



VISION ACADEMY
唯寻国际教育



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UKChO

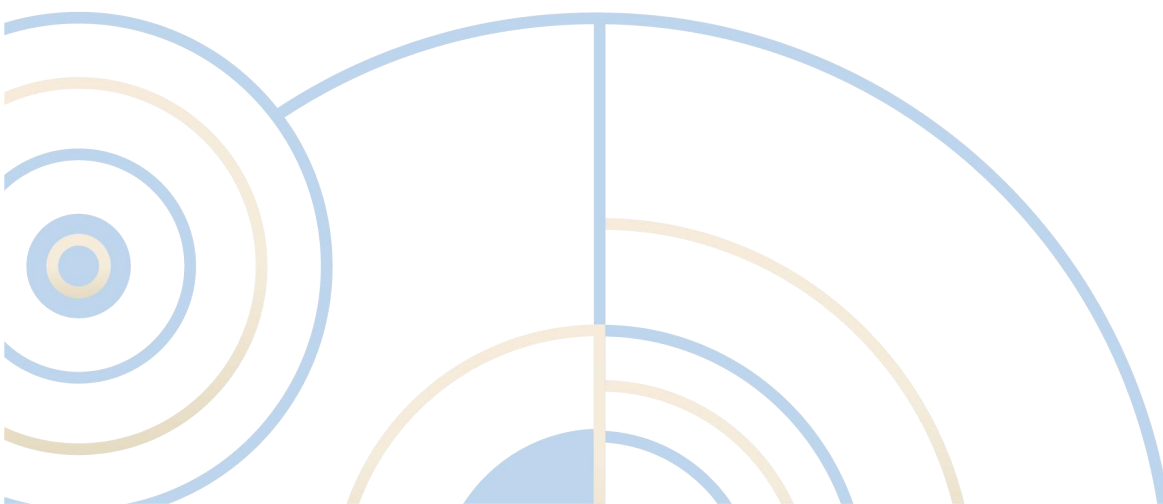
学生讲义

教育的本质是和更优秀的人在一起

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Lecture 6 Physical chemistry-Part 1

Test situation analysis

Testing points	Number of examinations in 2010-2021
Use standard enthalpy change to calculate the enthalpy change of reactions	28
Heat capacity	5
Hess' s law and the calculation of enthalpy change	8
Use bond energy to calculate the enthalpy change	1
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Intensive Teaching and Practicing

Point 1: Enthalpy changes

1.1 Review of enthalpy changes

1.1.1 Definition of enthalpy change

Enthalpy is a measure of the total energy of a system. We can measure the ΔH that takes place during a physical or a chemical change.

$$\Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

The units of enthalpy change are kilojoules per mole (kJ mol^{-1}).

ΔH for an exothermic reaction is negative.

ΔH for an endothermic reaction is positive.

For an exothermic reaction, $H_{\text{reactants}} > H_{\text{products}}$, so ΔH is negative. For an endothermic reaction, $H_{\text{reactants}} < H_{\text{products}}$, so ΔH is positive.

1.1.2 Standard enthalpy changes

⇒ An enthalpy change under standard conditions :

a pressure of 101 kPa, a temperature of 298K

- a temperature of 298K (25°C)

called a **standard enthalpy change** and has the symbol ΔH^\ominus

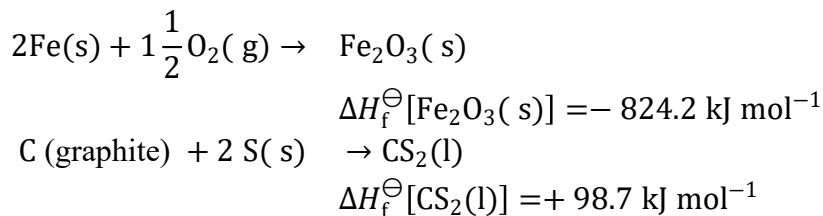
☞ **Standard enthalpy change of reaction, ΔH_r^\ominus**

The standard enthalpy change of reaction, ΔH_r^\ominus is the enthalpy change when the amounts of reactants shown in the stoichiometric equation react to give products under standard conditions. The reactants and products must be in their standard states. The symbol for standard enthalpy change of reaction is ΔH_r^\ominus

☞ **Standard enthalpy change of formation, ΔH_f^\ominus**



The standard enthalpy change of formation, ΔH_f^\ominus is the enthalpy change when one mole of a compound is formed from its elements under standard conditions. The reactants and products must be in their standard states.



By definition, the standard enthalpy change of formation of any element in its standard state is zero.

$$\Delta_r H^\ominus = \sum \Delta H_f^\ominus(\text{Products}) - \sum \Delta H_f^\ominus(\text{Reactants})$$

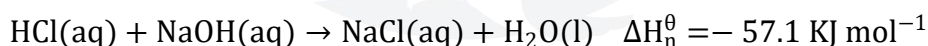
☞ Standard enthalpy change of combustion, ΔH_c^\ominus

The standard enthalpy change of combustion, ΔH_c^\ominus is the enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions.

☞ Standard enthalpy change of neutralisation, ΔH_n^\ominus

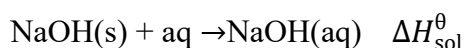
The standard enthalpy change of neutralisation (ΔH_n^\ominus) is the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions. Neutralization is always exothermic.

For example:



☞ Standard enthalpy change of solution, ΔH_{sol}^\ominus

The standard enthalpy change of solution (ΔH_{sol}^\ominus) is the enthalpy change when one mole of solute is dissolved in a solvent to form an infinitely dilute solution.



1.2 Heat Capacity

Heat Capacity and Calorimetry

The heating of a cool body by a warmer body is an important form of energy





transfer between two systems. The amount of heat transferred between two bodies may be quantified by the heat transfer equation:

$$q = mc\Delta T$$

The energy transferred as heat (the enthalpy change) is given by the relationship:

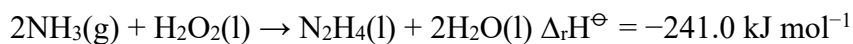
$$\Delta H = -mc\Delta T$$

Specific heat capacity has units of $\text{J g}^{-1}\text{K}^{-1}$ or $\text{J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$. Units that are also encountered are $\text{kJ kg}^{-1}\text{K}^{-1}$ or $\text{J kg}^{-1}\text{K}^{-1}$.

Specific heat capacity of water is $4.18\text{J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$ or $4.18\text{J g}^{-1}\text{ K}^{-1}$

Example 1.(source,UKChO,2013,1b)

(b) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.



Work out the standard enthalpy change for the decomposition of hydrazine to its elements.

The standard enthalpy changes of formation in kJ mol^{-1} are:

NH_3 : -46.1 ; H_2O_2 : -187.8 ; H_2O : -285.8

Exercise 1.(source,UKChO,2014,5f)

When $(\text{CH}_4)_8(\text{H}_2\text{O})_6$ is burnt in excess oxygen at 298 K, the enthalpy change of combustion is $-6690.4 \text{ kJ mol}^{-1}$.

(f)

Use the data below to determine the enthalpy change when methane hydrate is formed from methane and water at 298 K.

Standard enthalpy changes of formation at 298 K in kJ mol^{-1} :

CH_4 : -74.8 , H_2O : -285.8 , CO_2 : -393.5



Point 2: Hess's law and the calculation of enthalpy change of reaction

2.1 Hess's law

Hess's law states that 'the total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same'.

If we know the value for ΔH_1 (for the conversion of A to C) and ΔH_2 (for the conversion of C to B) we can work out the value of the enthalpy change ΔH_r for the conversion of A into B using this cycle. Hess's law states that the enthalpy change for the direct conversion of A to B is exactly the same as the enthalpy change for the indirect route between A and B. Therefore, in this case:

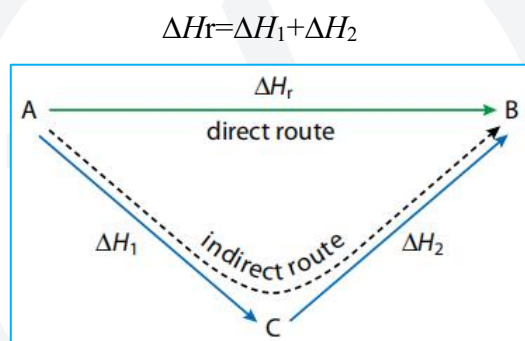
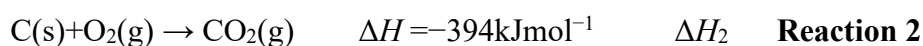
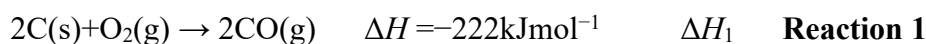


Fig 2.1 An enthalpy cycle

—IB chemistry 2nd edition P196

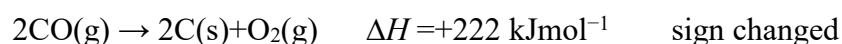
For example: Given these enthalpy changes:



⇒ Manipulating the equations

In this method we rearrange the equations for the data given to produce the equation for the reaction corresponding to the enthalpy change we have to find.

First, **Reaction 1** is reversed to give 2CO on the left-hand side, as in the overall equation:

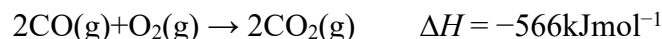




Now **Reaction 2** is multiplied by two to give 2CO_2 on the right-hand side, as in the overall equation:



We now have 2CO on the left-hand side and 2CO_2 on the right-hand side, as in the overall equations. The two equations and their enthalpy changes are now added together and common terms cancelled to produce the overall equation and its enthalpy change:



The relationship between the various enthalpy changes in the above example can be seen in an enthalpy level diagram (Figure 2.4). Downward arrows represent exothermic processes.

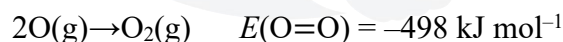
2.2 Bond energies and enthalpy changes

2.2.1 Bond energy

Bond enthalpy is the enthalpy change when **one mole of** covalent bonds, in a gaseous molecule, is broken under standard conditions.

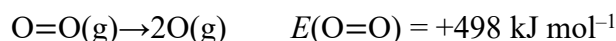
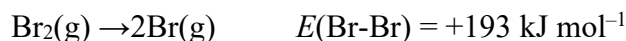
Enthalpy changes are due to the breaking and forming of bonds. Breaking bonds requires energy. The energy, is needed to overcome the attractive forces joining the atoms together.

⇒ **Energy is released when new bonds are formed.**



⇒ **Energy is absorbed when bonds are broken.**

The bond energy for double and triple bonds refers to a mole of double or triple bonds.



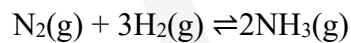
In a chemical reaction:

- if the energy needed to break bonds is less than the energy released when new bonds are formed, the reaction will release energy and is exothermic.
- if the energy needed to break bonds is more than the energy released when new bonds are formed, the reaction will absorb energy and is endothermic.

2.2.2 Calculating enthalpy changes using bond energies

We can use bond enthalpies to calculate the enthalpy change of a reaction that we cannot measure directly.

For example, the reaction for the Haber process



The enthalpy cycle for this reaction is shown in **Figure 2.2**. The relevant bond energies are:

$$E(\text{N}\equiv\text{N}) = 945 \text{ kJmol}^{-1}$$

$$E(\text{H}-\text{H}) = 436 \text{ kJmol}^{-1}$$

$$E(\text{N}-\text{H}) = 391 \text{ kJmol}^{-1}$$

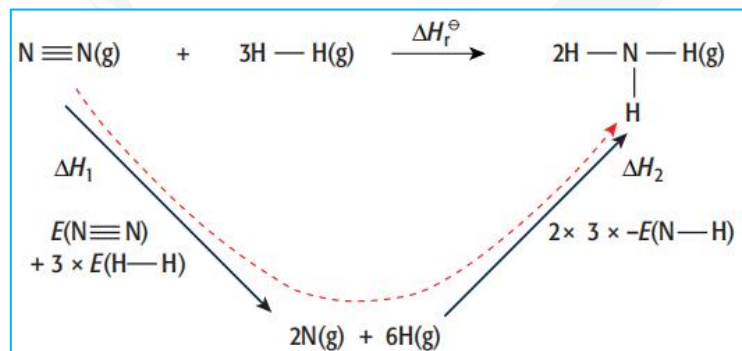


Figure 2.2 The enthalpy cycle for ammonia synthesis. The dashed line shows the two-step route

— 《Cambridge International AS and A Level Chemistry Coursebook 2nd Edition Lawrie Ryan》 P101

Note in these calculations that:

- one triple bond in nitrogen is broken
- three single bonds in hydrogen are broken



- six single N–H bonds in hydrogen are formed (because each of the two ammonia molecules has three N–H bonds)
- values for bond breaking are positive, as these are endothermic, and values for bond forming are negative, as these are exothermic.

$$\Delta H_r = \Delta H_1 + \Delta H_2$$

ΔH_r = enthalpy change for bonds broken + enthalpy change for bonds formed

$$\Delta H_r = 945 + 3 \times 436 + (-2 \times 3 \times 391) = -93 \text{ kJ mol}^{-1}$$

The overall process is sometimes summarised as:

$$\Delta H_r = \sum(\text{bonds broken}) - \sum(\text{bonds made})$$





Point 3: Entropy and Gibbs free energy

3.1 Introducing entropy

Entropy is a measure of the dispersal of energy at a specific temperature. Entropy can also be thought of as a measure of the randomness or disorder of a system. The higher the randomness or disorder, the greater the entropy of the system. A **system** is the part under investigation. In chemistry this is the chemical reaction itself, i.e. reactants being converted to products.

Entropy can also be thought of as a dispersal of energy, either from the system to the surroundings or from the surroundings to the system. The system becomes energetically more stable when it becomes more disordered.

Entropy is given the symbol S . The units of entropy are $\text{J K}^{-1} \text{mol}^{-1}$. S^\ominus is called **standard entropy**. It is possible to work out values for standard entropies for substances – for example, the standard entropy of $\text{H}_2(\text{g})$ is $131 \text{ J K}^{-1} \text{mol}^{-1}$, and the standard entropy of $\text{NaCl}(\text{s})$ is $72.4 \text{ J K}^{-1} \text{mol}^{-1}$.

3.2 Entropy changes in reactions

3.2.1 Comparing entropy values

You should be familiar with several simple rules concerning entropies:

- Gases have higher entropy values than liquids. Liquids have higher entropy values than solids.

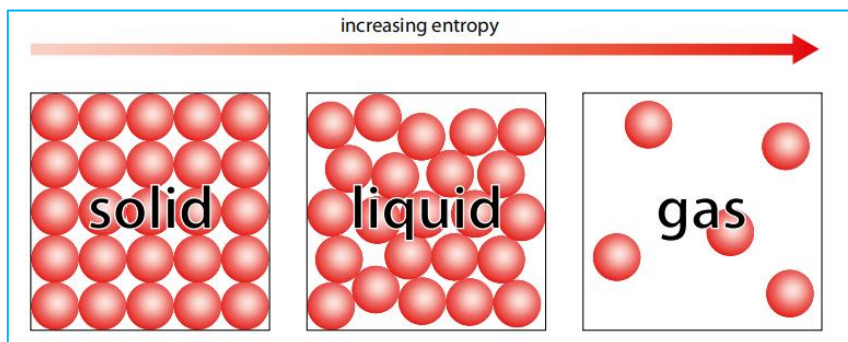
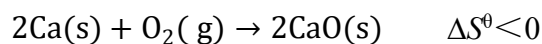
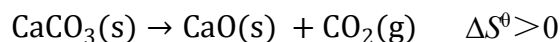


Figure 3.1 — IB chemistry 2nd edition P226

- An **increase** in number of moles of **gas**: ΔS^\ominus +ve (entropy **increases**).
- A **decrease** in number of moles of **gas**: ΔS^\ominus -ve (entropy **decreases**).



For example:



- Simpler substances with fewer atoms have lower entropy values than more complex substances with a greater number of atoms. For example, CO has a lower entropy value than CO₂
- For similar types of substances, harder substances have a lower entropy value. For example, diamond has a lower entropy value than graphite

3.2.2 Calculating entropy change for a reaction

An entropy change is represented by the symbol ΔS . The standard entropy change, S^θ , that has taken place at the completion of a reaction is the difference between the standard entropies of the products and the standard entropies of the reactants.

$$S^\theta = \sum S^\theta_{\text{products}} - \sum S^\theta_{\text{reactants}}$$

3.3 Gibbs free energy

Spontaneous reaction: one that occurs without any outside influence.

Whether a reaction will be spontaneous or not under a certain set of conditions can be deduced by looking at how the **entropy of the Universe** changes as the reaction occurs. The second law of thermodynamics states that for a process to occur spontaneously it must result in an increase in the entropy of the Universe.

The total entropy change is given by:

$$\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

If the universe entropy change increases, the entropy change is positive. The reaction will then occur spontaneously. We say that the reaction occurs spontaneously

When heat is given out in a chemical reaction, the surroundings get hotter and the particles move around more – therefore the entropy of the surroundings increases. So the entropy change of the surroundings can be related to the enthalpy change of the system. A new equation can be derived from the equation of the entropy change above. The new equation is:



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

ΔG is called the change in **Gibbs free energy**, or just the **free energy change**.
Under standard conditions, we have ΔG^θ , which is the **standard free energy change**.

for a reaction to be spontaneous, ΔG for the reaction must be negative.

Calculating ΔG^θ

The standard free energy change for a reaction can be calculated using the equation:

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

Extension:

The entropy change of the surroundings depends on the temperature and is given by:

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

$[-\Delta H$ because an exothermic reaction (ΔH negative) causes the entropy of the surroundings to increase ($\Delta S_{\text{surroundings}}$ positive)]

$$\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

$$\Delta S_{\text{universe}} = \frac{-\Delta H_{\text{system}}}{T} + \Delta S_{\text{system}}$$

$$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

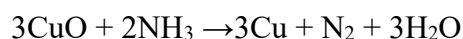
$-T\Delta S_{\text{universe}}$ is given the symbol ΔG .



The change in ox. nos. are -2 for the copper and $+3$ for the nitrogen. To balance the ox. no. changes, we need to multiply the copper by 3 and the nitrogen in the ammonia by 2. The total ox. no. changes are then balanced (-6 and $+6$). Note that we do not multiply the N_2 by 2 because there are already two atoms of nitrogen present. Once these ratios have been fixed you must not change them.

⇒ Step 4 Balance the atoms.

There are six hydrogen atoms in the $2NH_3$ on the left. These are balanced with six on the right (as $3H_2O$). This also balances the number of oxygen atoms. The final equation is



4.1.2 Half-equations (electron-half-equations)

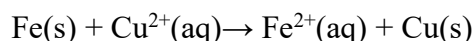
We can divide a reaction into two separate equations, one showing oxidation and the other showing reduction. We call these **half-equations**.

Any redox reaction is made up of two half-reactions : in one of them electrons are being lost (an oxidation process) and in the other one those electrons are being gained (a reduction process)

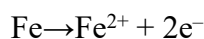
When writing a half-equation , one need follow subsequent steps :

- Write the corresponding product and mark the change of ox. no.
- According to the change of ox. no., write the number of electrons lost /gained.
- Balance the electrons by adding hydrogen ions (if in an acidic condition) or by adding hydroxide ions (if in an alkaline condition)
- Balance the hydrogen by adding water.

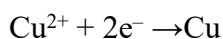
There is an simple example :



■ Each iron atom loses two electrons to form an Fe^{2+} ion. The iron atoms have been oxidised.



■ Each copper(II) ion gains two electrons. The copper ions have been reduced.



However, if the two reactions are separated, as in Figure 4.1, exactly the same reaction occurs, except that instead of the electrons being transferred directly from the Zn to the Cu^{2+} they are transferred via the external circuit.

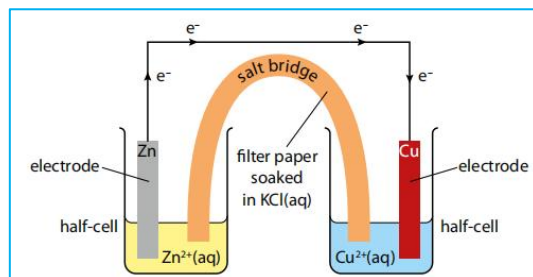


Fig 4.1 a voltaic cell

—IB chemistry 2nd edition

Reduction occurs at the cathode
Oxidation occurs at the anode

4.2 Standard electrode potential

When a metal is put into a solution of its ions an electrical double layer is formed. An electric potential (voltage) is established between the metal and the metal ions in solution. We call this value the **electrode potential**, E .

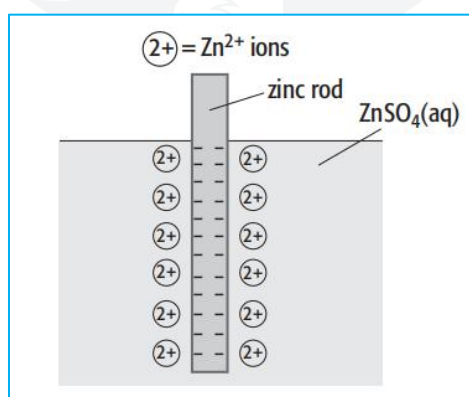


Fig 4.2 The separation of charge when a zinc rod is placed in a solution of Zn^{2+} ions results in an electrical double layer

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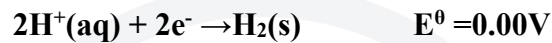


Standard conditions are:

- concentration of ions at 1.00mol dm^{-3}
- a temperature of 25°C (298K)
- any gases should be at a pressure of 1 atmosphere (101kPa)
- the value of the electrode potential of the half-cell is measured relative to the standard hydrogen electrode.

Under these conditions, the electrode potential we measure is called the **standard electrode potential**. This has the symbol, E^θ . It is spoken of as ‘E standard’.

The **standard hydrogen electrode** is one of several types of half-cell that can be used as reference electrodes.

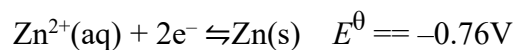
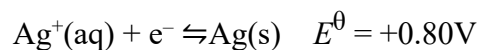


4.3 Using E^θ values to predict cell voltages

4.3.1 Using E^θ values to predict cell voltages

The voltage measured is the difference between the E^θ values of the two half-cells. we call this value the **standard cell potential**.

For the electrochemical cell shown in [Figure 4.3](#), the two relevant half-equations are:



The voltage of this cell is $+0.80 - (-0.76) = +1.56\text{V}$

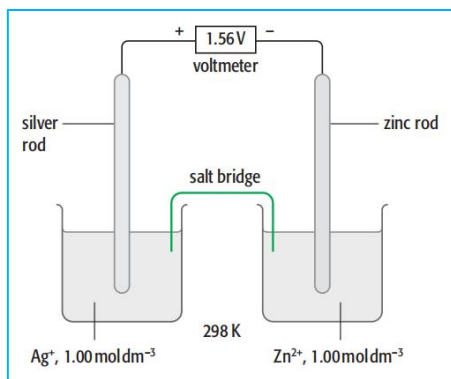


Figure 4.3 An Ag^+/Ag , Zn^{2+}/Zn electrochemical cell

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Note that in order to calculate the cell voltage, we always subtract the less positive E^\ominus value from the more positive E^\ominus value.

Chemists often use a shorthand notation (cell-diagram convention) for describing the reactions that go on in a voltaic cell.



oxidation

reduction

anode

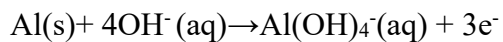
cathode

A **single vertical line** represents a phase boundary (between solid and aqueous solution here) and the **double line** indicates the salt bridge. Reading from left to right we can see that Zn is oxidised to Zn^{2+} and that Cu^{2+} is reduced to Cu. The reaction at the anode is shown by convention on the left and that at the cathode on the right.

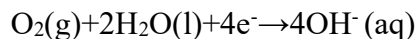
$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$



【Example 2】 In the aluminum-air battery, an aluminum anode is oxidized in alkaline solution:



At the carbon-air cathode, oxygen is reduced by the half-reaction:



for which the standard reduction potential $E^{\ominus}(\text{O}_2, \text{OH}^{\ominus}) = +0.40 \text{ V}$. The standard voltage of the cell $E^{\ominus}_{\text{cell}} = 2.71 \text{ V}$. We may conclude that the standard reduction potential at the anode, $E^{\ominus}(\text{Al}^{3+}, \text{Al})$, is: (Source: 2008, CCC, a, 20)

- A. +3.11 V B. +2.31 V C. 0.00 V D. -2.31 V E. -3.11 V





4.4 Standard cell potentials and ΔG

The standard cell potential and the standard free energy change (ΔG) are related by the equation:

$$\Delta G = -nFE$$

where n is the number of electrons transferred in a particular redox reaction and F is the Faraday constant, which is equal to the charge on one mole of electrons and has a value of approximately $96\,500\text{Cmol}^{-1}$.

Both E_{cell} and ΔG can be used to predict whether a reaction is spontaneous or not

$E_{\text{cell}}^{\ominus}$	ΔG^{\ominus}	Spontaneous?
positive	negative	spontaneous
negative	positive	non-spontaneous
0	0	at equilibrium

Table 4.4 The relationship between E_{cell} , ΔG and spontaneity

【Example 3】

Calculate ΔG for the reaction: $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$

The cell potential can be worked out from the standard electrode potentials

($\text{Zn}^{2+}/\text{Zn} = -0.76\text{ V}$ and $\text{Ag}^+/\text{Ag} = +0.80\text{ V}$):



Summary

Point 1

- Energy changes in chemical reactions that lead to heating or cooling are called enthalpy changes (ΔH).
- Standard enthalpy changes are compared under standard conditions of pressure, 10^5Pa (100 kPa), and temperature, 298K (25 °C).

$$\Delta H^\ominus_r = \sum \Delta H^\ominus_f(\text{products}) - \sum \Delta H^\ominus_f(\text{reactants})$$

Point 2

- Hess's law states that 'the total enthalpy change for a chemical reaction is _____ the route by which the reaction takes place'.
- Use bond energy to calculate the enthalpy change

$$\Delta H_r = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

Point 3

- Entropy (S) is related to the degree of randomness or disorder in a system. The greater the disorder, the _____ the entropy.
- Gibbs free energy is related to the _____ change of reaction and _____ change of the system by the $\Delta G = \Delta H - T\Delta S$.
- Spontaneous (feasible) chemical changes involve a decrease in Gibbs free energy (ΔG is _____).

Point 4

- Reduction occurs at the cathode; Oxidation occurs at the anode

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

- Standard cell potentials and ΔG

$$\Delta G = -nFE^\ominus_{\text{cell}}$$



QUIZ

Question 1.(source,UKChO,2010,3c)

Iodine forms the fluorides IF, IF₃, IF₅ and IF₇. Their standard enthalpy changes of formation are shown in the table.

	IF	IF ₃	IF ₅	IF ₇
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-95.4	-486	-843	-962.5

When the oxidation number of iodine is between 0 and +7 there is a possibility that it will disproportionate to the compound with iodine in its next highest oxidation number, and elemental iodine. For example, IF₃ might disproportionate to give IF₅ and I₂.

(c)

- i) Give the equations for the theoretical disproportionation reactions of IF, IF₃ and IF₅.
- ii) Calculate the standard enthalpy change for each of these reactions.
- iii) Only one of IF, IF₃ and IF₅, does not disproportionate – suggest which one.

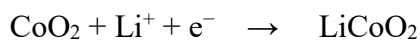
Question 2.(source,UKChO,2018,1a)

Lithium-ion batteries have intercalated lithium compounds as the electrode material. Intercalation is the reversible inclusion or insertion of a molecule (or ion) into materials with layered structures.

When being discharged, the cathode is cobalt oxide with intercalated lithium ions, and the anode is graphite with intercalated lithium ions. In the process of charging and discharging, lithium ions move from one electrode to the other through an electrolyte. The electrolyte is usually a lithium salt dissolved in an organic solvent.

If the battery is handled according to the manufacturer's instructions, then elemental lithium is never formed in the battery.

- (a) When being discharged, the half-reaction at the cathode may be assumed to be



- (i) What is the oxidation state of cobalt in CoO₂?
- (ii) What is the oxidation state of cobalt in LiCoO₂?



(source, UKChO, 2018, 1b)

(b) If the battery is overcharged, Li metal can form on one of the electrodes and this can pose a serious fire risk. At which electrode would Li be formed? Circle the correct answer in the answer booklet.

- A. At the anode, which is the cobalt oxide electrode.
- B. At the cathode, which is the cobalt oxide electrode.
- C. At the anode, which is the graphite electrode.
- D. At the cathode, which is the graphite electrode.



Question 3.(source,UKChO,2018,2a)

The Haber process is used to make ammonia, the main use of which is in fertilisers that are often sprayed on crops. Around 1% of the entire global energy supply is used in the Haber process and so research groups are looking to find more sustainable methods of producing ammonia.



In answering this question you may need to use the following relationships and constants

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

$$G^\theta = -nFE^\theta_{cell}$$

where:

n is the number of electrons transferred in the equation for the cell reaction

F is Faraday's constant (the charge carried by a mole of electrons), which is equal to $9.65 \times 10^4 \text{ C mol}^{-1}$

E^θ_{cell} is the electrochemical cell potential, in volts ($1 \text{ V} = 1 \text{ J C}^{-1}$)

$$Q = I t$$

where:

Q is the electric charge, in coulombs

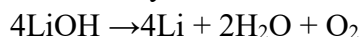
I is the current, in amperes

t is the time, in seconds

$$1 \text{ tonne} = 1 \times 10^6 \text{ g}$$

One recently published approach to making ammonia uses the following three-step method:

Step 1 Electrolysis of molten lithium hydroxide at 750 K to form lithium metal



Step 2 Reaction of lithium metal with nitrogen to form lithium nitride

Step 3 Reaction of lithium nitride with water to re-form lithium hydroxide and ammonia

Thus the lithium hydroxide formed in **Step 3** can be re-used in **Step 1** and the process can be repeated.

(a) State the two half-equations that combine to give the overall equation in **Step 1**.



(source, UKChO, 2018, 2b)

The table below gives the thermochemical data (to 3 significant figures) for **Step 1**.

At 750K	LiOH	Li	H ₂ O	O ₂
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-446	+15.0	-268	+15.8
$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	+128	+63.7	+224	+236

(b) Calculate the following for **Step 1** at 750 K.

- (i) H^\ominus in kJ mol^{-1}
- (ii) S^\ominus in $\text{J K}^{-1} \text{mol}^{-1}$
- (iii) G^\ominus in kJ mol^{-1}

Question 4. (source, UKChO, 2020, 2a)

Carbon dioxide emissions from fossil fuels are a major factor in climate change. Hydrogen is a potential alternative to fossil fuels, providing ‘clean energy’ with only water as a byproduct. The UK government is investigating converting the natural gas grid to carry hydrogen instead.



For this question, assume all processes take place at 298 K.

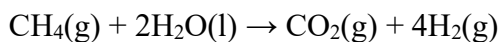
Enthalpy change of formation of $\text{CH}_4(\text{g})$, $\Delta_f H^\ominus = -74.8 \text{ kJ mol}^{-1}$

Enthalpy change of formation of $\text{CO}_2(\text{g})$, $\Delta_f H^\ominus = -393.5 \text{ kJ mol}^{-1}$

Enthalpy change of formation of $\text{H}_2\text{O}(\text{l})$, $\Delta_f H^\ominus = -285.8 \text{ kJ mol}^{-1}$

Entropy change of formation of $\text{H}_2\text{O}(\text{l})$, $\Delta_f S^\ominus = -163.0 \text{ J K}^{-1} \text{mol}^{-1}$

One low cost method for producing hydrogen is reforming methane. Though this produces CO_2 , this can be easily captured. The reforming process can be represented by the overall reaction:

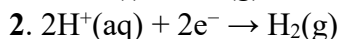
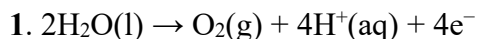


(a) Calculate the enthalpy change for this reaction.

(source, UKChO, 2020, 2b)

Electrolysis of water is another method of producing hydrogen. On a large scale, it currently costs more than reforming methane.

In polymer electrolyte membrane electrolysis, protons are transferred through a membrane between the two electrodes. The two half reactions are:



(b) Which of these half reactions occurs at the cathode?

(source, UKChO, 2020, 2c-2e)

The overall cell reaction is as follows:



(c) Calculate the enthalpy change for the overall cell reaction.

$$\text{Given that } \Delta G^\ominus = -nFE^\ominus \text{ and } \Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

where n = moles of electrons transferred in the overall equation, F = Faraday constant

(d) Calculate the cell potential, E^\ominus , for the overall cell reaction in V.

(if you do not get an answer to this question, use -1.13 V in further calculations)

(e) What is the standard electrode potential for half reaction 1?

(source, UKChO, 2020, 2f-2g)

Enthalpy change of formation of $\text{CH}_4(\text{g})$, $\Delta H^\ominus_f = -74.8 \text{ kJ mol}^{-1}$

Enthalpy change of formation of $\text{CO}_2(\text{g})$, $\Delta H^\ominus_f = -393.5 \text{ kJ mol}^{-1}$

Enthalpy change of formation of $\text{H}_2\text{O}(\text{l})$, $\Delta H^\ominus_f = -285.8 \text{ kJ mol}^{-1}$

Entropy change of formation of $\text{H}_2\text{O}(\text{l})$, $\Delta S^\ominus_f = -163.0 \text{ J K}^{-1} \text{ mol}^{-1}$

To replace natural gas within appliances such as boilers or furnaces, there needs to be a similar amount of heat released per second from burning fuel.

(f) What is the standard enthalpy change of combustion of CH_4 ?

(g) What is the standard enthalpy change of combustion of H_2 ?

When fuel gases are supplied under the same pressure, the heat released per second in a burner may be expressed using:

$$\text{heat released per second} \propto \frac{\text{standard enthalpy change of combustion}}{\sqrt{\text{relative molecular mass}}}$$

(h) What is the ratio of heat released per second in a burner fuelled by hydrogen compared to in the same burner fuelled by methane?

Assume hydrogen and methane are supplied under the same pressure.

Question 5.(source, UKChO, 2011, 1a)

The ingredients of a 'salt and vinegar flavour baked corn snack' are listed as:

- maize
- vegetable oil
- flavouring
- salt

A small bag typically contains 22 g of the snack.

The snack was analysed as follows:

Calorimetry

A 2.0 g sample of the snack was burnt completely. The temperature of the water in the calorimeter rose by 20.9°C . The calorimeter contained 500 g of water.

The specific heat capacity of water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$

$1 \text{ KJ} \equiv 0.239 \text{ dietary calories}$

a) Calculate the number of dietary calories in a typical small bag of the snack.

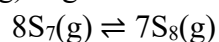


Question 6.(source,UKChO,2012,1a)



Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is a form of S_8 . In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

In the gas phase, the different ring sizes are in equilibrium; the equation for the equilibrium between $S_7(g)$ and $S_8(g)$ is given below:



(a) Given that the S–S bond strength in S_7 is $260.0 \text{ kJ mol}^{-1}$ and in S_8 is $263.3 \text{ kJ mol}^{-1}$, calculate the enthalpy change for the forward reaction.

(source,UKChO,2012,1c)

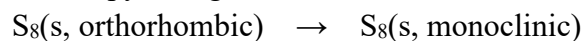
In the solid phase, S_8 crystallises in two well known forms: orthorhombic and monoclinic.

The enthalpy changes of combustion of these two forms are as follows:

$$\Delta_c H^\ominus (S_{8, \text{orthorhombic}}, 298 \text{ K}) = -296.8 \text{ kJ mol}^{-1}$$

$$\Delta_c H^\ominus (S_{8, \text{monoclinic}}, 298 \text{ K}) = -297.1 \text{ kJ mol}^{-1}$$

(c) i) Determine the enthalpy change at 298 K for the reaction

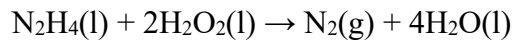


ii) Which is the more stable form at 298 K?

Question 7.(source, UKChO, 2013, 1c)

(c) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture, known as ‘C-Stoff’, and hydrogen peroxide (‘T-Stoff’).

(i) Hydrogen peroxide reacts with the hydrazine as shown in the equation.



State the oxidation number of nitrogen and oxygen in the reactants and products.

(ii) Hydrogen peroxide oxidises the methanol to carbon dioxide and water.

Write a balanced equation for this reaction.

(iii) The fighter plane would hold 225 litres of hydrazine and 862 litres of methanol. Use the following standard enthalpy changes and densities to calculate the heat energy evolved under standard conditions for the combustion of this quantity of rocket fuel. Assume that all the hydrazine and methanol are fully combusted.

$$\Delta_c H^\ominus (\text{N}_2\text{H}_4) = -622.2 \text{ kJ mol}^{-1}$$

$$\text{Density of N}_2\text{H}_4 = 1.021 \text{ g cm}^{-3}$$

$$\Delta_c H^\ominus (\text{CH}_3\text{OH}) = -726.0 \text{ kJ mol}^{-1}$$

$$\text{Density of CH}_3\text{OH} = 0.7918 \text{ g cm}^{-3}$$

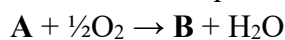
Question 8.(source, UKChO, 2014, 4c)

Bombardier beetles get their name from the defence mechanism that they have when attacked, whereby they shoot a hot chemical spray at their attackers. In their abdomen they have two separate chambers, one containing an aqueous solution of hydrogen peroxide and the other an aqueous solution of an organic compound, denoted here as **A**.

When the beetle is attacked, fluid from both chambers is squirted into a mixing chamber which contains enzymes. One of these enzymes, *catalase*, catalyses the breakdown of hydrogen peroxide into oxygen and water.

The temperature of the mixture ejected from bombardier beetles has been measured to reach the boiling point of water, considerably hotter than the beetle's body temperature, which matches the surroundings (20 °C).

Some of the intermediates produced during the breakdown of hydrogen peroxide react with the organic compound, **A**, to give a product **B**. The overall equation for the reaction can be considered as the result of **A** reacting with all of the oxygen produced by the hydrogen peroxide as in the equation below.



(b) Write an overall equation for the reaction of hydrogen peroxide with **A** to form **B**.

(c) (i) Calculate the amount of energy needed to heat 1 dm³ of this mixture by this amount. Assume the specific heat capacity of the mixture is the same as that of pure water, 4.18 J g⁻¹ K⁻¹ and that the density of the mixture is the same as that of pure water, 1.00 g cm⁻³.

(ii) Assuming equal volumes of the two solutions are mixed, what is the minimum concentration of the hydrogen peroxide solution in the beetle's hydrogen peroxide chamber?

The standard enthalpy change for the overall reaction (your answer to part (b)) per mole of **A** is -203 kJ mol⁻¹.



Question 9. (source, UKChO, 2015, 5g, 5h)

The 'usable energy' may be taken to be the energy released when the syngas undergoes complete combustion to form carbon dioxide and water at room temperature and pressure. The standard enthalpy changes of combustion for H_2 and CO are given below.

	CO(g)	$\text{H}_2(\text{g})$
Standard enthalpy change of combustion, $\Delta_c H^\ominus / \text{kJ mol}^{-1}$	-283	-286

(g)

(i) Calculate the energy released (the standard enthalpy change) when the sample of syngas produced from the experiment undergoes complete combustion.

Supplementary information: Composition of the syngas:

0.0196 mol of H_2 and 0.0115 mol of CO

(h)

(i) Given the standard enthalpy changes of combustion ($\Delta_c H^\ominus$) for heptane ($n = 7$) and octane ($n = 8$) are -4816 and $-5470 \text{ kJ mol}^{-1}$ respectively, calculate $\Delta_c H^\ominus$ of dodecane ($n = 12$).

(ii) By constructing an appropriate Hess' cycle, calculate the standard enthalpy change for the production of dodecane from syngas.

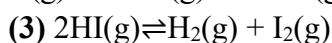
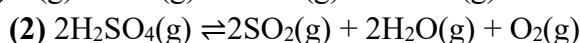
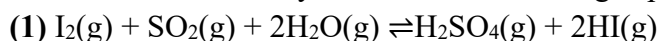


Question 10.(source,UKChO,2016,1a)

Daily fluctuations in energy usage and in energy generation from renewables lead to a need for energy storage methods. Energy may be stored chemically using the sulfur- iodine cycle. The cycle has also been proposed as a means of producing hydrogen fuel more efficiently than by electrolysis.



At high temperature the sulfur-iodine cycle involves the three gas-phase equilibria:



(a) Use the data and the equations at the end of the question to answer the following questions for **reaction (3)**.

(i) Calculate the standard enthalpy change at 298 K, $\Delta_r H^\ominus$ (298 K).

(ii) Calculate the standard entropy change at 298 K, $\Delta_r S^\ominus$ (298 K).

(iii) Calculate the standard Gibbs energy change at 298 K, $\Delta_r G^\ominus$ (298 K).

(iv) Calculate the equilibrium constant, K_{298} , at 298 K.

(v) Calculate the equilibrium constant, K_{723} , at 723 K. Assume $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ independent of temperature.

Data:

	HI(g)	H ₂ (g)	I ₂ (g)	H ₂ O(g)
$\Delta_f H^\ominus$ (298 K) / kJ mol ⁻¹	26.5		62.4	-242
S (298 K) / J K ⁻¹ mol ⁻¹	207	131	261	189

Useful equations: $\Delta S^\ominus = \sum S^\ominus(\text{products}) - \sum S^\ominus(\text{reactants})$

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

$$\Delta G^\ominus = -RT \ln K$$

Useful constant: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

(source, UKChO, 2016, 1b)

(b) Conditions are chosen so that the three equilibrium reactions above all proceed from left to right. Assuming that the products of reaction (1) are all consumed in reactions (2) and (3), write an overall equation for the sulfur-iodine cycle.

(source, UKChO, 2016, 1c)

(c) The standard enthalpy change of reaction at 298 K for **reaction (2)** is +439 kJ mol⁻¹. Use the value of $\Delta_f H$ (298 K) for H₂O(g) in the table to calculate the standard enthalpy change of reaction at 298 K for **reaction (1)**.

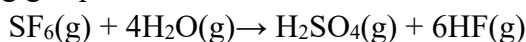
(source, UKChO, 2016, 1d)

(d) How much energy, per mol of sulfur atoms at 298 K, is stored with one revolution around the sulfur-iodine cycle?

Question 11. (source, UKChO, 2016, 2g)

Both elemental sulfur and tungsten react with fluorine gas to form the hexafluorides. SF_6 and WF_6 are both gases at room temperature and pressure, with WF_6 being the most dense gas known under these conditions. WF_6 is extremely toxic due to its rapid reaction with water to form two substances. In contrast, SF_6 is inert in water and non-toxic.

Consider the following gas-phase reaction:



(g) (i) Would you expect the standard entropy change for this reaction to be positive or negative?

(ii) Use the data below to calculate the standard enthalpy change for this reaction.

	SF_6	H_2O	H_2SO_4	HF
$\Delta_f H^\ominus$ (298 K) / kJ mol^{-1}	-1210	-242	-735	-273

(iii) Which of the following is correct regarding the reaction between SF_6 and water? Circle one answer in your answer booklet.

- A. SF_6 is kinetically stable and thermodynamically stable
- B. SF_6 is kinetically stable but thermodynamically unstable
- C. SF_6 is kinetically unstable but thermodynamically stable
- D. SF_6 is kinetically unstable and thermodynamically unstable.

Question 12. (source, UKChO, 2017, 5a)

How strong a base is may be defined by its proton affinity. The proton affinity of species X^- , $\text{PA}(\text{X}^-)$, is given by the standard enthalpy change of the reaction:



(a) Using the data in the table below, calculate the proton affinity of the methyl anion, $\text{PA}(\text{CH}_3^-)$, in kJ mol^{-1} .

Reaction 1	$\text{CH}_4 \rightarrow \text{H}^\bullet + \text{CH}_3^\bullet$	439 kJ mol^{-1}
Reaction 2	$\text{H}^\bullet \rightarrow \text{H}^+ + \text{e}^-$	$2.18 \times 10^{-18} \text{ J}$
Reaction 3	$\text{CH}_3^\bullet + \text{e}^- \rightarrow \text{CH}_3^-$	$-7.52 \text{ kJ mol}^{-1}$

Question 13.(source,UKChO,2019,1e)

One method of industrially manufacturing CO₂ involves the Haber–Bosch process.



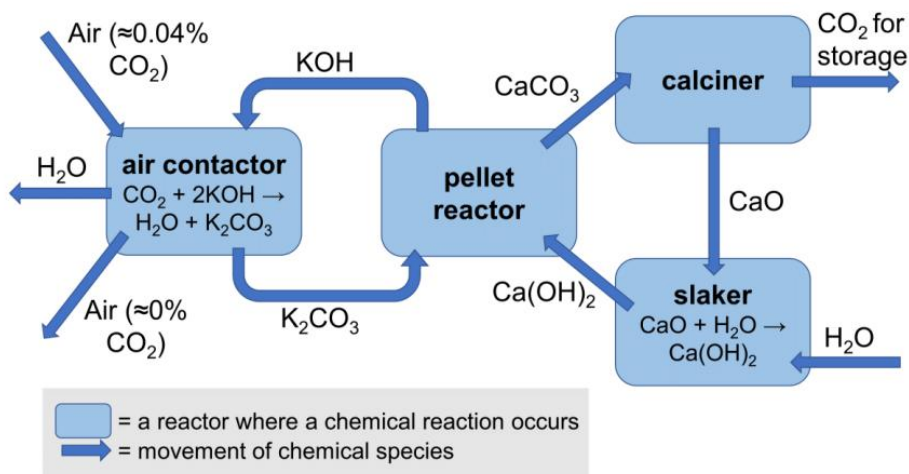
The standard enthalpies of formation of CO(g), CO₂(g) and H₂O(g) are –110.5, –393.5 and –241.1 kJ mol⁻¹ respectively.

(e) Calculate the enthalpy of reaction for the reaction between CO and steam to form CO₂ and H₂.

Question 14.(source,UKChO,2021,2e-f)

Direct air capture is a process which takes carbon dioxide directly from the air therefore avoiding any sulfur dioxide contamination. However, this process can be expensive to run due to the energy required to overcome thermodynamic barriers.

A scheme for a direct air capture process based on calcium looping is shown below.



(e) Write an equation for the reaction in the pellet reactor.

(f) Calculate the standard enthalpy change for the reaction which occurs in the air



contactor.

Standard enthalpy change of formations, $\Delta_f H^\ominus$, at 298 K in kJ mol^{-1} :

CaO	-635.1
CaCO ₃	-1206.9
Ca(OH) ₂	-986.1
KOH	-424.8
K ₂ CO ₃	-1151.2
CO ₂	-393.5
H ₂ O	-285.8

(source, UKChO, 2021, 2g)

(g) Tick the correct statement that describes the standard enthalpy change at 298 K for the sum of the reactions in the four reactors.

- The standard enthalpy change is positive.*
- The standard enthalpy change is zero.*
- The standard enthalpy change is negative.*
- More information is needed to calculate the standard enthalpy change.*

(h) Tick the two correct statements about the entropy changes in this process.

- The entropy change of the universe is positive.*
- The entropy change of the universe is negative.*
- The entropy change of the universe is zero.*
- More information is needed to calculate the entropy change of the universe.*
- The entropy change of this direct air capture process is positive.*
- The entropy change of this direct air capture process is negative.*
- The entropy change of this direct air capture process is zero.*
- More information is needed to calculate the entropy change of this direct air capture process.*

Question 15. (source, UKChO, 2020, 6a-6c)

This question is about anammox and ladderanes

Anammox is an abbreviation for **anaerobic ammonium oxidation**. Despite being a crucial part of the nitrogen cycle, the bacteria responsible for this process were only identified as recently as 1999. In the membranes of these bacteria an unusual class of lipids were found. These lipids contained several fused cyclobutane rings. Such molecules are called ladderanes due to their resemblance to the rungs of a ladder.



The mechanism of ammonium oxidation is believed to involve several different nitrogen-containing species:

- nitrogen gas
- the ammonium ion
- the nitrite ion (NO_2^-)
- hydrazine (NH_2NH_2)
- hydroxylamine (NH_2OH).

(a) (i) Give the oxidation state of the nitrogen atom in nitrogen gas and in the ammonium ion.

(ii) Give the oxidation state of the nitrogen atom in the nitrite ion (NO_2^-), hydrazine (NH_2NH_2), and hydroxylamine (NH_2OH).

The reaction takes place over three steps, all of which can be assumed to take place under acidic conditions.

(b) Using your oxidation states from part (a), write equations for the following steps in the cycle.

(i) Step 1: The half-equation for conversion of nitrite to hydroxylamine.

(ii) Step 2: The reaction of the ammonium ion and hydroxylamine to give hydrazine.

(iii) Step 3: The half equation for the conversion of hydrazine to nitrogen gas.

(c) Hence, write an overall reaction equation for the anammox process.



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