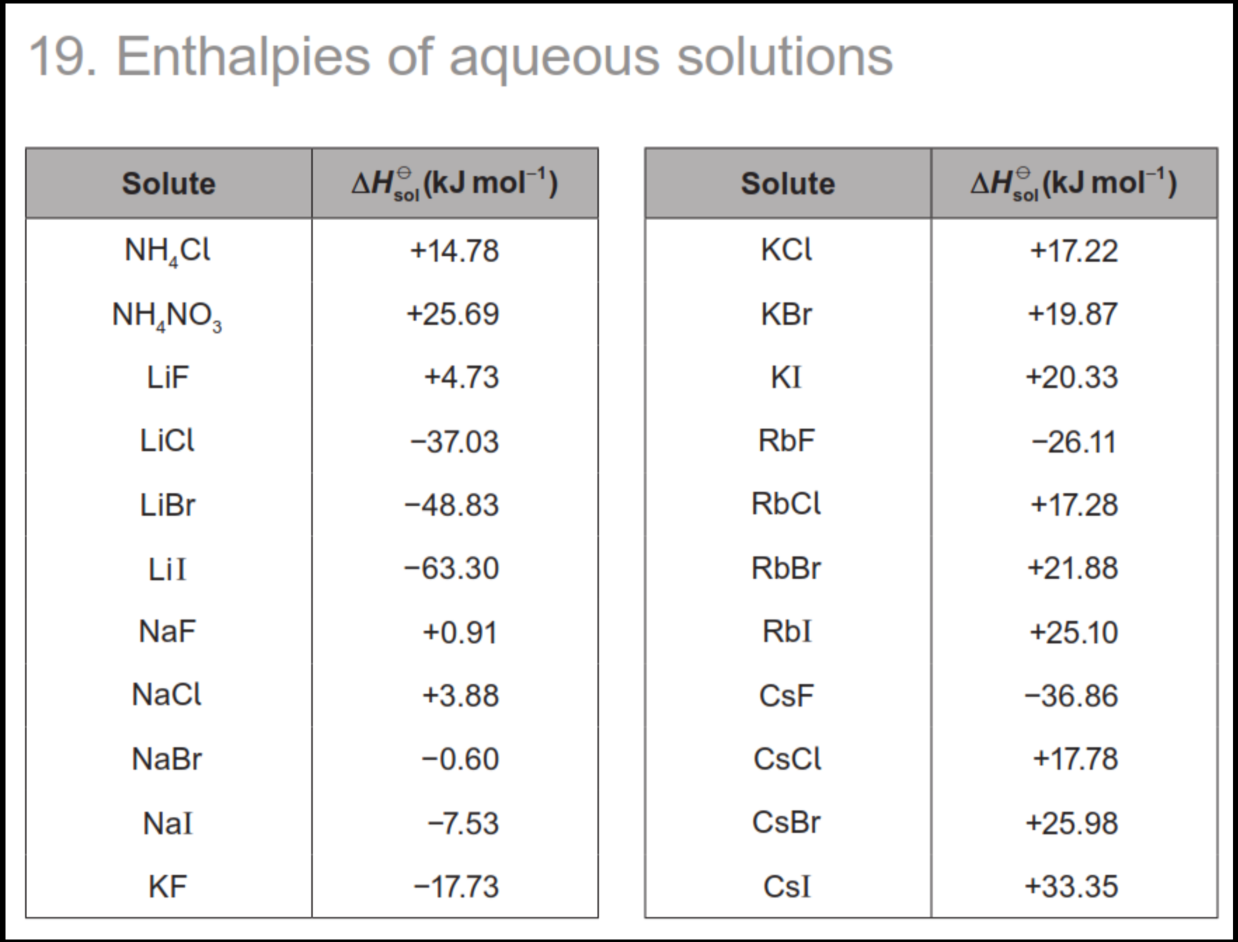
Enthalpy of solution ($\Delta H^\ominus_{sol}$)



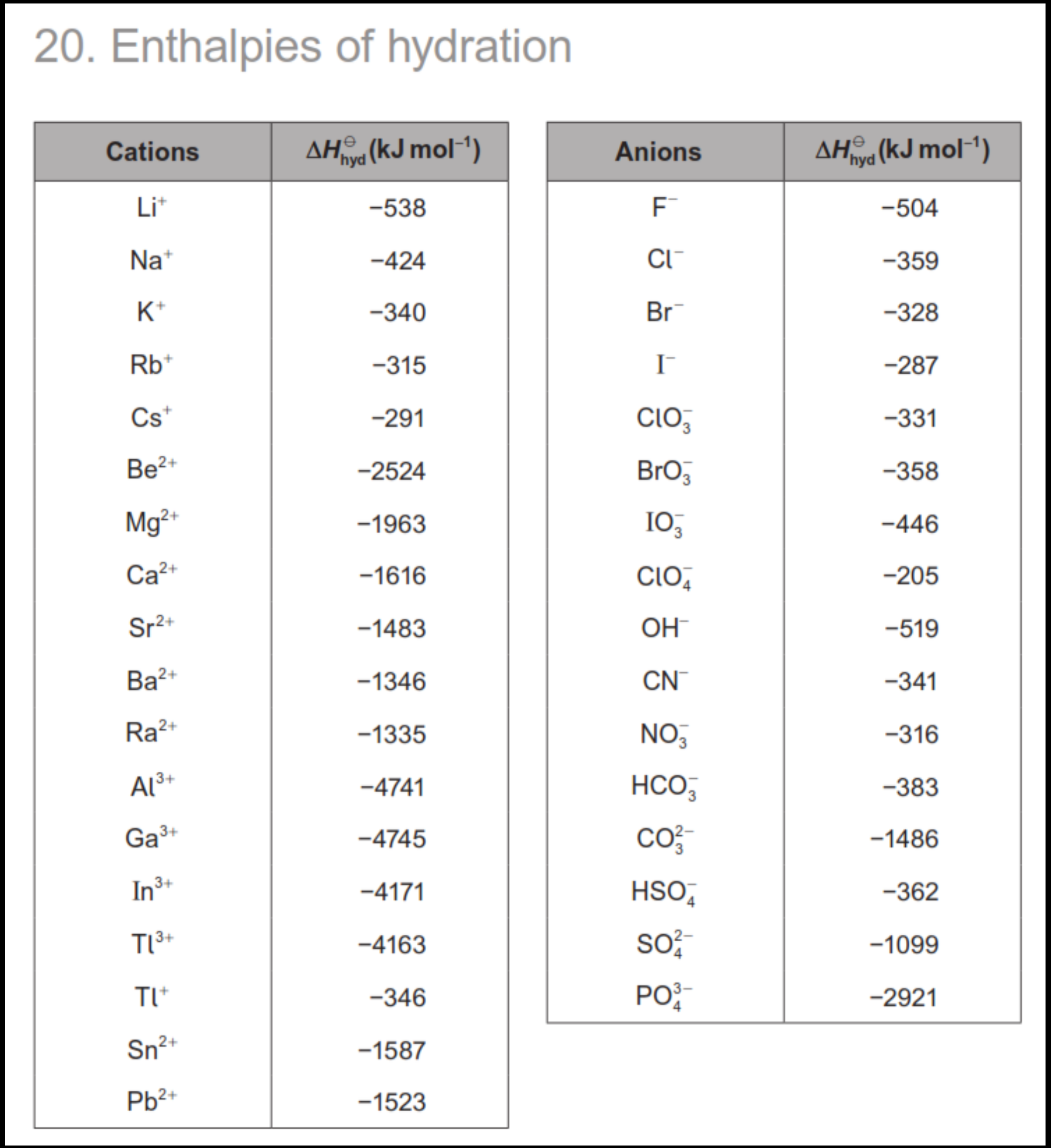
18. Lattice enthalpies at 298 K (experimental values)



19. Enthalpies of aqueous solutions

Solute	$\Delta H^\ominus_{sol}$ (kJ mol^{-1})
NH_4Cl	+14.78
NH_4NO_3	+25.69
LiF	+4.73
LiCl	−37.03
LiBr	−48.83
LiI	−63.30
NaF	+0.91
NaCl	+3.88
NaBr	−0.60
NaI	−7.53
KF	−17.73

Solute	$\Delta H^\ominus_{sol}$ (kJ mol^{-1})
KCl	+17.22
KBr	+19.87
KI	+20.33
RbF	−26.11
RbCl	+17.28
RbBr	+21.88
RbI	+25.10
CsF	−36.86
CsCl	+17.78
CsBr	+25.98
CsI	+33.35



20. Enthalpies of hydration

Cations	$\Delta H^\ominus_{hyd}$ (kJ mol^{-1})
Li^+	−538
Na^+	−424
K^+	−340
Rb^+	−315
Cs^+	−291
Be^{2+}	−2524
Mg^{2+}	−1963
Ca^{2+}	−1616
Sr^{2+}	−1483
Ba^{2+}	−1346
Ra^{2+}	−1335
Al^{3+}	−4741
Ga^{3+}	−4745
In^{3+}	−4171
Tl^{3+}	−4163
Tl^+	−346
Sn^{2+}	−1587
Pb^{2+}	−1523

Anions	$\Delta H^\ominus_{hyd}$ (kJ mol^{-1})
F^-	−504
Cl^-	−359
Br^-	−328
I^-	−287
ClO_3^-	−331
BrO_3^-	−358
IO_3^-	−446
ClO_4^-	−205
OH^-	−519
CN^-	−341
NO_3^-	−316
HCO_3^-	−383
CO_3^{2-}	−1486
HSO_4^-	−362
SO_4^{2-}	−1099
PO_4^{3-}	−2921

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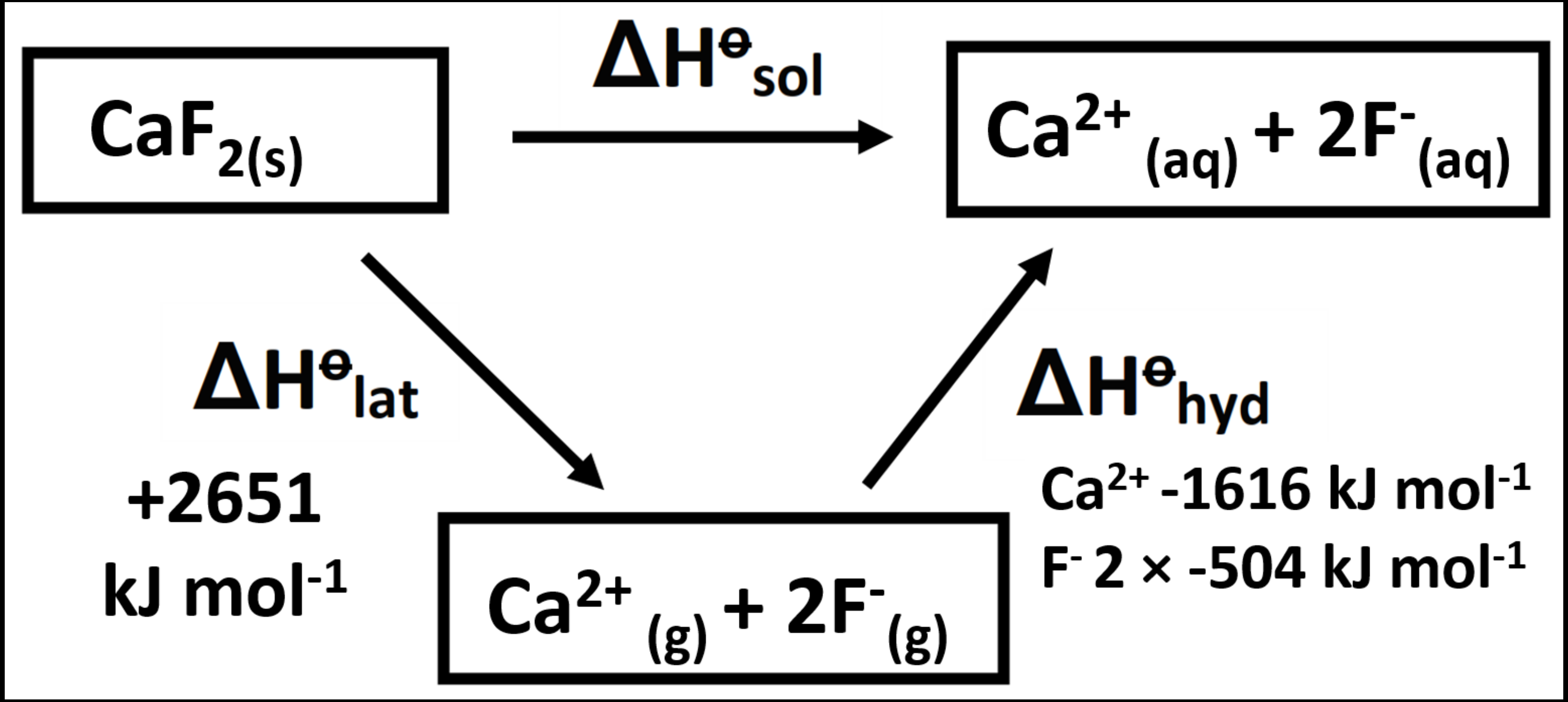
Enthalpy of solution ($\Delta H^{\ominus}_{sol}$)

Use the data in sections 18 and 20 to calculate the enthalpy change of solution $\Delta H^{\ominus}_{sol}$ of CaF_2.


$CaF_{2(s)}$
$\Delta H^{\ominus}_{sol}$
$Ca^{2+}{}_{(aq)} + 2F^{-}{}_{(aq)}$
$\Delta H^{\ominus}_{lat}$
+2651
kJ mol^{-1}
$\Delta H^{\ominus}_{hyd}$
Ca^{2+} -1616 kJ mol^{-1}
F^{-} 2 × -504 kJ mol^{-1}
$Ca^{2+}{}_{(g)} + 2F^{-}{}_{(g)}$

Enthalpy of solution ($\Delta H^{\ominus}_{sol}$)

Use the data in sections 18 and 20 to calculate the enthalpy change of solution $\Delta H^{\ominus}_{sol}$ of CaF_2.

$$\Delta H^{\ominus}_{sol} = \Delta H^{\ominus}_{lat} + \Delta H^{\ominus}_{hyd}$$

$$\Delta H^{\ominus}_{sol} = +2651 + (-1616 + 2 \times -504)$$

$$\Delta H^{\ominus}_{sol} = +27.0 \text{ kJ mol}^{-1}$$

Enthalpy of solution ($\Delta H^\ominus_{sol}$)

Use the data in sections 19 and 20 to calculate the lattice enthalpy of NH_4Cl.

$$\Delta H^\ominus_{lat} = \Delta H^\ominus_{sol} - \Delta H^\ominus_{hyd}$$

$$\Delta H^\ominus_{lat} = +14.78 + (-307 + -359)$$

$$\Delta H^\ominus_{lat} = +680\ \text{kJ mol}^{-1}$$

Enthalpy of solution ($\Delta H^{\ominus}_{sol}$)

The solubility of an ionic compound depends on the magnitude of the $\Delta H^{\ominus}_{lat}$ compared to the $\Delta H^{\ominus}_{hyd}$.

If the $\Delta H^{\ominus}_{lat}$ is greater than the $\Delta H^{\ominus}_{hyd}$, the $\Delta H^{\ominus}_{sol}$ is endothermic.

If the $\Delta H^{\ominus}_{lat}$ is less than the $\Delta H^{\ominus}_{hyd}$, the $\Delta H^{\ominus}_{sol}$ is exothermic.

An exothermic $\Delta H^{\ominus}_{sol}$ favours the dissolving process.

Whether an ionic compound with an endothermic $\Delta H^{\ominus}_{sol}$ is soluble or not depends on the ΔS.

Enthalpy of solution ($\Delta H^{\ominus}_{sol}$)

The change in entropy is also a factor that determines the solubility of an ionic compound.

NaCl has a $\Delta H^{\ominus}_{sol}$ of +3.9 kJ mol^{-1}.

NaCl is soluble in water because the increase in entropy makes up for the endothermic $\Delta H^{\ominus}_{sol}$.

$$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Ionic compounds with a $+\Delta H^{\ominus}_{sol}$ are only soluble if the change in entropy is large enough to outweigh it.

Enthalpy of solution ($\Delta H^{\ominus}_{sol}$)

The dissolving of ammonium nitrate has a $\Delta H^{\ominus}_{sol}$ of +25.7 kJ mol^{-1} and a ΔS of +108 J K^{-1} mol^{-1}. Determine the spontaneity of the dissolving process at 25°C.

$$\Delta G = \Delta H - \mathrm{T}\Delta S$$

$$\Delta G = 25.7 - (298 \times 0.108)$$

$$\Delta G = -6.48 \text{ kJ mol}^{-1}$$

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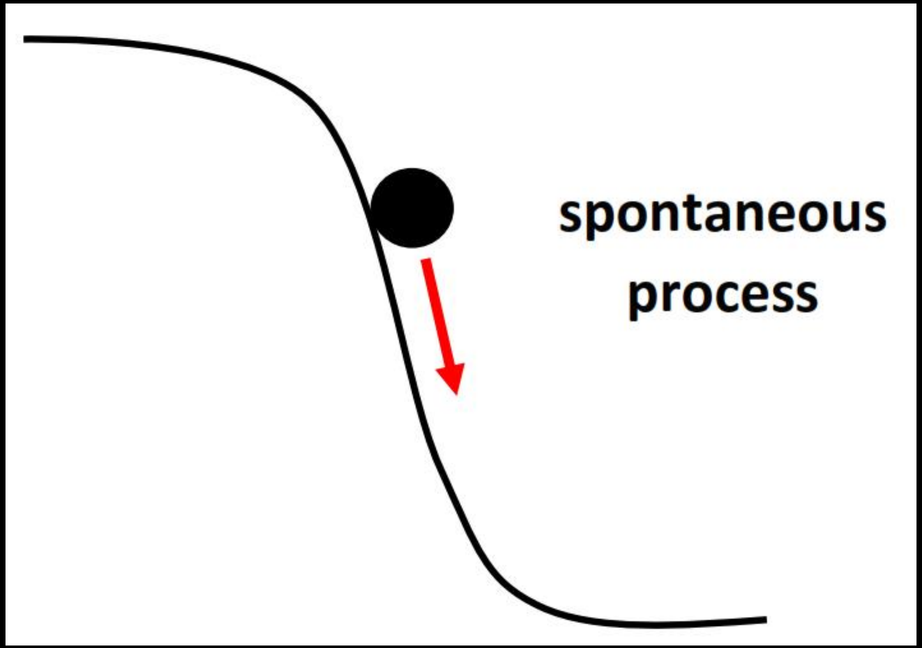
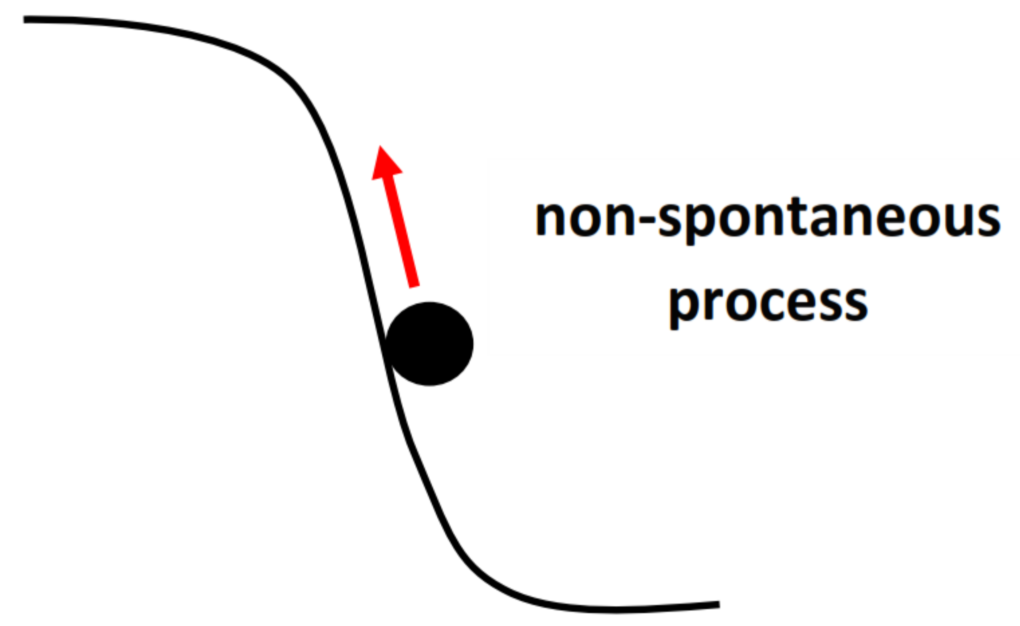
Entropy and spontaneity

Entropy and spontaneity

A spontaneous process is a process that occurs without adding energy (other than the energy required to overcome the energy barrier).


spontaneous process


non-spontaneous process

Entropy and spontaneity

Spontaneous processes can be either fast or slow.

Combustion is a fast spontaneous process.

Rusting is a slow spontaneous process.

Entropy and spontaneity

According to the second law of thermodynamics, for a spontaneous process the change in entropy of the universe (ΔS_{total}) must be positive.

$$\boxed{\Delta S_{(total)} = \Delta S_{(system)} + \Delta S_{(surroundings)}}$$

For a spontaneous process:

$$\boxed{\Delta S_{(total)} > 0}$$

Entropy and spontaneity

The temperature of the surroundings affects the $\Delta S_{\text{(surroundings)}}$ when heat is added.

$$\boxed{\Delta S_{\text{(surroundings)}} = -\frac{\Delta H_{\text{system}}}{\text{T}}}$$

Heat added to low temperature surroundings has a greater effect than heat added to high temperature surroundings.

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Entropy and spontaneity

$$\Delta S_{\text{(surroundings)}} = -\frac{\Delta H_{\text{system}}}{\text{T}}$$

$$H_2O_{(l)} \rightarrow H_2O_{(s)}$$

$\Delta S_{\text{(system)}} = -22.0\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Delta H_{\text{(system)}} = -6.01\ \text{kJ mol}^{-1}$

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Entropy and spontaneity

$H_2O_{(l)} \rightarrow H_2O_{(s)}$ at -10°C (263 K)

$$\Delta S_{(\text{surroundings})} = -\frac{-6010}{263}$$

$\Delta S_{(\text{surroundings})} = +22.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Delta S_{(\text{total})} = -22.0 + 22.9 = +0.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

Freezing is spontaneous at 263 K (-10°C)

Entropy and spontaneity

$H_2O_{(l)} \rightarrow H_2O_{(s)}$ at 10°C (283 K)

$$\Delta S_{(\text{surroundings})} = -\frac{-6010}{283}$$

$$\Delta S_{(\text{surroundings})} = +21.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{(\text{total})} = -22.0 + 21.2 = -0.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Freezing is non-spontaneous at 283 K (10°C)

Entropy and spontaneity

For a spontaneous process:

$$\Delta S_{(total)} > 0$$

$H_2O_{(l)} \rightarrow H_2O_{(s)}$ at 263 K $\Delta S_{(total)} > 0$

$H_2O_{(l)} \rightarrow H_2O_{(s)}$ at 283 K $\Delta S_{(total)} < 0$

Entropy and spontaneity

Exothermic reaction – heat lost by the system is gained by the surroundings.

$\Delta H_{(\text{system})} < 0$

$\Delta S_{(\text{surroundings})} > 0$

Endothermic reaction – heat gained by the system is lost by the surroundings.

$\Delta H_{(\text{system})} > 0$

$\Delta S_{(\text{surroundings})} < 0$

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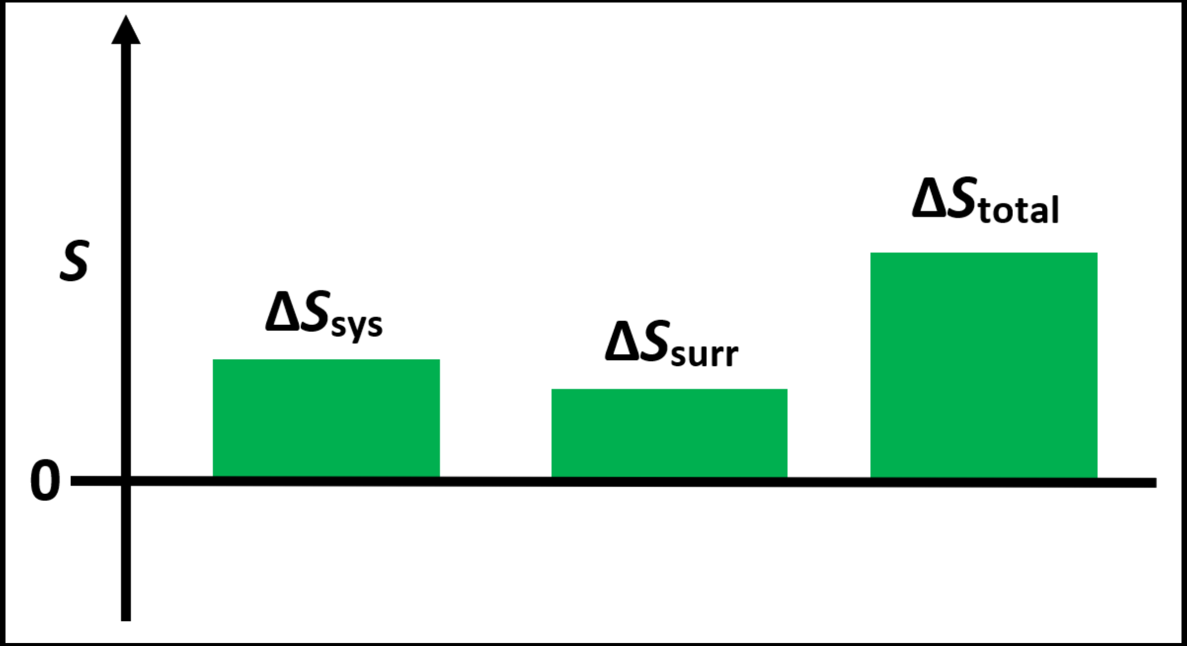
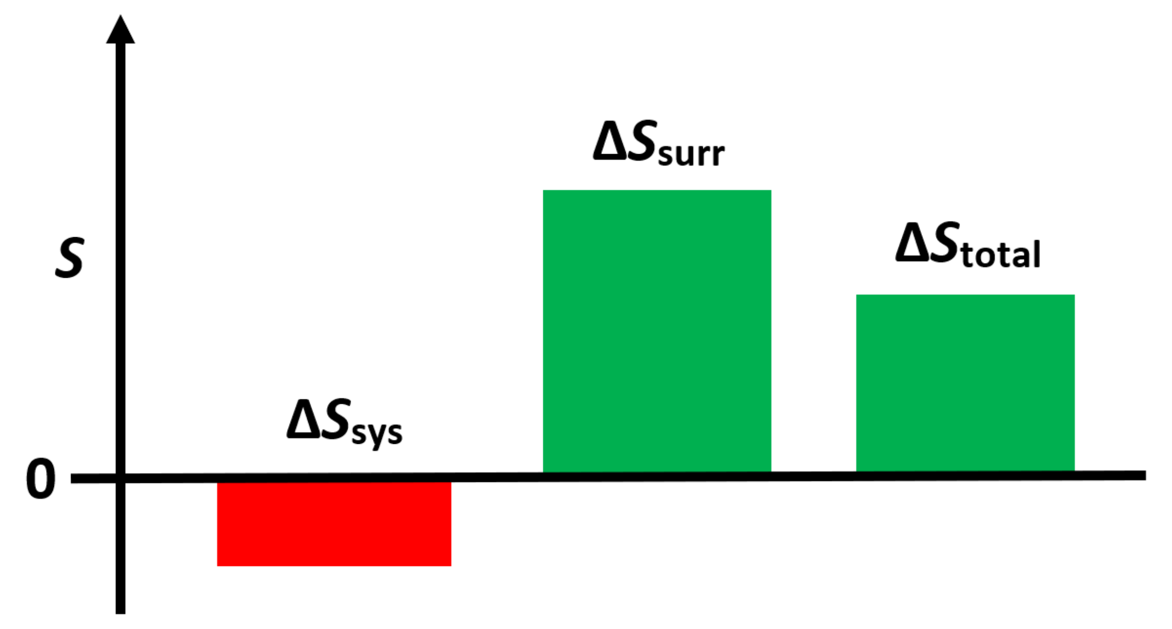
Entropy and spontaneity

$\Delta H_{(sys)} < 0 \quad \Delta S_{(sys)} > 0$



$\Delta S_{(total)}$ is positive irrespective of $\Delta S_{(surr)}$

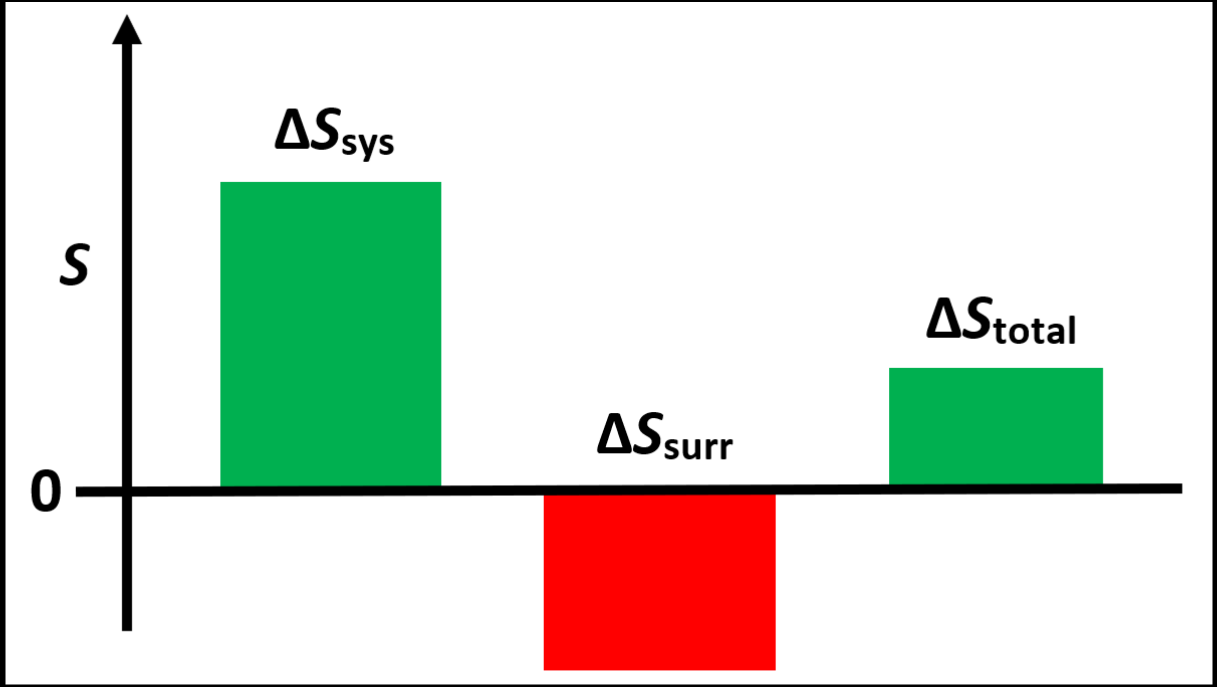
$\Delta H_{(sys)} < 0 \quad \Delta S_{(sys)} < 0$



$\Delta S_{(total)}$ can only be positive if $\Delta S_{(surr)} > \Delta S_{(sys)}$

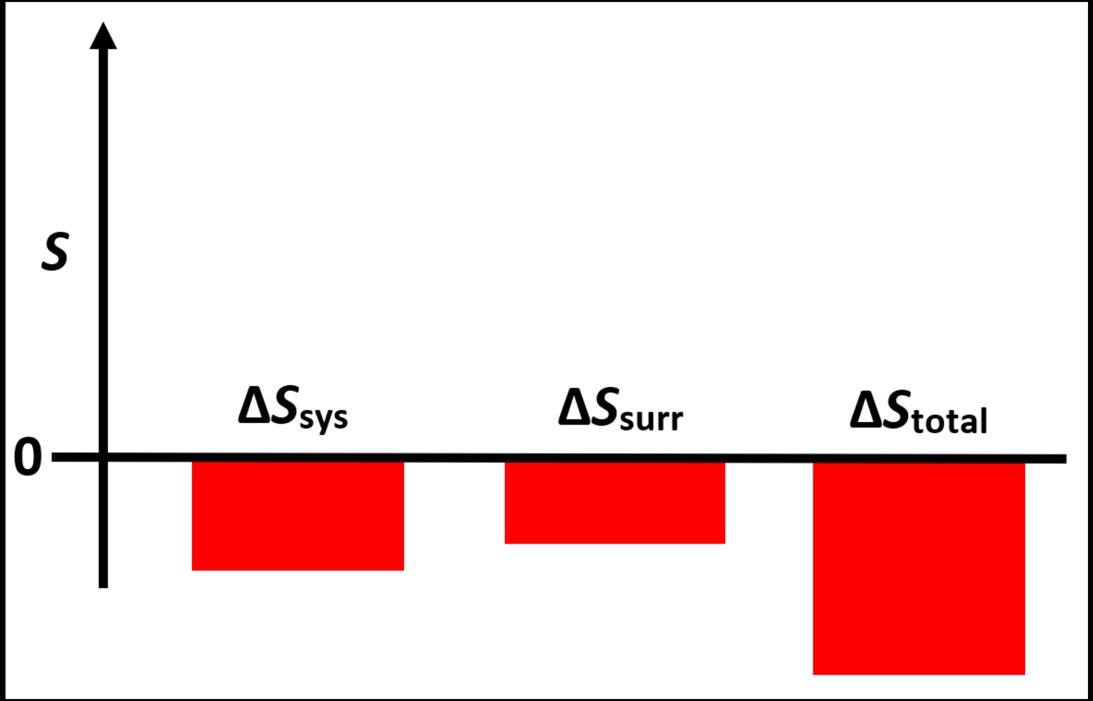
Entropy and spontaneity

$\Delta H_{(sys)} > 0$ $\Delta S_{(sys)} > 0$



$\Delta S_{(total)}$ can only be positive if $\Delta S_{(surr)} < \Delta S_{(sys)}$

$\Delta S_{(sys)} < 0$ $\Delta S_{(surr)} < 0$



$\Delta S_{(total)}$ can never be positive

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Entropy and spontaneity

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(g)}$$

$\Delta S_{(sys)} > 0$ $\Delta S_{(surr)} > 0$ $\Delta S_{(total)} > 0$

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$$

$\Delta S_{(sys)} < 0$ $\Delta S_{(surr)} >> 0$ $\Delta S_{(total)} > 0$

$$Ba(OH)_2 \bullet 8H_2O_{(s)} + 2NH_4NO_{3(s)} \rightarrow Ba(NO_3)_{2(aq)} + 2NH_{3(aq)} + 10H_2O_{(l)}$$

$\Delta S_{(sys)} >> 0$ $\Delta S_{(surr)} < 0$ $\Delta S_{(total)} > 0$

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Entropy (S)

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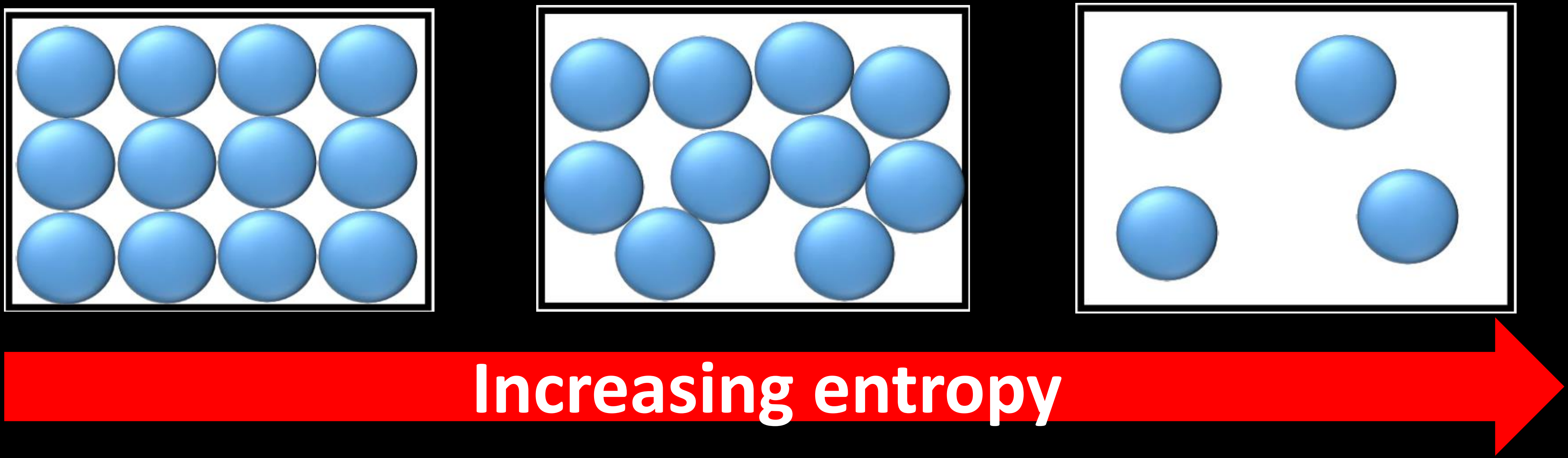
Entropy (*S*)

Entropy (*S*) refers to the distribution of available energy among the particles in a system.

The more ways in which the energy can be distributed, the higher the entropy.



Entropy (S)

$$S = k \ln W$$

k – the Boltzmann constant (R/L = 1.38×10^{-23} J mol^{-1})

W – number of different microstates

A microstate is the arrangement of each molecule in the system at a single instant.

The greater the number of microstates, the greater the number of ways that energy can be distributed.

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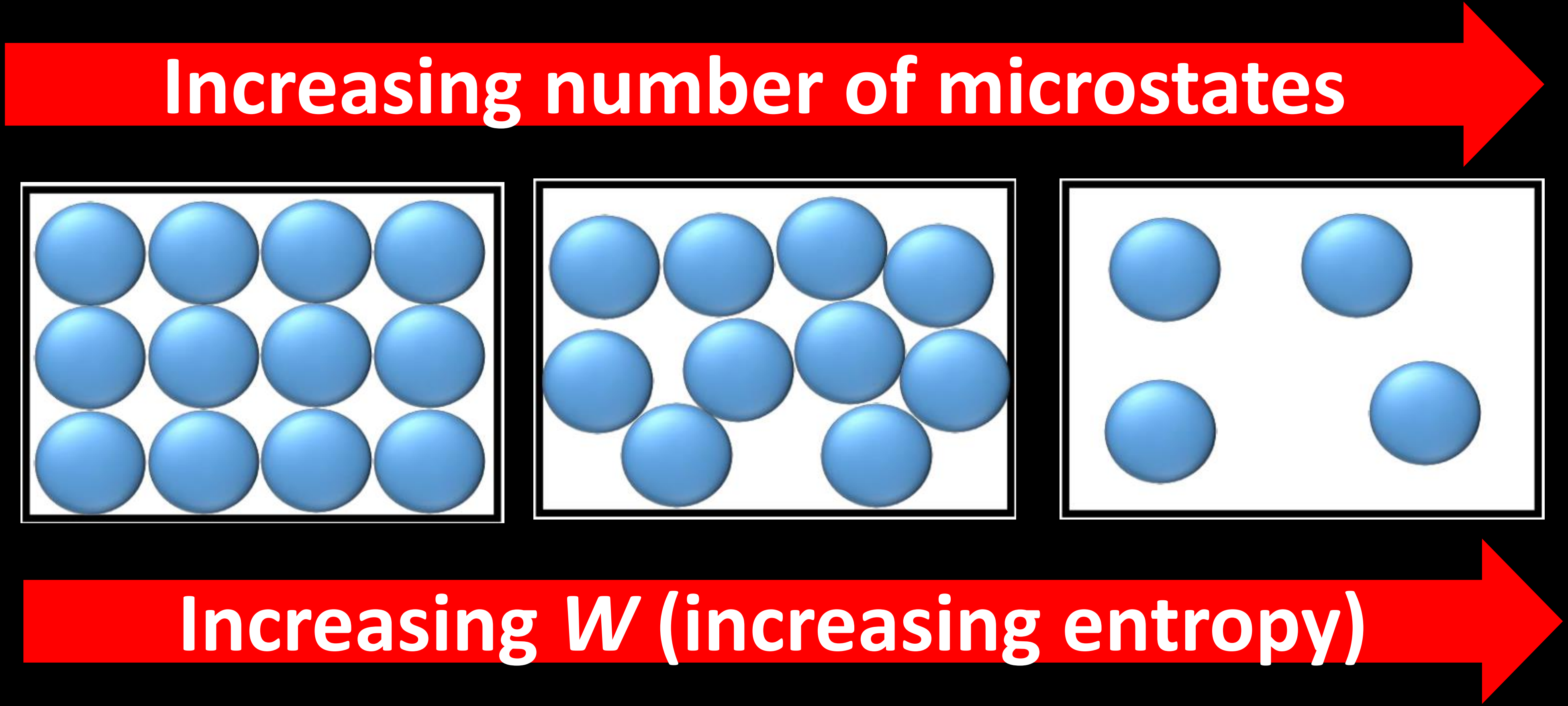
Entropy (S)

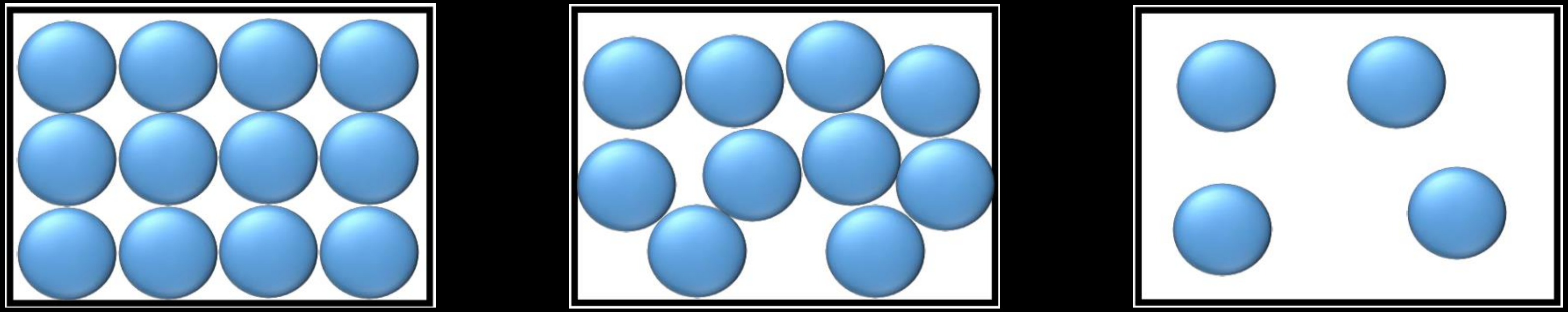
A microstate is the arrangement of each molecule in the system at a single instant.


Increasing number of microstates

Increasing *W* (increasing entropy)

Entropy (S)

State of matter	Absolute entropy ($S^\ominus$) J K^{-1} mol^{-1}
$H_2O_{(s)}$	41.3
$H_2O_{(l)}$	70.0
$H_2O_{(g)}$	188



solids < liquids < gases

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Predicting entropy changes (ΔS)

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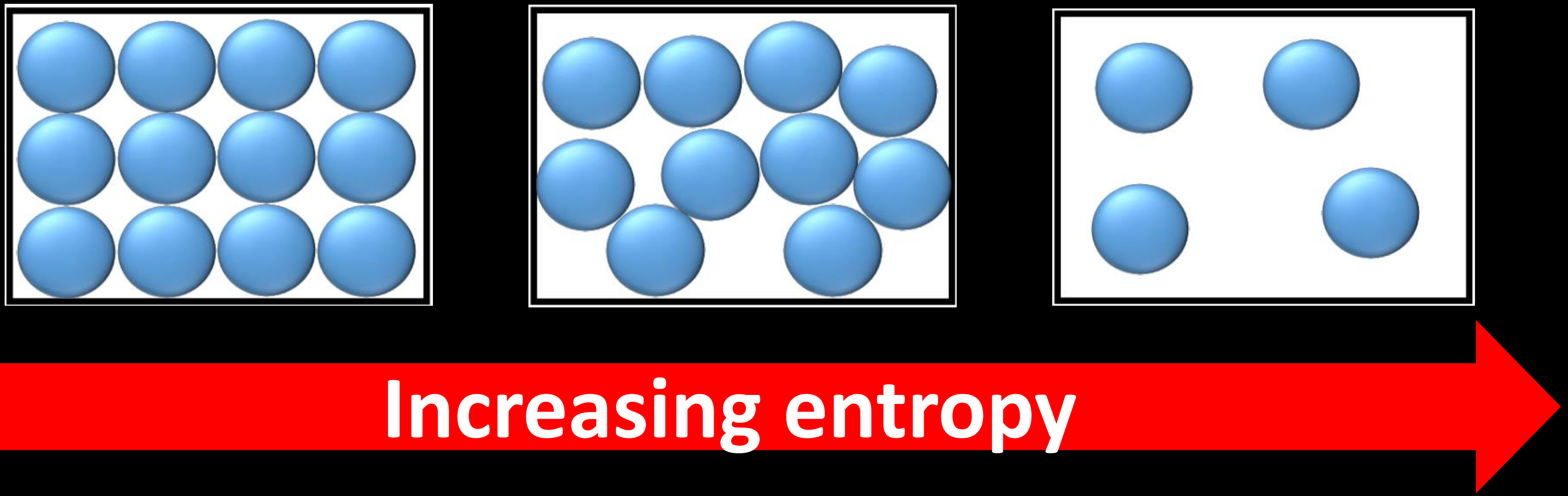
Entropy (S)

A system with fewer ways to distribute energy has a lower entropy.

A system with more ways to distribute energy has a higher entropy.


Increasing entropy

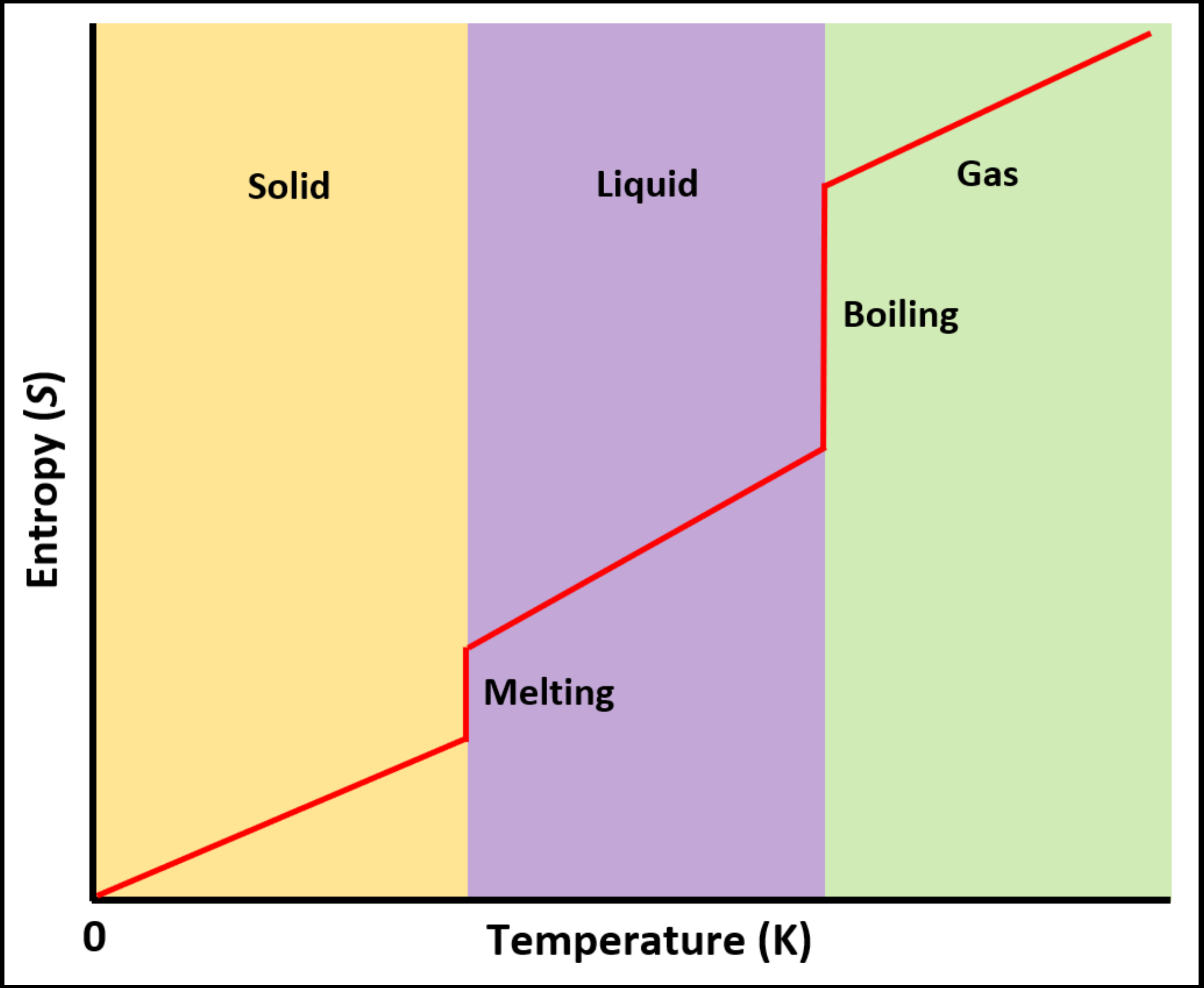
Predicting entropy changes (ΔS)

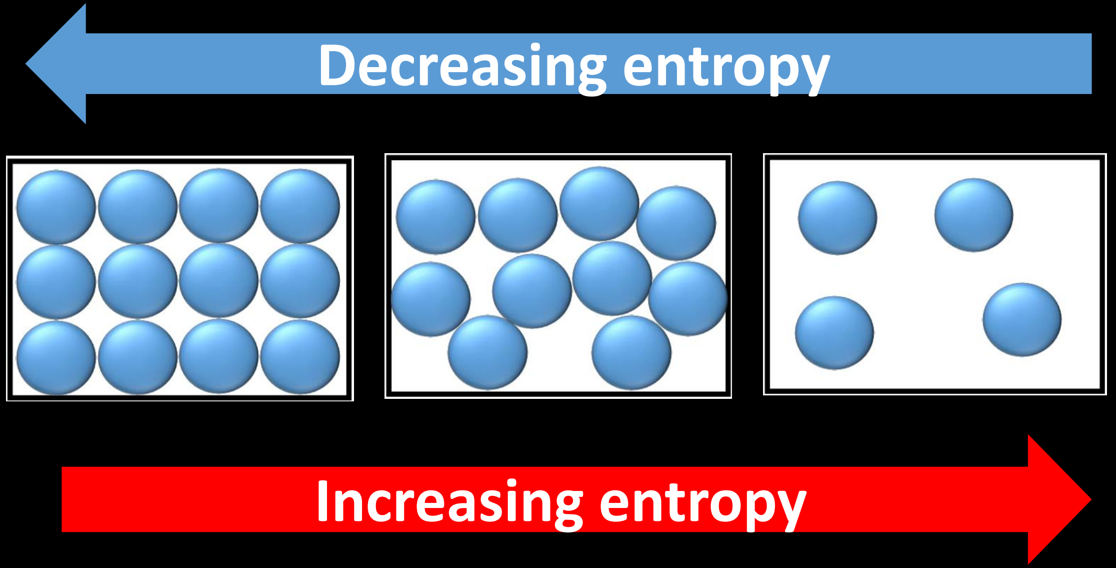
Factors that can change the entropy of a system:

- changes in temperature
- changes of state (freezing, evaporating)
- dissolving (or crystallisation)
- changes in amounts of gaseous reactants or products

Predicting entropy changes (ΔS)

Entropy increases as temperature increases.





Decreasing entropy

Increasing entropy

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \quad +\Delta S$$

$$H_2O_{(g)} \rightarrow H_2O_{(l)} \quad -\Delta S$$

Predicting entropy changes (Δ*S*)

Factors that increase entropy (positive entropy change, +Δ*S*)

Dissolving	$NaCl_{(s)} \rightarrow Na^+_{(aq)}\ Cl^-_{(aq)}$
Increase in mol of gas	$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$ $CH_{4\ (g)} + H_2O_{(g)} \rightarrow 3H_{2(g)} + CO_{(g)}$

Predicting entropy changes (Δ*S*)

Factors that decrease entropy (negative entropy change, -Δ*S*)

Crystallisation	$Na^{+}_{(aq)}\ Cl^{-}_{(aq)} \rightarrow NaCl_{(s)}$
Decrease in mol of gas	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$ $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

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Predicting entropy changes (ΔS)

$$Na_2CO_{3(s)} + 2HCl_{(aq)} \rightarrow CO_{2(g)} + 2NaCl_{(aq)} + H_2O_{(l)}$$

Positive entropy change due to increase in mol of gas

$$AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$$

Negative entropy change due to formation of solid in products

$$2S_2O_3{}^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow S_4O_6{}^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$$

Negligible entropy change due to same amount (in mol) of aqueous reactants and products

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

Negative entropy change due to decrease in mol of gas

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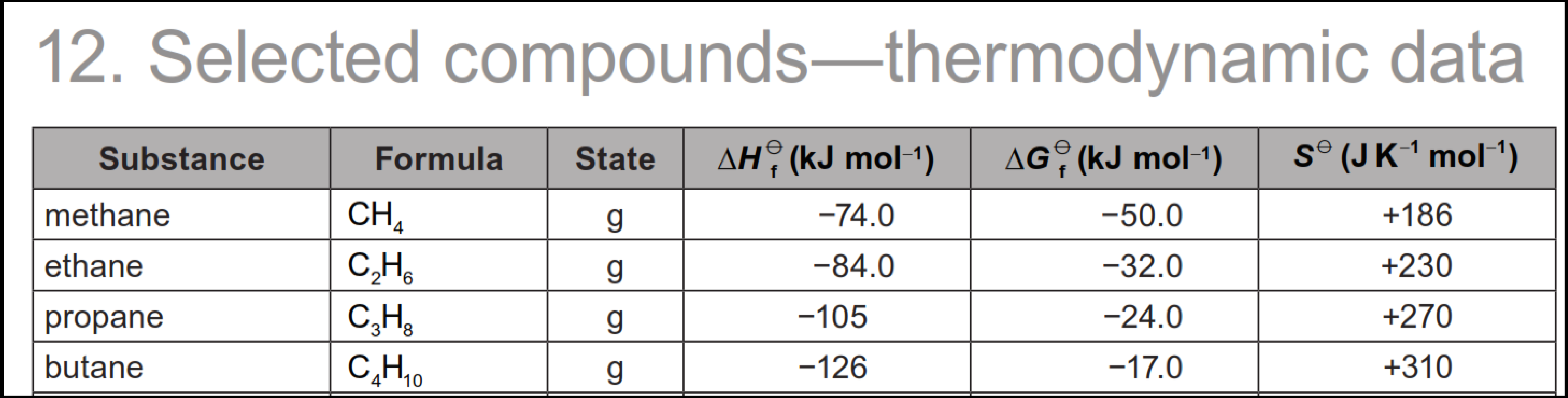
Standard entropy change ($\Delta S^{\ominus}$)

Standard entropy change ($\Delta S^{\ominus}$)

$$\Delta S^{\ominus}_{\text{reaction}} = \sum S^{\ominus}_{\text{products}} - \sum S^{\ominus}_{\text{reactants}}$$



12. Selected compounds—thermodynamic data

Substance	Formula	State	$\Delta H^{\ominus}_f$ (kJ mol^{-1})	$\Delta G^{\ominus}_f$ (kJ mol^{-1})	$S^{\ominus}$ (J K^{-1} mol^{-1})
methane	CH_4	g	−74.0	−50.0	+186
ethane	C_2H_6	g	−84.0	−32.0	+230
propane	C_3H_8	g	−105	−24.0	+270
butane	C_4H_{10}	g	−126	−17.0	+310

Absolute entropy values ($S^{\ominus}$) are always positive.

The unit of $S^{\ominus}$ is J K^{-1} mol^{-1}.

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Standard entropy change ($\Delta S^{\ominus}$)

$$\Delta S^{\ominus}_{\text{reaction}} = \sum S^{\ominus}_{\text{products}} - \sum S^{\ominus}_{\text{reactants}}$$

Use the absolute entropy values ($S^{\ominus}$) in Table 12 of the IB chemistry data booklet.

Input the values into the equation, remembering to multiply by the coefficients in the balanced equation.

Check that the sign of the entropy change corresponds to the change in entropy of the reaction.

When using the equation $\Delta G = \Delta H - T\Delta S$, convert the ΔS to kJ K^{-1} mol^{-1} by dividing by 1000.

Standard entropy change ($\Delta S^\ominus$)

$$N_2H_{4\,(l)} + O_{2\,(g)} \rightarrow N_{2\,(g)} + 2H_2O_{\,(g)}$$

$$\Delta S^\ominus_{reaction} = \sum S^\ominus_{products} - \sum S^\ominus_{reactants}$$

$$\Delta S^\ominus_{reaction} = (192 + 2 \times 188) - (121 + 205)$$

$$\Delta S^\ominus = +242\ J\ K^{-1}\ mol^{-1}$$

	$S^\ominus$ (J K^{-1} mol^{-1})
$N_2H_{4(l)}$	121
$O_{2(g)}$	205
$N_{2(g)}$	192
$H_2O_{(g)}$	188

The ΔS is positive because in the reaction 1 mol of liquid and 1 mol of gas have become 3 mol of gas.

Standard entropy change ($\Delta S^\ominus$)

$$C_2H_4\ (g) + H_2\ (g) \xrightarrow{Ni} C_2H_6\ (g)$$

$$\Delta S^\ominus_{reaction} = \sum S^\ominus_{products} - \sum S^\ominus_{reactants}$$

	$S^\ominus$ (J K^{-1} mol^{-1})
C_2H_4	220
H_2	131
C_2H_6	230

$$\Delta S^\ominus_{reaction} = (230) - (131 + 220)$$

$$\Delta S^\ominus = -121\ J\ K^{-1}\ mol^{-1}$$

The ΔS is negative because in the reaction 2 mol of gas have become 1 mol of gas.

Standard entropy change ($\Delta S^{\ominus}$)

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

$$\Delta S^{\ominus}_{reaction} = \sum S^{\ominus}_{products} - \sum S^{\ominus}_{reactants}$$

$$\Delta S^{\ominus}_{reaction} = (2 \times 193) - (192 + 3 \times 131)$$

	$S^{\ominus}$ (J K^{-1} mol^{-1})
N_2	192
H_2	131
NH_3	193

$$\Delta S^{\ominus} = -199 \text{ J K}^{-1}\text{ mol}^{-1}$$

The ΔS is negative because in the reaction 4 mol of gas have become 2 mol of gas.

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Calculating changes in Gibbs free energy (ΔG)

Gibbs free energy (Δ*G*)

The change in Gibbs free energy (Δ*G*) can be calculated using the following equation:

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

ΔG – Gibbs free energy change (kJ mol^{-1})
ΔH – change in enthalpy (kJ mol^{-1})
T – temperature in kelvin, K
ΔS – change in entropy (J K^{-1} mol^{-1})

Gibbs free energy (ΔG)

For a spontaneous process, ΔG is negative.

For a non-spontaneous process, ΔG is positive.

Spontaneity	ΔG	E_{cell}	K_c
Spontaneous	–	+	Large
Non-spontaneous	+	–	Small

Gibbs free energy (Δ*G*)

Calculate the Δ*G* for the following reaction at 298 K, given the following data.

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

	$\Delta H_f^\ominus$ (kJ mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})
$N_{2\,(g)}$	0	191.5
$H_{2\,(g)}$	0	130.6
$NH_{3\,(g)}$	-46.1	192.3

Gibbs free energy (ΔG)

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

$$\Delta S^{\ominus}_{reaction} = \sum S^{\ominus}_{products} - \sum S^{\ominus}_{reactants}$$

$$\Delta S^{\ominus}_{reaction} = (2 \times 192.3) - (191.5 + 3 \times 130.6)$$

$$\Delta S^{\ominus}_{reaction} = 384.6 - 583.3$$

$$\Delta S^{\ominus}_{reaction} = -198.7\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Gibbs free energy (ΔG)

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

$$\Delta H^{\ominus}_{\text{reaction}} = \sum H_f^{\ominus}{}_{\text{products}} - \sum H_f^{\ominus}{}_{\text{reactants}}$$

$$\Delta H^{\ominus}_{\text{reaction}} = (-46.3 \times 2) - (0)$$

$$\Delta H^{\ominus}_{\text{reaction}} = -92.6 \text{ kJ mol}^{-1}$$

Gibbs free energy (ΔG)

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

$$\Delta G = -92.6 - (298 \times -0.1987)$$

$$\Delta G = -33.4 \text{ kJ mol}^{-1}$$

Negative value for Δ*G* means that the reaction is spontaneous at 298 K.

Gibbs free energy (ΔG)

At what temperature does the reaction become non-spontaneous?

$$>0 = -92.6 - (T \times -0.1987)$$

$$T = >(92.6 / 0.1987)$$

$$T = > 466\ K$$

$$\Delta G = -92.6 - (467 \times -0.1987)$$

$$\Delta G = +0.193\ kJ\ mol^{-1}$$

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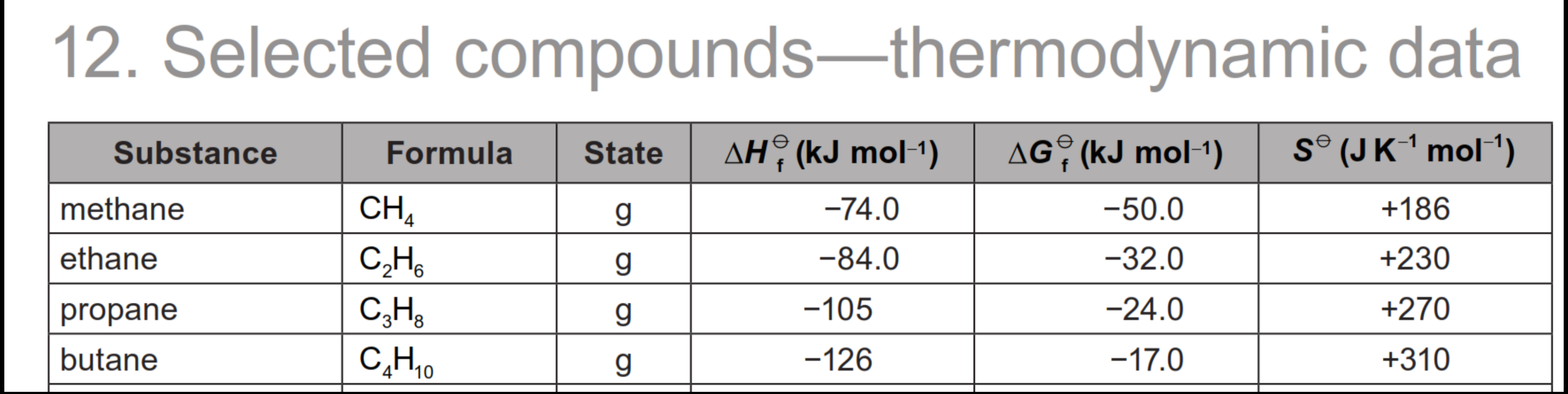
Calculating standard Gibbs free energy changes ($\Delta G^{\ominus}$) using $\Delta G_f^{\ominus}$ values

Calculating $\Delta G^{\ominus}$

The standard Gibbs free energy change ($\Delta G^{\ominus}$) is the change in Gibbs free energy measured under standard conditions (100 kPa and 298 K).

$$\Delta G^{\ominus} = \Sigma\Delta G_f^{\ominus}\,_{\text{products}} - \Sigma\Delta G_f^{\ominus}\,_{\text{reactants}}$$



12. Selected compounds—thermodynamic data

Substance	Formula	State	$\Delta H_f^{\ominus}$ (kJ mol^{-1})	$\Delta G_f^{\ominus}$ (kJ mol^{-1})	$S^{\ominus}$ (J K^{-1} mol^{-1})
methane	CH_4	g	−74.0	−50.0	+186
ethane	C_2H_6	g	−84.0	−32.0	+230
propane	C_3H_8	g	−105	−24.0	+270
butane	C_4H_{10}	g	−126	−17.0	+310

Calculating $\Delta G^{\ominus}$

The standard change in Gibbs free energy ($\Delta G^{\ominus}$) is the change in Gibbs free energy measured under standard conditions (298 K and 100 kPa).

$$\Delta G^{\ominus} = \Sigma\Delta G_f^{\ominus}{}_{\text{products}} - \Sigma\Delta G_f^{\ominus}{}_{\text{reactants}}$$

$\Delta G_f^{\ominus}$ - standard Gibbs free energy of formation is the change in Gibbs free energy when one mole of a compound is formed from its elements in their standard states under standard conditions (100 kPa and 298 K).

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Calculating $\Delta G^{\ominus}$

$\Delta G_f^{\ominus}$ - standard Gibbs free energy of formation is the change in Gibbs free energy when one mole of a compound is formed from its elements in their standard states under standard conditions (100 kPa and 298 K).

$$2C_{(graphite)} + 3H_{2\ (g)} + \tfrac{1}{2}O_{2\ (g)} \rightarrow C_2H_5OH_{\ (l)}$$

$\Delta G_f^{\ominus}$ C_2H_5OH = –175 kJ mol^{-1}

Calculating $\Delta G^{\ominus}$

$$C_2H_{4\,(g)} + H_2O_{\,(g)} \xrightarrow{H_2SO_4} C_2H_5OH_{\,(l)}$$

	$\Delta G_f^{\ominus}$ (kJ mol^{-1})
C_2H_4	+68.0
H_2O	–228.6
C_2H_5OH	–175

$$\Delta G^{\ominus} = \Sigma\Delta G_f^{\ominus}{}_{\text{products}} - \Sigma\Delta G_f^{\ominus}{}_{\text{reactants}}$$

Calculating $\Delta G^{\ominus}$

$$C_2H_{4\,(g)} + H_2O_{\,(g)} \xrightarrow{H_2SO_4} C_2H_5OH_{\,(l)}$$

	$\Delta G_f^{\ominus}$ (kJ mol^{-1})
C_2H_4	+68.0
H_2O	–228.6
C_2H_5OH	–175

$$\Delta G^{\ominus} = (-\ 175) - \ (68.0 + -\ 228.6)$$

Calculating $\Delta G^{\ominus}$

$$C_2H_{4\,(g)} + H_2O_{(g)} \xrightarrow{H_2SO_4} C_2H_5OH_{(l)}$$

	$\Delta G_f^{\ominus}$ (kJ mol^{-1})
C_2H_4	+68.0
H_2O	–228.6
C_2H_5OH	–175

$$\Delta G^{\ominus} = -14.4 \text{ kJ mol}^{-1}$$

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Factors that affect the spontaneity of a chemical reaction

Gibbs free energy (ΔG)

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

For a spontaneous process, ΔG must be negative.

ΔH	ΔS	Temperature
negative	positive	any
negative	negative	low/high
positive	negative	any
positive	positive	low/high

Exothermic reactions

Exothermic reaction with an increase in entropy.

ΔH	ΔS	T	ΔG	Spontaneity
negative	positive	any	negative	spontaneous

An exothermic reaction with an increase in entropy is spontaneous at any temperature.

$$\Delta G = \Delta H - \mathrm{T}\Delta S$$

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Exothermic reactions

Exothermic reaction with a decrease in entropy.

ΔH	ΔS	T	ΔG	Spontaneity
negative	negative	low	negative	spontaneous

An exothermic reaction with a decrease in entropy is spontaneous only at low temperatures.

ΔG will be negative only at low temperatures; at high T, ($T\Delta S$) makes ΔG positive.

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

Endothermic reactions

Endothermic reaction with a decrease in entropy.

ΔH	ΔS	T	ΔG	Spontaneity
positive	negative	any	positive	non-spontaneous

An endothermic reaction with a decrease in entropy is non-spontaneous at any temperature.

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

Endothermic reactions

Endothermic reaction with an increase in entropy.

ΔH	ΔS	T	ΔG	Spontaneity
positive	positive	high	negative	spontaneous

An endothermic reaction with an increase in entropy is spontaneous only at high temperatures.

ΔG will be negative only at high temperatures ($T\Delta S > \Delta H$); at low temperatures $\Delta H > T\Delta S$.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

Example reactions

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(g)}$$

$\Delta H < 0 \quad \Delta S > 0 \quad \Delta G < 0$ at any temp

$$Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

$\Delta H < 0 \quad \Delta S < 0 \quad \Delta G < 0$ at T < 4525 K

$$2N_2O_{(g)} + O_{2(g)} \rightarrow 4NO_{(g)}$$

$\Delta H > 0 \quad \Delta S > 0 \quad \Delta G < 0$ at T > 994 K

Example reactions

$$3O_{2(g)} \rightarrow 2O_{3(g)}$$

$\Delta H > 0$ $\Delta S < 0$ $\Delta G > 0$ at any temp

How to determine the temperature at which a reaction becomes spontaneous.

$$\Delta G = \Delta H - \mathrm{T}\Delta S$$

$$0 = \Delta H - \mathrm{T}\Delta S$$

$$\mathrm{T}\Delta S = \Delta H$$

$$\mathrm{T} = \Delta H \div \Delta S$$

Summary

ΔS

$\Delta H < 0 \quad \Delta S > 0$ Spontaneous at any temperature	$\Delta H > 0 \quad \Delta S > 0$ Spontaneous at high temperatures
$\Delta H < 0 \quad \Delta S < 0$ Spontaneous at low temperatures	$\Delta H > 0 \quad \Delta S < 0$ Non-spontaneous at any temperature

ΔH