Name: ______________________ Date: __________ Period: ______

HL IB Chem Thermodynamics - Guided Notes

Slide 3: Which has more entropy?

- Solid, liquid or gas?
- $NaCl_{(aq)}$ or $NaCl_{(s)}$?
- CO or CO_2?
- NaCl and water or $NaCl_{(aq)}$?
- $N_{2(g)} + O_{2(g)}$ or $2NO_{(g)}$?
- H_2O at room temperature or H_2O at 50^{o}C?

Slide 4: Which has more entropy?

- Solid, liquid or gas? **Solid < Liquid < Gas** (more disorder)
- **$NaCl_{(aq)}$** or $NaCl_{(s)}$? A solution has more randomness than a solid
- CO or **CO_2**? The more atoms there are the more entropy (possible arrangements)
- NaCl and water or **$NaCl_{(aq)}$**? A solution has more arrangements and motion than a solute and solvent
- $N_{2(g)} + O_{2(g)}$ or $2NO_{(g)}$? **Too close to tell** (stays the same)
- H_2O at room temperature or **H_2O at 50^{o}C?** More temp = more kinetic energy/movement

Slide 5: Entropy and temperature

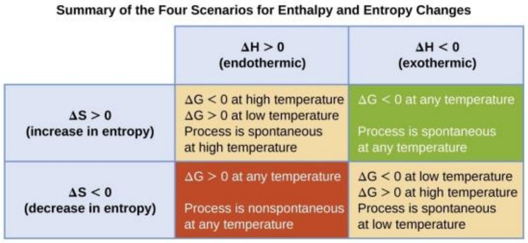
- As temp _____________, the entropy increases.
- Particles can gain energy and can be _____________ in more ways.
- Sudden _____________ in entropy at melting and boiling points.
- Much bigger _____________ at the boiling point.
- Entropy jumps more here as gas _____________ have more movement (and so disorder) than liquid or solid particles.

Slide 6: Standard entropy SƟ

- _____________ entropy is at 100 kPa and 298 K **(in data books)**.
- The units are J K^{-1} mol^{-1} => ensure your units are _____________!
- Standard entropy can be _____________:
- **E.g. due to _____________**
- NO_2 = 240 J K^{-1} mol^{-1} NO = 211 J K^{-1} mol^{-1}
- This is due to the fact there are more ways we can arrange the _____________.
- **E.g. due to _____________ state**
- $H_2O_{(g)}$ = 699 J K^{-1} mol^{-1} $H_2O_{(l)}$ = 189 J K^{-1} mol^{-1}
- **_____________ endothermic reactions occur due to favourable entropy values.**

Slide 7: Standard entropy SƟ

- If S is bigger than 0 there is an _____________ in entropy. The reaction is feasible.
- If S is less than 0, there is a _____________ in entropy.
- **_____________ endothermic reactions occur due to favourable entropy values.**


Summary of the Four Scenarios for Enthalpy and Entropy Changes

	ΔH > 0 (endothermic)	**ΔH < 0 (exothermic)**
ΔS > 0 (increase in entropy)	ΔG < 0 at high temperature ΔG > 0 at low temperature Process is spontaneous at high temperature	ΔG < 0 at any temperature Process is spontaneous at any temperature
ΔS < 0 (decrease in entropy)	ΔG > 0 at any temperature Process is nonspontaneous at any temperature	ΔG < 0 at low temperature ΔG > 0 at high temperature Process is spontaneous at low temperature

Slide 8: Entropy change

- Can be measured using 3 _____________:
- **Entropy of system**
- **$\Delta S = \sum S^{\theta}$products - $\sum S^{\theta}$_____________**
- **Entropy of _____________**
- $\Delta S_{surroundings} = -{}^{\Delta H}/_{T}$ J $mol^{-1}K^{-1}$
- **Total entropy change**
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
- _____________ data is section 13 of data booklets
- **Learn these _____________!**

Slide 9: Entropy change example 1

- Calculate the total entropy change for the following reaction under standard conditions. 2Ca + $O_2 \rightarrow$ 2CaO

- $\Delta S_{system} = \Delta S_{products} - \Delta S_{reactants}$
- = (2 x 40) - [(2 x 41.6)+205]
- = 80-2882 = -208.2 J K^{-1} mol^{-1}
- $\Delta S_{surroundings} = -{}^{\Delta H}/_{T} = -\,{}^{(-1270x1000)}/_{298}$ (standard temp)
- = 4261.7 J K^{-1} mol^{-1}
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
- = -208.2 + 4261.7
- = 4053.5 J K^{-1} mol^{-1}

- This number is positive (above 0), so means reaction is kinetically feasible at standard conditions.
- $\Delta H^{\ominus} = -12270$ kJ mol^{-1}
- **$\Delta S^{\ominus}$ (J K^{-1} mol^{-1})**
- Ca = 41.6
- O_2 = 205
- CaO = 40

Slide 10: Entropy change example 2

- Does NaBr dissolve in solution at 298 K?
- $\Delta S^{\ominus}_{system} = 55.0$ J K^{-1} mol^{-1}
- $NaBr_{(s)} \rightarrow Na^{+}_{(aq)} + Br^{-}_{(aq)}$ $\Delta H^{\ominus} = -0.6$ kJ mol^{-1}
- $\Delta S_{surroundings} = -{}^{\Delta H}/_{T} = -\,{}^{(-0.6x1000)}/_{298}$ (standard temp)
- $= +2.05$ J K^{-1} mol^{-1}
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
- $= 55.0 + 2.05$
- $= +57.0$ J K^{-1} mol^{-1}
- This number is positive (above 0), so means reaction is kinetically feasible at standard conditions.

Slide 11: Questions

- 1. For each of the following reactions, indicate whether you would expect the entropy of the system to increase or decrease, and explain why. If you cannot tell just by inspecting the equation, explain why.
- (a) $CH_3OH_{(l)} \rightarrow CH_3OH_{(g)}$
- (b) $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$
- (c) $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$
- (d) $2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(aq)}$
- 2. Predict which of the following reactions has a positive change in entropy.
- I. $2N_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{(g)}$
- II. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
- III. $Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

Slide 12: Questions

- 3. Predict which of the following reactions has a negative change in entropy.
- I. $2HgO_{(s)} \rightarrow 2\ Hg_{(l)} + O_{2(g)}$
- II. $Ba^{2+}_{(aq)} + SO_4^{2--}{}_{(aq)} \rightarrow BaSO_{4(s)}$
- III. $2\ H_2O_{2(l)} \rightarrow 2\ H_2O_{(l)} + O_{2(g)}$
- 4. Predict which of the following reactions has a negative change in entropy.
- I. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$
- II. $MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}$
- III. $PCl_{5(s)} \rightarrow PCl_{3(l)} + Cl_{2(g)}$

Slide 13: Check your work

- 1. For each of the following reactions, indicate whether you would expect the entropy of the system to increase or decrease, and explain why. If you cannot tell just by _____________ the equation, explain why.
- (a) $CH_3OH_{(l)} \rightarrow CH_3OH_{(g)}$ _____________
- (b) $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$ _____________
- (c) $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$ _____________
- (d) $2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(aq)}$ _____________
- 2. Predict which of the _____________ reactions has a positive change in entropy.
- I. $2N_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{(g)}$ **Too close to tell (v _____________ negative)**
- II. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ _____________
- III. $Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$ _____________

Slide 14: Check your work

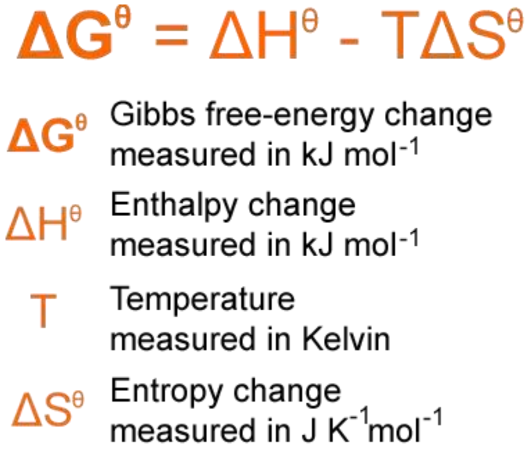
- 3. Predict which of the _____________ reactions has a negative change in entropy.
- I. $2HgO_{(s)} \rightarrow 2\ Hg_{(l)} + O_{2(g)}$ _____________
- II. $Ba^{2+}_{(aq)} + SO_4^{2--}{}_{(aq)} \rightarrow BaSO_{4(s)}$ _____________
- III. $2\ H_2O_{2(l)} \rightarrow 2\ H_2O_{(l)} + O_{2(g)}$ _____________
- 4. Predict which of the _____________ reactions has a negative change in entropy.
- I. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ _____________ **(too close to tell)**
- II. $MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}$ _____________
- III. $PCl_{5(s)} \rightarrow PCl_{3(l)} + Cl_{2(g)}$ _____________

Slide 15: Calculating entropy

- Similar to ____________ ΔH_f.
- **$\Delta S = \sum S^{\theta}$products - $\sum S^{\theta}$____________**
- $N_2 + 3H_2 \rightleftharpoons 2NH_3$
- ΔS^{θ} = (2 x 193) - (192 + 3x131)
- = -199 J K^{-1} mol^{-1}
- The ΔS is ____________ because in the reaction 4 moles of gas has become 2 moles of gas.

Slide 18: Gibbs Free Energy ΔG

- Named after Josiah Gibbs, an American ____________ who came up with the idea of working out free energy using entropy, enthalpy and temperature to work out if a reaction is feasible at a specific temperature.
- IN DATA BOOKS - 1



$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$$

ΔG^{θ}	Gibbs free-energy change measured in kJ mol^{-1}
ΔH^{θ}	Enthalpy change measured in kJ mol^{-1}
T	Temperature measured in Kelvin
ΔS^{θ}	Entropy change measured in J $K^{-1}mol^{-1}$

Slide 19: Gibbs Free Energy

- What do we mean by the term feasible/spontaneous?
- If **ΔG is negative or equal to zero**, then the reaction is **feasible**.
- If **ΔG is positive** then the reaction **isn't feasible**.
- **Feasible means that once a reaction has started, it will carry onto completion, without any energy being supplied to it.**
- **A spontaneous reaction is a reaction that occurs in a given set of conditions without intervention. Spontaneous reactions are accompanied by an increase in overall entropy, or disorder.**

Slide 20: The relationship between enthalpy and entropy

- Exothermic reactions **give out heat**, this **increases the entropy or disorder of the ____________ particles**, many exothermic reactions are spontaneous.

- Some ____________ reactions **have a positive value for ΔH** and are spontaneous at room temperature.
- **Enthalpy changes alone do not determine whether a reaction is ____________ or not.**
- There are ____________ from **both enthalpy and entropy**

Slide 21: More about Free Energy

- Free-energy change takes into account the changes in ____________ and entropy in the system. The formula below shows this:
- A negative ΔG doesn't guarantee a reaction will happen or tell you about its rate. Even if ΔG shows that a reaction is ____________ feasible, it might have a really high activation energy, or be so slow you wouldn't even notice it.
- Of system

Slide 22: Worked example 1

- **Calculate ΔG for the following reaction:**
- **$2Fe + 1\frac{1}{2} O_2 \rightarrow Fe_2O_3$ $\Delta H^{\ominus} = -822$ kJ mol^{-1}**
- $\Delta S_{system} = \Delta S_{products} - \Delta S_{reactants}$
- $= 90 - [(2 \times 27.2)+(1.5 \times 205)] = -271.9$ J K^{-1} mol^{-1}
- $\Delta G = \Delta H - T \Delta S$
- $= (-822 \times 1000) - [298 \times -271.9]$
- $= -740973.8$ J mol^{-1}
- Therefore this reaction should be feasible. However the rate is very slow (rusting). Could still have a high activation energy or law rate etc.
- **$\Delta S^{\ominus}$ (J K^{-1} mol^{-1})**
- $Fe_2O_3 = 90$
- $Fe = 27.2$
- $O_2 = 205$

Slide 23: Feasibility and temperature

- When calculating if a reaction is feasible without numbers to calculate it, split ΔG equation into 2 halves.
- $\Delta G = \mathbf{\Delta H - T \Delta S}$
- Feasible?
- Yes - As above certain temp.
- Yes - Always.
- Usually
- Never

Slide 24: ΔG is zero

- If **ΔG is zero,** a reaction is **in _____________**. This is often the case during phase transitions (e.g. bp/mp).
- You can find the _____________ when ΔG is zero by re-arranging the free-energy equation.
- **_____________ the equation to make T the subject:**
- This can now be used to calculate the _____________ at which a reactions become feasible.

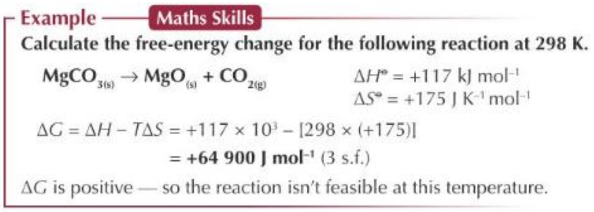
Slide 25: Worked example 2

- **Calculate the temperature at which a reaction becomes feasible**
- **$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$ $\Delta H^{\ominus} = +493\ kJ\ mol^{-1}$**
- Assume ΔG = 0 (lowest feasibility, so lowest temp).
- $\Delta S_{system} = \Delta S_{products} - \Delta S_{reactants}$
- = [(2x27.2)+(3x198)] - [90+(3x5.7)]
- = 648.4 - 107.1 = +541.3 $J\ K^{-1}\ mol^{-1}$
- ΔG = ΔH - T ΔS
- 0 = (493x1000) - [**X** x 541.3]
- **X** = (493x1000) / 541.3
- = 910.8 K
- Useful industrially to save energy etc.
- **$\Delta S^{\ominus}$ ($J\ K^{-1}\ mol^{-1}$)**
- Fe_2O_3 = 90
- Fe = 27.2
- C = 5.7
- CO = 198

Slide 26: Example

- Here are some examples of how to decide if a reaction is feasible at different temperatures:

Slide 27: Your turn



Example — **Maths Skills**

Calculate the free-energy change for the following reaction at 298 K.

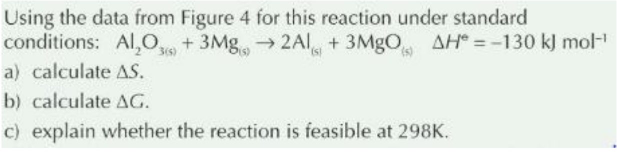
$\mathbf{MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}}$ $\Delta H^{\circ} = +117\ \text{kJ mol}^{-1}$

$\Delta S^{\circ} = +175\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Delta G = \Delta H - T\Delta S = +117 \times 10^{3} - [298 \times (+175)]$

$= \mathbf{+64\ 900\ J\ mol^{-1}}$ (3 s.f.)

ΔG is positive — so the reaction isn't feasible at this temperature.



Using the data from Figure 4 for this reaction under standard conditions: $Al_2O_{3(s)} + 3Mg_{(s)} \rightarrow 2Al_{(s)} + 3MgO_{(s)}$ $\Delta H^{\circ} = -130\ \text{kJ mol}^{-1}$

a) calculate ΔS.

b) calculate ΔG.

c) explain whether the reaction is feasible at 298K.

Slide 28: Check your work

- **$Al_2O + 3Mg \rightarrow 2Al + 3MgO$ $\Delta H^{\ominus} = -130\ kJ\ mol^{-1}$**
- $\Delta S_{system} = \Delta S_{products} - \Delta S_{reactants}$
- $= [(2\times28.3)+(3\times27.0)] - [51+(3\times32.5)]$
- $= 137.6 - 148.5 \quad = -10.9\ J\ K^{-1}\ mol^{-1}$
- $\Delta G \quad = \Delta H - T\ \Delta S$
- $\Delta G \quad = (-130\times1000) - [298 \times -10.9]$
- $= -126751.8\ J\ mol^{-1}$
- The ____________ is feasible at 298 K.

Slide 29: Your turn

- **Calculate the Gibbs free-energy at 298K for the following reaction:**
- **Is the reaction feasible at 298 K? Why?**
- ***Reaction is not feasible because ΔG is > 0 at 298 K***

Slide 30: Your turn

- **Calculate the Gibbs free-energy at 298K for the following reaction:**
- **Is the reaction feasible at 298 K? Why?**
- ***Reaction is feasible because ΔG is < 0 at 298 K***

Slide 31: Free energy graphs

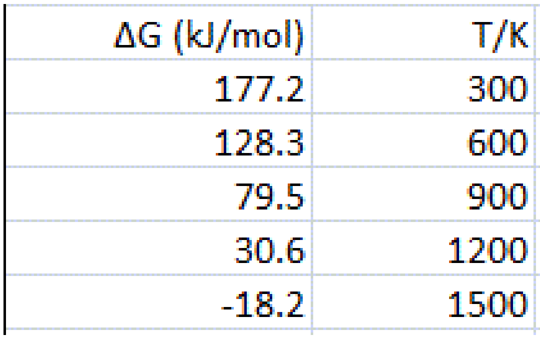
- You can use a free energy graph to work out _____________ and entropy change for a reaction.
- **The ΔG vs T is a straight line** and _____________ can be described using the equation **y=mx+c.**

Slide 32: Free energy graphs

- **So on a graph where ΔG is the y-axis, the gradient of the line (m) is equal to –ΔS and the y ____________ (c) is equal to ΔH.**
- **The entropy change is the same as the ____________ but with the opposite sign**
- -ΔS=
- **ΔH= +40 KJ mol^{-1}**

Slide 33: Free energy graphs

- **Your turn:**
- Plot a graph to ***calculate ∆H and ∆S*** for the decomposition of lithium carbonate using the data below.
- State the ***temperature at which the reaction is just feasible***.

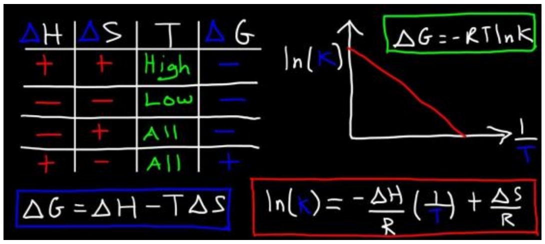


ΔG (kJ/mol)	T/K
177.2	300
128.3	600
79.5	900
30.6	1200
-18.2	1500

Slide 34: Free energy graphs

Slide 35: Gibbs free energy

- https://www.thinkib.net/chemistry/page/24608/mc-test-entropy-
  ____



ΔH	ΔS	T	ΔG
+	+	High	−
−	−	Low	−
−	+	All	−
+	−	All	+

$\Delta G = -RT\ln K$

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

$\ln(K) = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R}$

Slide 36: Your turn

Slide 37: Answers

Slide 38: Enthalpy of formation (ΔH^{Θ}_f): $3/2H_2(g) + 1/2N_2(g) \rightarrow NH_3(g)$

The enthalpy change when 1 mole of pure compound is formed from its constituent elements in their standard states at 298K and 100 kPa pressure.

EXOTHERMIC for most substances

Write enthalpy of formation equations for the following:

Potassium chloride
Methane (CH_4)
Carbon dioxide
Water
Magnesium oxide
Ethanoic acid (CH_3COOH)
Benzene (C_6H_6)
Glucose ($C_6H_{12}O_6$)
Aluminum nitrate
Copper (II) sulfate

- **Enthalpy of ____________**
- **____________ - Covered in SL**

Slide 39: First ionization energy (Ei): $M(g) \rightarrow M^+(g) + e^-$ ENDOTHERMIC

The first ionization enthalpy is the standard enthalpy change when a mole of gaseous atoms is converted into one mole of gaseous ions each with a single positive charge.

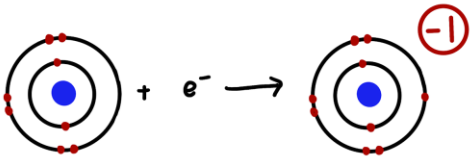
Second ionization energy - ENDOTHERMIC

- **Ionization energy**
- **____________ - Covered in bonding unit**

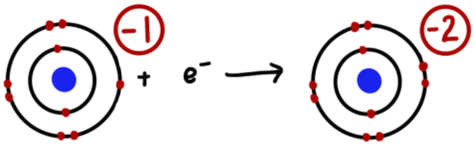
Slide 40: First electron affinity (Ea): M(g) + e- → M-(g) EXOTHERMIC for many non-metals
The first electron affinity is the standard enthalpy change when a mole of gaseous atoms is converted into one mole of gaseous ions each with a single negative charge.

Second electron affinity - endothermic as adding an e- to a -ve ion

- **Electron affinity**
- **____________ - Covered in bonding unit**



First Electron Affinity

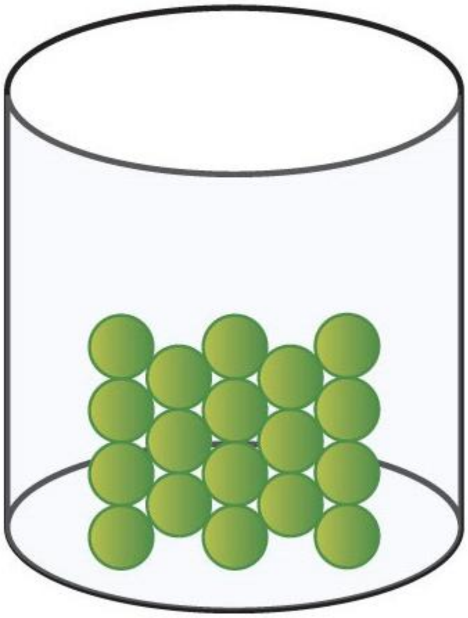


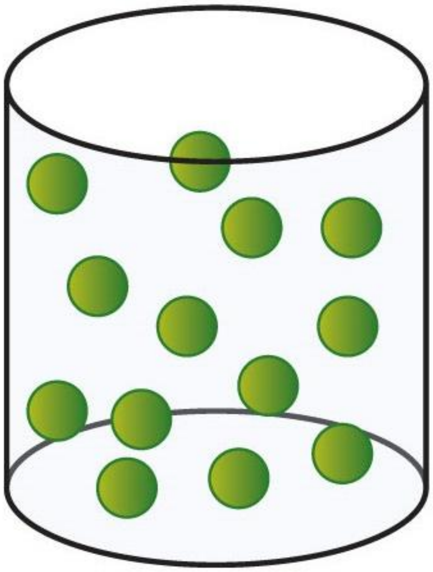
Second Electron Affinity

Slide 41: Enthalpy of atomization (ΔHΘat): Na(s) → Na(g) ENDOTHERMIC
The enthalpy change which accompanies the formation of one mole of gaseous atoms from the element in its standard state at 298 K and 100 kPa pressure.

Write enthalpy of atomization equations for the following:
Potassium
Chlorine
Oxygen
Carbon
Hydrogen
Sodium
Aluminum
Copper
Bromine
Nitrogen

- **Enthalpy of ____________**





Slide 42: Enthalpy of atomization (ΔHΘat): Na(s) → Na(g) ENDOTHERMIC

Potassium K(s) → K(g)
Chlorine ½ Cl2(g) → Cl(g)
Oxygen ½ O2(g) → O(g)
Carbon C(s) → C(g)
Hydrogen ½ H2(g) → H(g)
Sodium Na(s) → Na(g)
Aluminum Al(s) → Al(g)
Copper Cu(s) → Cu(g)
Bromine ½ Br2(g) → Br(g)
Nitrogen ½ N2(g) → N(g)

- **Check your work**

Slide 43: Bond dissociation (covalent bond) enthalpy (ΔH): H2(g) → 2H (g)
The bond dissociation enthalpy is the standard enthalpy change when a mole of gaseous molecules is broken down into separate gaseous atoms.
ENDOTHERMIC
Write bond dissociation equations for the following:
Chlorine
Oxygen
Methane (CH4)
Carbon dioxide
Water
Ethanoic acid (CH3COOH)
Benzene (C6H6)
Glucose (C6H12O6)
Ammonia
SO3

- **Bond ____________ (covalent bond) enthalpy**

Slide 44: Bond dissociation (covalent bond) enthalpy (ΔH): $H_2(g) \rightarrow 2H(g)$

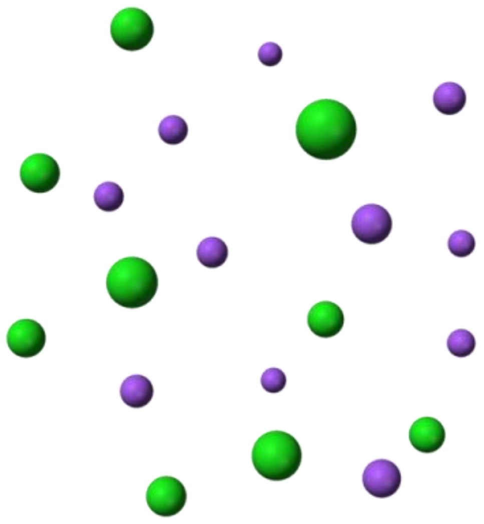
Chlorine $Cl_2(g) \rightarrow 2Cl(g)$
Oxygen $O_2(g) \rightarrow 2O(g)$
Methane $CH_4(g) \rightarrow C(g) + 4Cl(g)$
Carbon dioxide $CO_2(g) \rightarrow C(g) + 2O(g)$
Water $H_2O(l) \rightarrow 2H(g) + O(g)$
Ethanoic acid $CH_3COOH(l) \rightarrow 2C(g) + 2O(g) + 4H(g)$
Benzene $C_6H_6(l) \rightarrow 6C(g) + 6H(g)$
Glucose $C_6H_{12}O_6 \rightarrow 6C(g) + 6O(g) + 12H(g)$
Ammonia $NH_3(l) \rightarrow N(g) + 3H(g)$
$SO_3 \rightarrow S(g) + 3O(g)$

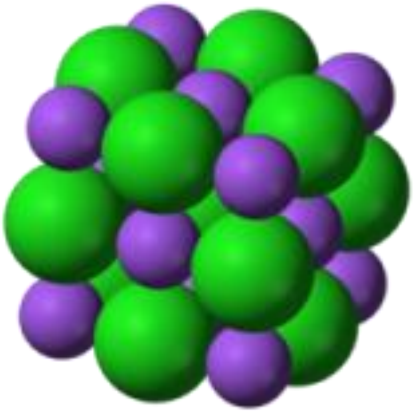
- Check your work

Slide 45: Lattice enthalpy - measure of the strength of forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces of attraction.

These forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them.

- Lattice enthalpy (of ____________)

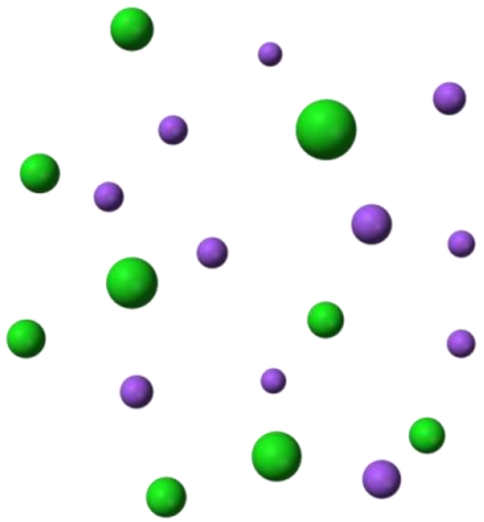


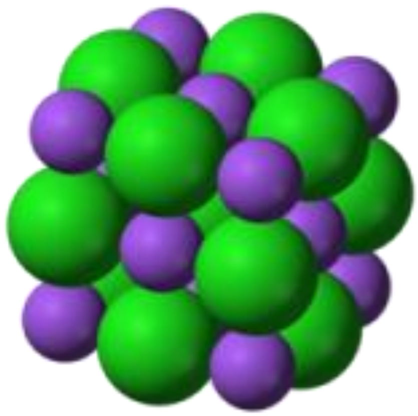


Slide 46: Lattice enthalpy ($\Delta H \Theta L$): $MgCl_2(s) \rightarrow Mg^{2+}(g) + 2Cl^{-}(g)$ ENDOTHERMIC
Energy change when 1 mole of pure ionic solid is broken up into its constituent gaseous ions at 298K and 100 kPa pressure (SATP).

Write the lattice enthalpy of dissociation equations for the following:
Potassium chloride
Potassium sulfide
Lithium bromide
Magnesium chloride
Magnesium oxide
Sodium fluoride
Sodium oxide
Aluminium chloride
Aluminum nitride
Aluminium oxide

- **Lattice enthalpy (of ____________)**





Slide 47: Lattice enthalpy (ΔH^{Θ}_{L}): $MgCl_2(s) \rightarrow Mg^{2+}(g) + 2Cl^-(g)$ ENDOTHERMIC

Potassium chloride $KCl(s) \rightarrow K^+(g) + Cl^-(g)$
Potassium sulfide $K_2S(s) \rightarrow 2K^+(g) + S^{2-}(g)$
Lithium bromide $LiBr(s) \rightarrow Li^+(g) + Br^-(g)$
Magnesium chloride $MgCl_2(s) \rightarrow Mg^{2+}(g) + 2Cl^-(g)$
Magnesium oxide $MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$
Sodium fluoride $NaF(s) \rightarrow Na^+(g) + F^-(g)$
Sodium oxide $Na_2O(s) \rightarrow 2Na^+(g) + O^{2-}(g)$
Aluminium chloride $AlCl_3(s) \rightarrow Al^{3+}(g) + 3Cl^-(g)$
Aluminum nitride $Al_2N_3(s) \rightarrow 2Al^{3+}(g) + 3N^{2-}(g)$
Aluminium oxide $Al_2O_3(s) \rightarrow 2Al^{3+}(g) + 3O^{2-}(g)$

- **Check your work**

Slide 48: Lattice enthalpy (ΔHΘL): Mg2+(g) + 2Cl-(g) → MgCl2(s) EXOTHERMIC

E.g. Na+(g) + Cl-(g) → NaCl(s)
Enthalpy change to form 1 mole of pure ionic solid from its constituent gaseous ions at 298K and 100 kPa pressure (SATP).

Write the lattice enthalpy of formation equations for the following:
Potassium chloride
Potassium sulfide
Lithium bromide
Magnesium chloride
Magnesium oxide
Sodium fluoride
Sodium oxide
Aluminium chloride
Aluminum nitride
Aluminium oxide

- **Lattice enthalpy of ____________**

Slide 49: Lattice enthalpy (ΔHΘL): Mg2+(g) + 2Cl-(g) → MgCl2(s) EXOTHERMIC

Potassium chloride K+(g) + Cl-(g) → KCl(s)
Potassium sulfide 2K+(g) + S2-(g) → K2S(s)
Lithium bromide Li+(g) + Br-(g) → LiBr(s)
Magnesium chloride Mg2+(g) + 2Cl-(g) → MgCl2(s)
Magnesium oxide Mg2+(g) + O2-(g) → MgO(s)
Sodium fluoride Na+(g) + F-(g) → NaF(s)
Sodium oxide 2Na+(g) + O2-(g) → Na2O(s)
Aluminium chloride Al3+(g) + 3Cl-(g) → AlCl3(s)
Aluminum nitride 2Al3+(g) + 3N2-(g) → Al2N3(s)
Aluminium oxide 2Al3+(g) + 3O2-(g) → Al2O3(s)

- **Check your work**

Slide 50: Lattice enthalpy

- For NaCl, the solid is more stable than gas ions by 787 kJ mol^{-1}
- 1 mol
- Lattice ____________ enthalpy
- $NaCl_{(s)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$ **+787 kJ mol^{-1}**
- Lattice ____________ enthalpy

- $Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(s)}$ **-787 kJ mol^{-1}**

Slide 51: Factors affecting lattice enthalpy:

Charges of ions

A bigger charge = stronger attraction/force

Ionic radii

A smaller ion = stronger attraction/force

A stronger attraction = more EXOTHERMIC/ENDOTHERMIC

- **Lattice enthalpy**
- **1+**
- **2+**
- **1+**
- **1+**

Slide 52: Enthalpy changes (for Born-Haber cycles)

- Enthalpy changes occur at many ____________ points in a reaction.
- Max Born and Fritz Haber came up with a cycle to show this, called a Born-Haber cycle.

Slide 53: Introduction to Born-Haber cycles

- Born-Haber cycles are like Hess' cycles, except they only show lattice ____________ for ionic compounds.
- They obey Hess' Law in that the total ____________ change of a reaction is the same no matter what the route taken.
- Add up all enthalpy in the cycle = 0 (because energy cannot be created or ____________).

Slide 55: Ionic compound (s)

- **Gas ions (g)**
- **____________ (std states)**
- **$\Delta H_{\text{formation}}$**

- **Metal ions, e^-'s, non-metal atoms (g)**
- **$\Delta H_{formation}$ = sum of all other ΔH's**
- **Born-Haber cycle ____________**

Slide 56: Introduction to Born-Haber cycles

- Copy the diagram and identify the type of enthalpy at each stage.
- **?**

Slide 57: Introduction to Born-Haber cycles

- Solid is always at the bottom.
- The left always shows us the elements that make up the compound.
- Do atomisations first, then ionisations.
- On right, electron affinity and lattice enthalpy of formation.
- **Calculate the lattice enthalpy of formation. Use what you already know (work backwards).**
- **?**

Slide 58: Introduction to Born-Haber cycles

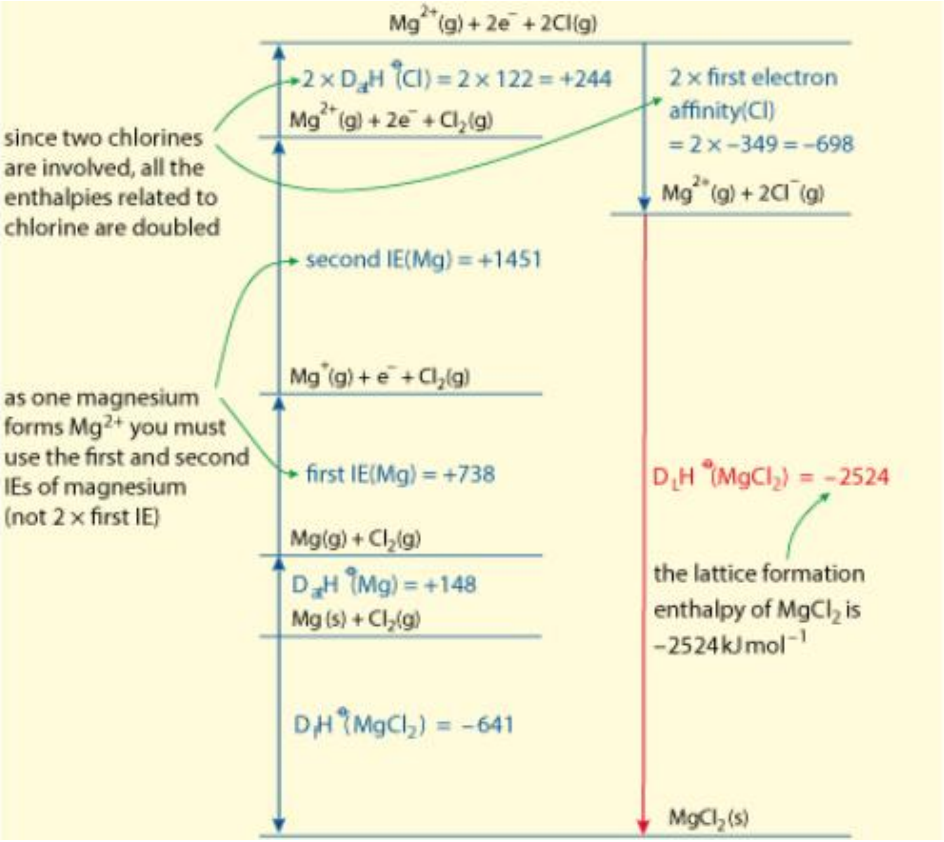
- Calculating the lattice enthalpy of formation.
- If you're going against the arrow, reverse the sign.
- **$(\Delta H^{\ominus}_{F}) = +107 +121+502-355+\Delta H^{\ominus}_{L}$**
- **$-411 = -375+\Delta H^{\ominus}_{L}$**
- **$(\Delta H^{\ominus}_{L}) = -786$ kJ mol^{-1}**
- **?**

- Note: This is lattice enthalpy of **formation**
- **Lattice enthalpy of dissociation would be +786 kJ**

Slide 59: Applying knowledge and understanding

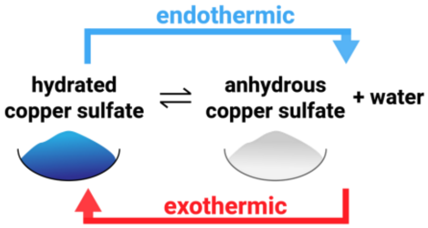
- Use the following values to construct the Born-Haber cycle for $MgCl_2$. What is the enthalpy of formation?
- ΔH_{2IE} Mg = +1451 kJ mol^{-1}
- ΔH_{at} Mg = +148 kJ mol^{-1}
- ΔH_{at} Cl = +122 kJ mol^{-1}
- Use data books!

Slide 60: MgCl2



Slide 61: Solutions: Reversible reactions

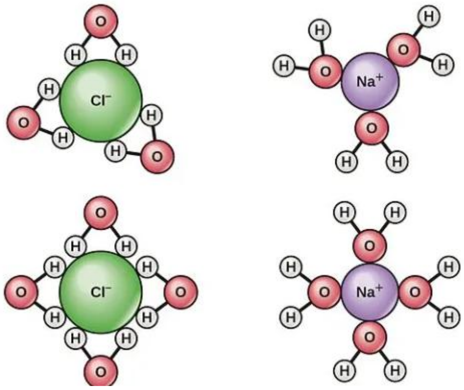
- $CuSO_4 + 5H_2O \rightarrow CuSO_4.5H_2O$
- $CuSO_4.5H_2O \rightarrow CuSO_4 + 5H_2O$

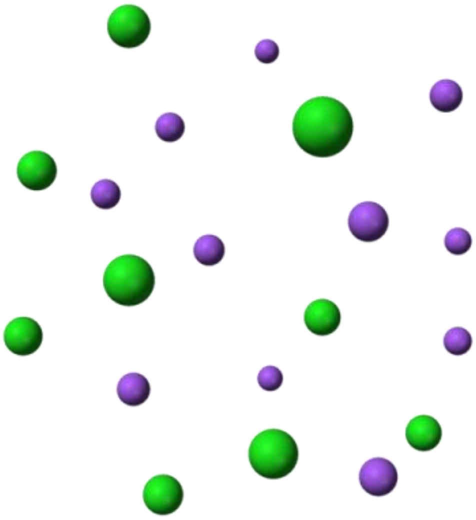


Slide 62: Enthalpy of hydration (ΔHΘhyd): Na+(g) + Cl-(g) → Na+(aq) + Cl-(aq)
The enthalpy change when 1 mole of gaseous ion is added to water to form a dilute solution
EXOTHERMIC

Write enthalpy of hydration
equations for the following:
Potassium chloride
Potassium sulfide
Lithium bromide
Magnesium chloride
Magnesium oxide
Sodium fluoride
Sodium oxide
Aluminium chloride
Aluminum nitride
Aluminium oxide

- **Enthalpy of _____________**





Slide 63: Enthalpy of hydration (ΔHΘhyd): Na+(g) + Cl-(g) → Na+(aq) + Cl-(aq)

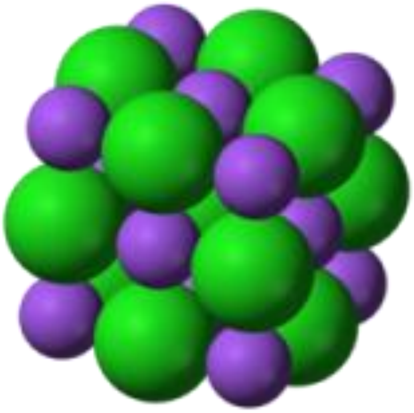
Potassium chloride K+(g) + Cl-(g) → K+(aq) + Cl-(aq)
Potassium sulfide 2K+(g) + S2-(g) → 2K+(aq) + S2-(aq)
Lithium bromide Li+(g) + Br-(g) → Li+(aq) + Br-(aq)
Magnesium chloride Mg2+(g) + 2Cl-(g) → Mg2+(aq) + 2Cl-(aq)
Magnesium oxide Mg2+(g) + 2O2-(g) → Mg2+(aq) + 2O2-(aq)
Sodium fluoride Na+(g) + F-(g) → Na+(aq) + F-(aq)
Sodium oxide 2Na+(g) + O2-(g) → 2Na+(aq) + O2-(aq)
Aluminium chloride Al3+(g) + 3Cl-(g) → Al3+(aq) + 3Cl-(aq)
Aluminum nitride Al3+(g) + N3-(g) → Al3+(aq) + N3-(aq)
Aluminium oxide 2Al3+(g) + 3O2-(g) → 2Al3+(aq) + 3O2-(aq)

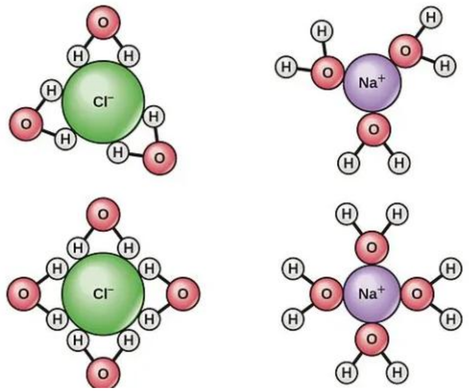
- **Check your work**

Slide 64: Enthalpy of solution (ΔHΘsol): NaCl(s) → Na+(aq) + Cl-(aq) EXO/ENDO
The enthalpy change when 1 mole of a substance is dissolved in a large excess of water in their standard states at 298K and 100 kPa pressure.

Write enthalpy of solution equations for the following:
Potassium chloride
Potassium sulfide
Lithium bromide
Magnesium chloride
Magnesium oxide
Sodium fluoride
Sodium oxide
Aluminium chloride
Aluminum nitride
Aluminium oxide

- **Enthalpy of solution**





Slide 65: Enthalpy of solution (ΔHΘsol): NaCl(s) → Na+(aq) + Cl-(aq)   EXO/ENDO

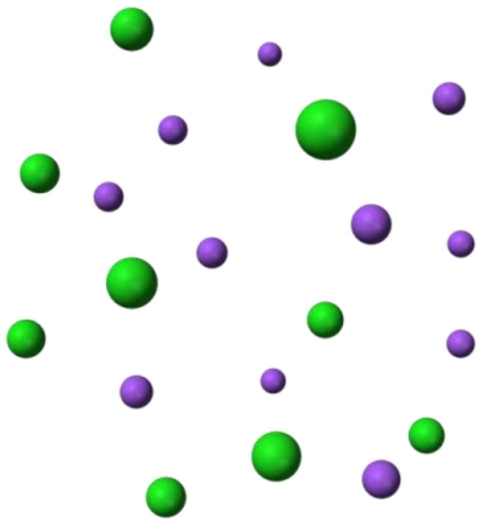
Potassium chloride KCl(s) → K+(aq) + Cl-(aq)
Potassium sulfide K2S(s) → 2K+(aq) + S2-(aq)
Lithium bromide LiBr(s) → Li+(aq) + Br-(aq)
Magnesium chloride MgCl2(s) → Mg2+(aq) + 2Cl-(aq)
Magnesium oxide MgO(s) → Mg2+(aq) + O2-(aq)
Sodium fluoride NaF(s) → Na+(aq) + F-(aq)
Sodium oxide Na2O(s) → 2Na+(aq) + O2-(aq)
Aluminium chloride AlCl3(s) → Al3+(aq) + 3Cl-(aq)
Aluminum nitride Al2N3(s) → 2Al3+(aq) + 3N2-(aq)
Aluminium oxide Al2O3(s) → 2Al3+(aq) + 3O2-(aq)

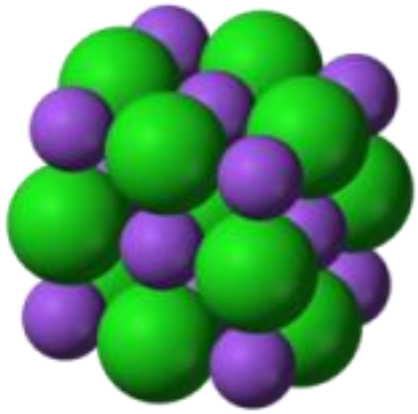
- **Check your work**

Slide 66: Dissolving compounds in water gives an enthalpy change.

ΔHΘlatt = solid ionic lattice breaking up into gas ions

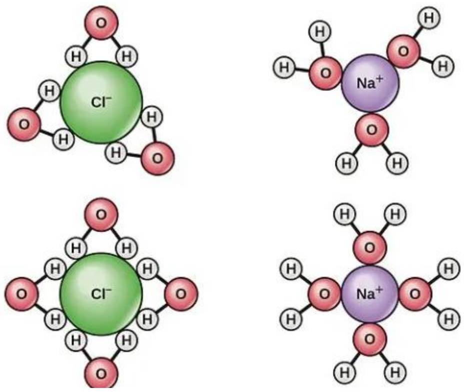
- **_____________ ionic compounds**
- Bond breaking - _____________



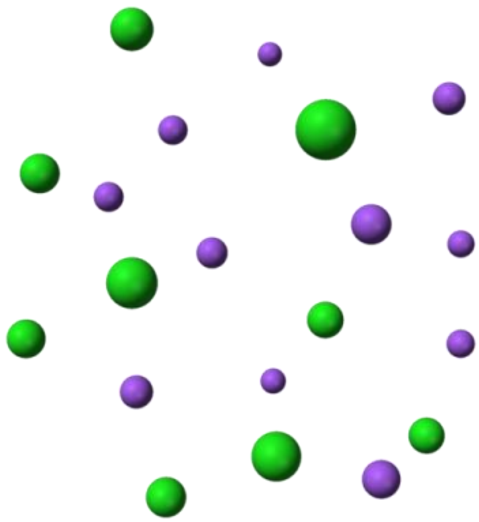


Slide 67: Dissolving compounds in water gives an enthalpy change.

ΔHΘhyd = gas ions attract water to form aqueous ions

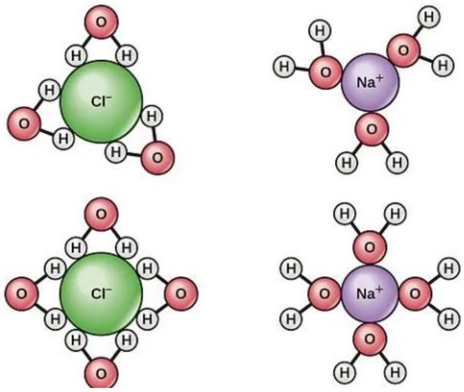


- _____________ **ionic compounds**
- Bond making - _____________

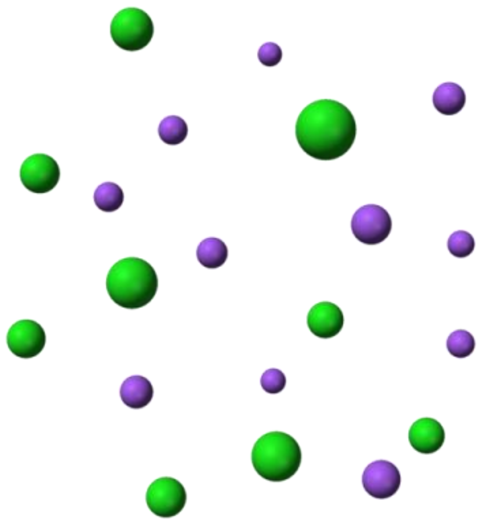


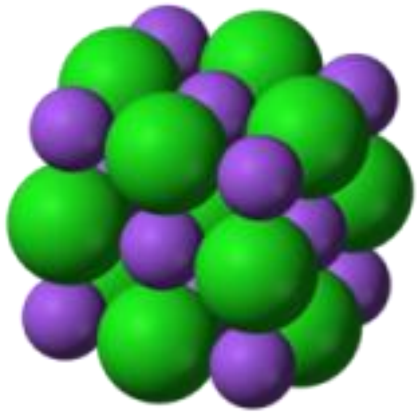
Slide 68: Dissolving compounds in water gives an enthalpy change.

ΔHΘsol = solid ionic lattice dissolves to form aqueous ions (2 step process - in reality happens all together)



- ____________ ionic compounds
- $\Delta H^{\ominus}_{hyd}$
- $\Delta H^{\ominus}_{latt}$
- $\Delta H^{\ominus}_{sol}$





Slide 69: Dissolving compounds in water gives an enthalpy change.

- **Dissolving compounds**
- **Always write solid salt on left**
- **Always write ____________ salt on right**

$$\begin{tikzcd}
\boxed{NaCl_{(s)}} \arrow[rr, "\Delta H^{\ominus}_{sol}"] \arrow[dr, "\Delta H^{\ominus}_{lat}"'] & & \boxed{Na^{+}_{(aq)} + Cl^{-}_{(aq)}} \\
& \boxed{Na^{+}_{(g)} + Cl^{-}_{(g)}} \arrow[ur, "\Delta H^{\ominus}_{hyd}"'] &
\end{tikzcd}$$

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

Slide 70: Dissolving compounds in water gives an enthalpy change.

- **Solution Enthalpy Practice**

- $\Delta H^{\ominus}_{sol} = +778 - 774 = +4\ \text{kJ mol}^{-1}$

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

Slide 71: HL - Entropy

- **Do now:**
- What changes are _____________ to particles as they move from a solid to a liquid. Think about energy.

Slide 72: Entropy

- Entropy is the measure of disorder in particles and hence the number of ways particles can arrange _____________ ($S^{\ominus}$).
- The more energy (quanta) _____________ have, the higher the entropy.
- More _____________ (more moles) =
- higher _____________. Due to more
- ways of _____________ the particles
- e.g. _____________ salts.
- Standard _____________ Conditions (SATP in data book)

Slide 73: Which has more entropy?

- Solid, liquid or gas?
- $NaCl_{(aq)}$ or $NaCl_{(s)}$?
- CO or CO_2?
- NaCl and water or $NaCl_{(aq)}$?
- $N_{2(g)} + O_{2(g)}$ or $2NO_{(g)}$?
- H_2O at room temperature or H_2O at 50°C?

Slide 74: Which has more entropy?

- Solid, liquid or gas? **Solid < Liquid < Gas** (more disorder)
- **$NaCl_{(aq)}$** or $NaCl_{(s)}$? A solution has more randomness than a solid
- CO or **CO_2**? The more atoms there are the more entropy (possible arrangements)
- NaCl and water or **$NaCl_{(aq)}$**? A solution has more arrangements and motion than a solute and solvent
- $N_{2(g)} + O_{2(g)}$ or $2NO_{(g)}$? **Too close to tell** (stays the same)
- H_2O at room temperature or **H_2O at 50°C?** More temp = more kinetic energy/movement

Slide 75: Entropy and temperature

- As temp _____________, the entropy increases.
- _____________ can gain energy and can be ordered in more ways.
- Sudden _____________ in entropy at melting and boiling points.
- Much bigger _____________ at the boiling point.
- Entropy jumps more here as gas _____________ have more movement (and so disorder) than liquid or solid particles.

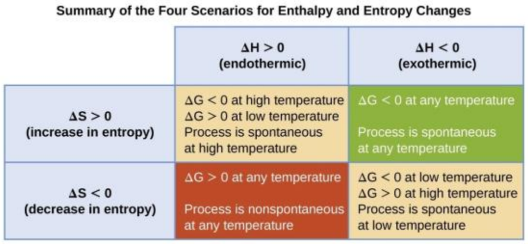
Slide 76: Standard entropy SƟ

- _____________ entropy is at 100 kPa and 298 K **(in data books)**.
- The units are $J\ K^{-1}\ mol^{-1}$ => ensure your units are _____________!
- Standard entropy can be _____________:
- **E.g. due to _____________**
- $NO_2 = 240\ J\ K^{-1}\ mol^{-1}$ $NO = 211\ J\ K^{-1}\ mol^{-1}$
- This is due to the fact there are more ways we can arrange the _____________.
- **E.g. due to _____________ state**
- $H_2O_{(g)} = 699\ J\ K^{-1}\ mol^{-1}$ $H_2O_{(l)} = 189\ J\ K^{-1}\ mol^{-1}$
- **_____________ endothermic reactions occur due to favourable entropy values.**

Slide 77: Standard entropy SƟ

- If S is bigger than 0 there is an _____________ in entropy. The reaction is feasible.

- If S is less than 0, there is a ____________ in entropy.
- **____________ endothermic reactions occur due to favourable entropy values.**



Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	**$\Delta H < 0$ (exothermic)**
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

Slide 78: Entropy change

- Can be measured using 3 ____________:
- **Entropy of system**
- **$\Delta S = \sum S^{\theta}products - \sum S^{\theta}$____________**
- **Entropy of ____________**
- $\Delta S_{surroundings} = -{}^{\Delta H}/_{T}$ ${}^{kJ\ mol-1}/_{K}$
- **Total entropy change**
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
- ____________ data is section 12 of data booklets
- **Learn these ____________!**

Slide 79: Entropy change example 1

- Calculate the total entropy change for the following reaction under standard conditions. $2Ca + O_2 \rightarrow 2CaO$

- $\Delta S_{system} = \Delta S_{products} - \Delta S_{reactants}$
- = (2 x 40) - [(2 x 41.6)+205]
- = 80-2882 = -208.2 J K^{-1} mol^{-1}
- $\Delta S_{surroundings}$ $= -{}^{\Delta H}/_{T}$ $= - {}^{(-1270x1000)}/_{298}$ (standard temp)
- = 4261.7 J K^{-1} mol^{-1}
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
- = -208.2 + 4261.7
- = 4053.5 J K^{-1} mol^{-1}
- This number is positive (above 0), so means reaction is kinetically feasible at standard conditions.
- $\Delta H^{\ominus}$ = -12270 kJ mol^{-1}
- **$\Delta S^{\ominus}$ (J K^{-1} mol^{-1})**
- Ca = 41.6
- O_2 = 205
- CaO = 40

Slide 80: Entropy change example 2

- Does NaBr dissolve in solution at 298 K?
- $\Delta S^{\ominus}_{system} = 55.0 \text{ J K}^{-1} \text{ mol}^{-1}$
- $NaBr_{(s)} \rightarrow Na^{+}_{(aq)} + Br^{-}_{(aq)}$ $\Delta H^{\ominus} = -0.6 \text{ kJ mol}^{-1}$
- $\Delta S_{surroundings} = -{}^{\Delta H}/_{T} = -{}^{(-0.6x1000)}/_{298}$ (standard temp)
- $= +2.05 \text{ J K}^{-1} \text{ mol}^{-1}$
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
- $= 55.0 + 2.05$
- $= +57.0 \text{ J K}^{-1} \text{ mol}^{-1}$
- This number is positive (above 0), so means reaction is kinetically feasible at standard conditions.

Slide 81: Questions

- 1. For each of the following reactions, indicate whether you would expect the entropy of the system to increase or decrease, and explain why. If you cannot tell just by inspecting the equation, explain why.
- (a) $CH_3OH_{(l)} \rightarrow CH_3OH_{(g)}$
- (b) $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$
- (c) $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$
- (d) $2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(aq)}$
- 2. Predict which of the following reactions has a positive change in entropy.
- I. $2N_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{(g)}$
- II. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
- III. $Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

Slide 82: Questions

- 3. Predict which of the following reactions has a negative change in entropy.
- I. $2HgO_{(s)} \rightarrow 2\ Hg_{(l)} + O_{2(g)}$
- II. $Ba^{2+}_{(aq)} + SO_4^{2--}{}_{(aq)} \rightarrow BaSO_{4(s)}$
- III. $2\ H_2O_{2(l)} \rightarrow 2\ H_2O_{(l)} + O_{2(g)}$
- 4. Predict which of the following reactions has a negative change in entropy.
- I. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$
- II. $MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}$

- III. $PCl_{5(s)} \rightarrow PCl_{3(l)} + Cl_{2(g)}$

Slide 83: Check your work

- 1. For each of the following reactions, indicate whether you would expect the entropy of the system to increase or decrease, and explain why. If you cannot tell just by ____________ the equation, explain why.
- (a) $CH_3OH_{(l)} \rightarrow CH_3OH_{(g)}$ ____________
- (b) $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$ ____________
- (c) $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$ ____________
- (d) $2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(aq)}$ ____________
- 2. Predict which of the ____________ reactions has a positive change in entropy.
- I. $2N_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{(g)}$ **Too close to tell (v ____________ negative)**
- II. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ ____________
- III. $Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$ ____________

Slide 84: Check your work

- 3. Predict which of the ____________ reactions has a negative change in entropy.
- I. $2HgO_{(s)} \rightarrow 2\,Hg_{(l)} + O_{2(g)}$ ____________
- II. $Ba^{2+}_{(aq)} + SO_4^{2--}{}_{(aq)} \rightarrow BaSO_{4(s)}$ ____________
- III. $2\,H_2O_{2(l)} \rightarrow 2\,H_2O_{(l)} + O_{2(g)}$ ____________
- 4. Predict which of the ____________ reactions has a negative change in entropy.
- I. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ ____________ **(too close to tell)**
- II. $MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}$ ____________
- III. $PCl_{5(s)} \rightarrow PCl_{3(l)} + Cl_{2(g)}$ ____________

Slide 85: Does the entropy increase or decrease?

Slide 86: Check your work

Slide 87: Calculating entropy

- Similar to ____________ ΔHf.
- **ΔS = ∑S$^{\theta}$products - ∑S$^{\theta}$____________**
- $N_2 + 3H_2 \rightleftharpoons 2NH_3$
- $\Delta S^{\theta} = (2 \times 193) - (192 + 3 \times 131)$
- $= -199\ J\ K^{-1}\ mol^{-1}$
- The ΔS is ____________ because in the reaction 4 moles of gas has become 2 moles of gas.
- **Values are in the data book are in ____________ 12.**