Chem Factsheet

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Disproportionation

To succeed in this topic you need to:
- **understand oxidation numbers (covered in Factsheet 11),**
- **be familiar with redox charts (examples are included in Factsheets 75 and 83,**
- **understand standard electrode potentials and electrochemical cells (covered in Factsheet 37).**

After working through this Factsheet you will:
- **have revised the basic principles of oxidation and reduction;**
- **know that disproportionation is a special kind of redox involving essentially one substance only;**
- **be able to predict disproportionation products from inspection of redox charts;**
- **be familiar with common examples of disproportionation;**
- **have revised the principles of electrochemical cells;**
- **be able to predict, from standard electrode potentials, the feasibility of disproportionation reactions;**
- **understand the difference between disproportionation and reproportionation.**

A disproportionation reaction is a special kind of redox reaction. To understand this topic, you must therefore begin by making sure you know the basic ideas of oxidation and reduction.

Remember *- Principles of oxidation and reduction*
- *Oxidation is a chemical change involving the loss of electrons, e.g.*

$$Na \rightarrow Na^+ + e^-$$

- *Reduction is a chemical change involving the gain of electrons, e.g.*

$$Cl + e^- \rightarrow Cl^-$$

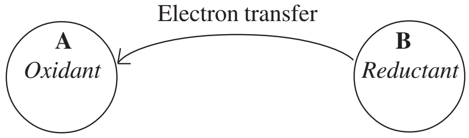
- *Oxidation and reduction must occur together. Whenever a chemical species (i.e. atom, molecule or ion) is oxidised, the electrons it loses are accepted by another species, which thus becomes reduced.*

A chemical reaction in which one species is oxidised while another is simultaneously reduced is known as an *oxidation-reduction* or *redox reaction.* Again make sure you know the basic principles.

Remember *- Principles of redox reactions*
- *Every reaction of this sort is a combination of two* **half-reactions**, *i.e. the oxidation of one species and the reduction of another.*
- ***Most*** *reactions involve essentially two substances, namely an* **oxidising agent** *and a* **reducing agent**.
- *Another substance (water, an acid or an alkali) may also be needed for the reaction to occur.*
- *The oxidising agent provides an* **oxidant**, *i.e. a species which brings about oxidation. Often, as in the case of Cl_2, an 'oxidising agent' and an 'oxidant' are one and the same thing.*
- *The reducing agent provides a* ***reductant***, *i.e. a species which brings about reduction. Often, as in the case of Zn, a 'reducing agent' and a 'reductant' are one and the same thing.*
- *During a redox reaction, electrons are transferred from the reductant to the oxidant.*
- *Because the reductant loses electrons, it becomes oxidised as the reaction occurs. Conversely, because the oxidant gains electrons, it becomes reduced.*

Fig 1. helps you to understand these basic principles.

Fig. 1 Reaction between an oxidant (A) and a reductant (B)



A causes the oxidation of **B** by removing electrons from it. In doing so, **A** accepts electrons, i.e. it is reduced.

B causes the reduction of **A** by giving electrons to it. In doing so, **B** loses electrons, i.e. it is oxidised.

What is the difference between disproportionation and redox?

Disproportionation is a kind of redox reaction involving one substance only. Part of it behaves as an oxidising agent and part as a reducing agent.

That part of the substance which acts as an **oxidising agent** becomes **reduced**, while the part which acts as a **reducing agent** becomes **oxidised**. This leads to the accepted definition of disproportionation.

Disproportionation is defined as the simultaneous oxidation and reduction of a single substance.*

** Chemists often talk about the disproportionation of ions (such as Cu^+ or ClO^-) in aqueous solution. For this reason, disproportionation can also be defined as the simultaneous oxidation and reduction of a single species.*

Prediction of products

Redox charts of elements, in which the principal molecules or ions are shown in order of oxidation number, are very useful in predicting the products of disproportionation reactions.

Species at the top of a redox chart cannot undergo disproportionation because they cannot be oxidised; neither can species at the bottom because they cannot be reduced. Between these extremes, many elements have species which could, in principle, undergo disproportionation.

Use of redox charts in predicting disproportionation products.
- *Locate the reacting molecule or ion on the redox chart.*
- *Look upwards to identify the oxidation product.*
- *Look downwards to identify the reduction product.*
- *Do not assume there will always be one move upwards (an increase of 1 in oxidation number) and one move downwards (a decrease of 1 in oxidation number)*
- *Movement up or down the chart ceases when a stable oxidation level is reached.*

If the change in oxidation number (ON) is the same in both directions, the product ions or molecules will be formed in a 1:1 ratio; otherwise the ratio will be different.

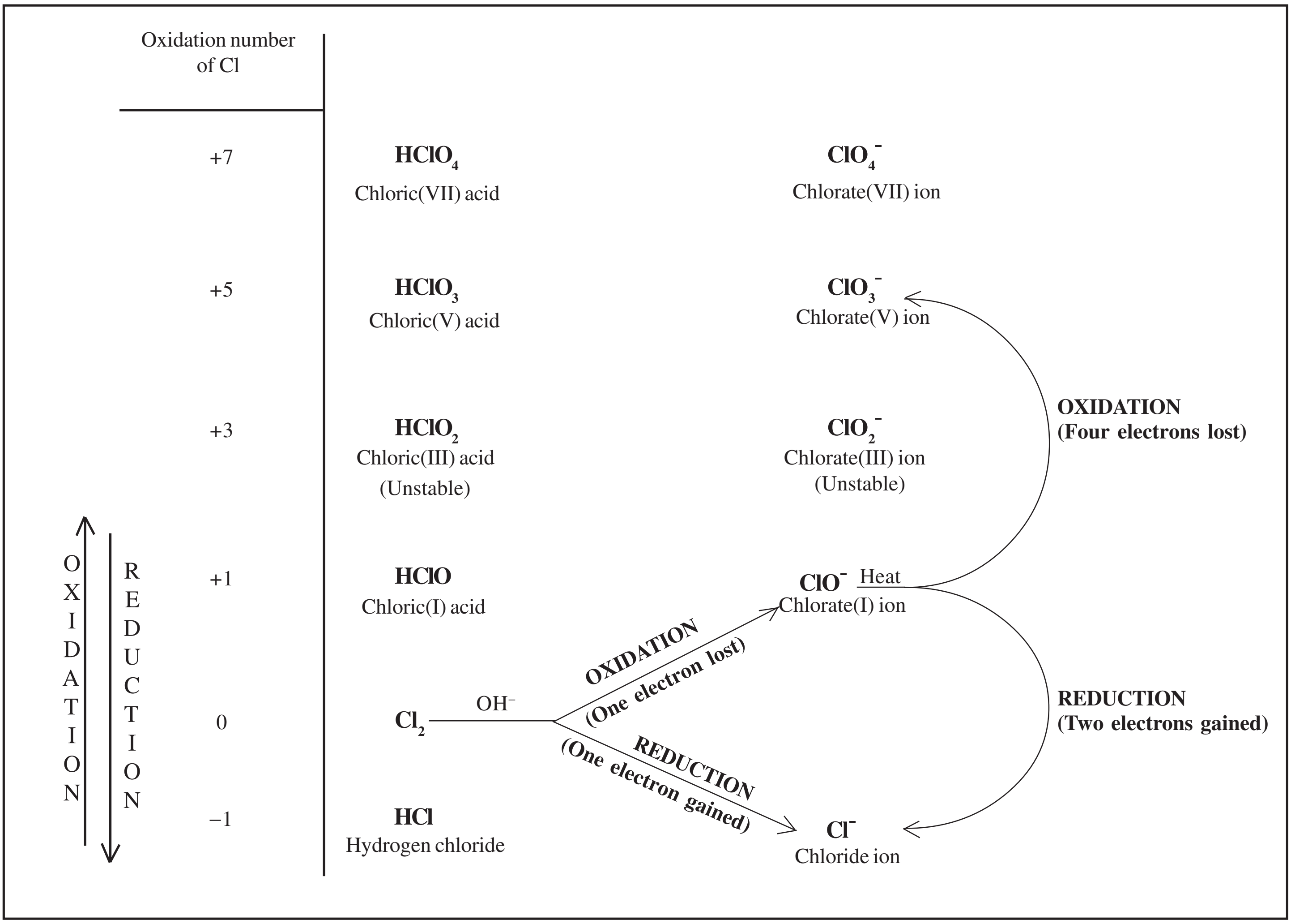
In all cases, the number of electrons lost on forming the oxidation product is equal to the number of electrons gained on forming the reduction product.

Here are some well known examples to illustrate these principles.

Halogens with alkalis

When chlorine is passed into cold, aqueous sodium hydroxide, it disproportionates to give a solution of sodium chloride, NaCl, and sodium chlorate(I), NaClO. The redox chart of chlorine (Fig. 2) helps to explain this.

Fig 2. Disproportionation of Cl_2 and ClO^- shown on the redox chart of chlorine



Reduction can lead only to Cl^- ions, but what about oxidation? Upward movement could conceivably give ClO^-, ClO_2^-, ClO_3^- or ClO_4^- ions, so why is the product ClO^-? The answer is that ClO^- ions are formed first and, because they are stable at room temperature, they stay as they are.

On oxidising Cl_2 to ClO^-, the ON of chlorine changes by +1, corresponding to a one electron loss. Reduction of Cl_2 to Cl^- changes it by -1, corresponding to a one electron gain. Because the number of electrons lost on oxidation is equal to the number gained on reduction, ClO^- and Cl^- ions are formed in a 1:1 ratio:

$$Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l) \qquad (1)$$

Bromine and iodine behave in a similar manner to chlorine. Other alkalis (e.g. KOH) behave like NaOH.

Thermal decomposition

Many thermal decomposition reactions involve disproportionation. If chlorine is passed into *hot* aqueous sodium hydroxide, the products are sodium chloride and sodium chlorate(V), $NaClO_3$, because the ClO^- ion which is formed at first is unstable at temperatures above 70 °C and undergoes disproportionation.

- Reduction of ClO^- cannot give chlorine, because Cl_2 and OH^- would immediately react together, but continues down the chart to give Cl^-.
- Oxidation of ClO^- does not stop at the unstable ClO_2^- ion but proceeds further to the more stable ClO_3^- ion at the +5 oxidation level.

Remember - *Vertical movements on redox charts stop at stable oxidation levels.*

On going from ClO^- to Cl^- the ON of Cl changes by -2, corresponding to a two electron gain. From ClO^- to ClO_3^- it changes by +4, corresponding to a four electron loss. Consequently, in the equation, ClO_3^- and Cl^- ions appear in a 1:2 ratio:

$$3ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq) \qquad (2)$$

To obtain the overall ionic equation for the reaction between Cl_2 and OH^- at temperatures > 70 °C, multiply Equation (1) × 3 and add to Equation (2):

$$3Cl_2(g) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$$

Exam Hint - *Not all thermal decompositions are disproportionation reactions. For example, in the decomposition of calcium carbonate the oxidation numbers of all the elements remain unchanged:*

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ON of Ca	*+2*	*+2*	
ON of C	*+4*		*+4*
ON of O	*-2*	*-2*	*-2*

Non-metal oxides with water

Most non-metal oxides are *acid anhydrides*, i.e. acids without water. They dissolve in water to give acids and, although reactions occur, there is no change in the ON of the non-metal, e.g.

$$\begin{array}{llllll} & SO_3(s) & + & H_2O(l) & \rightarrow & H_2SO_4(aq) \\ \text{ON of S} & +6 & & & & +6 \end{array}$$

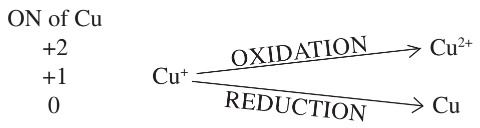
$$\begin{array}{llllll} & P_4O_{10}(s) & + & 6H_2O(l) & \rightarrow & 4H_3PO_4(aq) \\ \text{ON of P} & +5 & & & & +5 \end{array}$$

However, a few non-metal oxides react with water to give a mixture of two acids and are thus described as *mixed anhydrides*. A well known example is nitrogen dioxide, which dissolves in water to give a mixture of nitrous acid and nitric acid. Here, the ON of the principal element (N) is simultaneously increased and decreased, so the reaction is a disproportionation:

$$\begin{array}{llllllll} & 2NO_2(g) & + & H_2O(l) & \rightarrow & HNO_2(aq) & + & HNO_3(aq) \\ \text{ON of N} & +4 & & & & +3 & & +5 \end{array}$$

Ions in aqueous solution

Copper(I) sulphate (an uncommon compound) is a white solid. On dissolving it in water you'd expect to see a colourless solution, but what actually appears is a blue solution of ordinary copper(II) sulphate and a red-brown precipitate of metallic copper. Copper(I) ions in solution always undergo disproportionation:



The equation for the reaction is:

$$Cu_2SO_4(s) \ + \ aq \ \rightarrow \ CuSO_4(aq) \ + \ Cu(s)$$

> ***Exam Hint -*** *Although silver is immediately below copper in the Periodic Table, Ag^+ ions do not behave in the same way as Cu^+ ions. If you are asked to explain this, you must base your argument on $E^\ominus$ values - see below.*

Feasibility of disproportionation

Although redox charts suggest the possibility of disproportionation reactions and help you to predict the identity of the products, they will not tell you whether such reactions take place. In reality, only a tiny number of possible disproportionations actually occur. To find out the feasibility of a disproportionation reaction, you must use standard electrode potentials.

A standard electrode potential (symbol $E^\ominus$) is a property of a redox *system*, i.e. a solution containing equal concentrations (1 mol dm^{-3}) of an oxidant and chemically related reductant, such as $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$. It is defined as the potential that develops on a piece of platinum dipped into the system at a temperature of 298 K, referred to a standard hydrogen electrode assumed to have a potential of 0.00 V.

$E^\ominus$ values of systems provide a useful measure of their oxidising or reducing powers.

> **Remember -** *Significance of $E^\ominus$ values*
> - *The more +ve an $E^\ominus$ value, the more strongly oxidising is the system.*
> - *Negative $E^\ominus$ values indicate reducing systems: the more –ve the value, the greater the reducing power.*
> - *A system will oxidise any other system with a less +ve (or more –ve) $E^\ominus$ value.*

To use $E^\ominus$ values to predict whether a proposed disproportionation reaction will actually occur, you need to imagine that the reaction is taking place in an electrochemical cell. You must therefore be familiar with the construction and operation of such cells.

> **Remember -** *Principles of electrochemical cells*
> - *A cell is a device for carrying out a redox reaction in such a way that energy is released as electrical energy rather than heat.*
> - *The two half-reactions (i.e. oxidation and reduction) are carried out in separate half-cells connected by a salt bridge.*
> - *Each half-cell is a system comprising an oxidant and related reductant. It may consist of a metal dipping into a solution containing its ions (e.g. Zn(s) in contact with $Zn^{2+}(aq)$), or it may comprise a 'redox electrode' consisting of Pt immersed in a solution containing a mixture of ions (or molecules) in an oxidised state and related ions (or molecules) in the reduced state.*
> - *As a result of the redox reaction, the metal of one half-cell becomes +vely charged while that of the other half-cell becomes –vely charged. The half-cells are therefore referred to, respectively, as the +ve and –ve poles of the cell.*
> - *The system with the more +ve $E^\ominus$ value is always the +ve pole of the cell.*
> - *Reduction occurs at the +ve pole of a cell and oxidation at the –ve pole.*

The maximum potential difference (i.e. voltage) that a cell can develop is known as its electromotive force (e.m.f.) or *cell potential*, symbol E_{cell}. For cells in general it is the difference between the potentials of its electrodes under conditions of zero current flow:

$$E_{cell} \ = \ E_+ \ - \ E_-$$

For a cell consisting of two standard electrodes (all that is relevant to A-level), its standard cell potential is given by Equation (3):

$$E^\ominus_{cell} \ = \ E^\ominus_+ \ - \ E^\ominus_- \qquad (3)$$

where $E^\ominus_+$ and $E^\ominus_-$ refer to the standard electrode potentials ($E^\ominus$ values) of the systems at the +ve and -ve poles respectively.

Bearing in mind that reduction occurs at the +ve pole and oxidation at the -ve one, Equation (3) can be rewritten:

$$E^\ominus_{cell} \ = \ E^\ominus_{reduction} \ - \ E^\ominus_{oxidation} \qquad (4)$$

where $E^\ominus_{reduction}$ and $E^\ominus_{oxidation}$ refer to the standard electrode potentials ($E^\ominus$ values) of the systems in the half cells where reduction and oxidation respectively are occurring.

> **Remember -** *Equation (4) spells* **REDOX**:
> $E^\ominus_{cell} \ = \ E^\ominus_{\textbf{RED}uction} \ - \ E^\ominus_{\textbf{OX}idation}$

This is the equation that you need to answer questions on disproportionation. Imagine that the proposed reaction is taking place in an electrochemical cell, with oxidation in one half-cell and reduction in the other. Calculate the e.m.f. of the cell by applying Equation (4) and see whether the value is +ve or –ve.

> *Significance of the result*
> - *If $E^\ominus_{cell}$ is negative, disproportionation will not occur. (It is impossible to have a cell with a –ve e.m.f.)*
> - *If $E^\ominus_{cell}$ is positive, disproportionation* will *occur.*
> - *If $E^\ominus_{cell}$ is positive, but with a value < ~0.3 V, the reaction will not proceed to completion. (A dynamic equilibrium is established.)*

Example

	$E^\ominus$/V
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15

Does the copper(I) ion disproportionate in aqueous solution under standard conditions?

Answer The proposed reaction is:

$$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

Oxidation

Reduction

$$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$$
$$= +0.52 - (+0.15) = +0.37\ V$$

The value is positive and > 0.3 V, so this disproportionation will go to completion.

> ***Exam Hint*** *- Never change the sign of an $E^\ominus$ value!*
> *It is conventional, as in the above example, to quote an $E^\ominus$ value alongside the system to which it relates, written in the form of an ionic half-equation for a reduction process (i.e. with the oxidised species on the LHS). As a result, students may argue that if $E^\ominus$ is, say, +x V for a reduction process, it must be -x V for the reverse change, i.e. the oxidation process.*
>
> *THIS IS WRONG! $E^\ominus$ values do not refer to reactions but to systems, and their quoted values and signs should be substituted unchanged into Equation (4).*

Practice questions

1 Most nitrates decompose on heating to give the metal oxide together with nitrogen dioxide and oxygen, e.g.

$2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$

By considering the oxidation numbers of the elements involved, show that this reaction is a disproportionation.

2 Explain, using oxidation numbers, whether or not each of the following thermal decomposition reactions involves disproportionation.
- (a) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
- (b) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$
- (c) $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$
- (d) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

3 Chlorine dioxide, ClO_2, is a mixed anhydride. Use the redox chart of chlorine (p. 2) to predict the acids that it will form with water, and write an equation for the reaction.

4 Use the following data to predict whether or not the silver(I) ion disproportionates in aqueous solution under standard conditions.

	$E^\ominus$/V
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Ag^{2+}(aq) + e^- \rightleftharpoons Ag^+(aq)$	+1.98

5 Use the following standard electrode potentials to explain why, under acidic conditions, potassium manganate(VI) dissolves in water to form a purple solution and a brown precipitate, but under alkaline conditions it just gives a green solution.

	$E^\ominus$/V
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.60
$MnO_4^-(aq) + e^- \rightleftharpoons MnO_4^{2-}(aq)$	+0.56

6 When a mixed solution of ammonium chloride and sodium nitrite is boiled, reproportionation occurs between ammonium ions and nitrite ions so that a new nitrogen-containing species is formed.
- (a) What species is this?
- (b) Use changes in oxidation number to justify your answer to (a).
- (c) Write an equation for the reaction.

Reproportionation

This is essentially the opposite of disproportionation.

> *Reproportionation occurs when two species containing the same element in different oxidation states react together to give a single species in which the element is present in a third, intermediate oxidation state.*

For example, when ammonium nitrate is heated, the ammonium ion is oxidised, the nitrate ion is reduced, and all nitrogen finishes up as dinitrogen monoxide:

	NH_4^+	$NO_3^-(s)$	$\rightarrow$	$N_2O(g) + 2H_2O(l)$
ON of N	-3	+5		+1

Dinitrogen monoxide is formed from both NH_4^+ and NO_3^- ions because, as in ordinary disproportionation, the number of electrons lost on oxidation must be equal to the number gained on reduction. Oxidation of NH_4^+ to N_2O corresponds to a four electron loss (ON increase from -3 to +1), and the gain of four electrons by NO_3^- takes the ON down from +5 to +1, again producing N_2O.

Answers

1. $2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$

	$2Mg(NO_3)_2$		$2MgO$	$4NO_2$	O_2
ON of N	+5			+4	
ON of O	-2		(-2)	(-2)	0

The changes in ON show that N is reduced and O is oxidised, i.e. disproportionation occurs.

2. (a) Yes. ON of Cl falls, from +5 to -1; that of O increases from -2 to 0.
   (b) No. ON of all elements remain constant.
   (Na = +1, H = +1, C = +4 and O = -2 in both reactants and products.)
   (c) No. ON of all elements remain constant.
   (N = -3, H = +1 and Cl = -1 in both reactants and products.)
   (d) Yes. ON of O changes from -1 in H_2O_2 to -2 in H_2O and 0 in O_2.

3 ClO_2 forms chloric(V) acid by oxidation and chloric(III) acid by reduction.

$2ClO_2(g) + H_2O(l) \rightarrow HClO_3(aq) + HClO_2(aq)$

4 The proposed reaction is:

$$2Ag^+(aq) \rightarrow Ag^{2+}(aq) + Ag(s)$$

Oxidation

Reduction

$$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$$
$$\therefore E^\ominus_{cell} = +0.80 - (+1.98) = -1.18\ V$$

Because the value is negative, this disproportionation will not occur.

5 Disproportionation of the manganate(VI) ion is possible, as shown by positive e.m.f.

$$3MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 4OH^-(aq)$$

Oxidation

Reduction

$$E^\ominus_{cell} = +0.60 - (+0.56) = +0.04\ V$$

The very low e.m.f. shows that the reaction is reversible. In acidic solution OH^- ions are removed and equilibrium is disturbed to the RHS, but in alkaline solution the excess of OH^- ions disturbs it to the LHS.

6 (a) N_2
  (b) Oxidation of NH_4^+ to N_2 increases ON by 3; hence a three-electron loss.
  Reduction of NO_2^- to N_2 decreases ON by 3; hence a three-electron gain.
  (c) $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

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