Chem Factsheet

www.curriculum-press.co.uk Number 173

The Chemistry of Breathalysers

This Chem Factsheet gives general guidance on this topic and the answers that are provided are "best answers". However, in some cases, other answers will gain equal/partial credit.

Before starting this Factsheet, make sure you understand redox chemistry, redox potentials, fuel cells and infrared spectrometry.

1. Introduction

A breathalyser is an instrument that tests exhaled breath to give an estimation of the amount of alcohol in the blood (Blood Alcohol Content, BAC). Ethanol in blood can pass into the gas of the lungs. Hence, by using a breathalyzer to measure the ethanol in exhaled breath, an *estimation* of alcohol in the blood can be obtained.

The breathalyzer was introduced in the U.K. in 1967. A breathalyser provides an indication of the need to measure BAC accurately, but this has to be done using a *blood sample*. The current legal upper limit for BAC is: 0.35 mg/l = 0.08% BAC.

2. Three Types of Breathalyser

Type 1. The Potassium Dichromate(VI) Crystals and Sulfuric Acid Breathalyser

This was the breathalyzer introduced into the UK in 1967. The person being tested had to blow through a tube containing acidified potassium dichromate on a silica support.. If there was ethanol in the breath, the *orange crystals would turn green* to an extent depending upon the amount of ethanol. The colour change was measured by photometry. The ethanol reduces the orange $Cr_2O_7^{2-}$ ions to green Cr^{3+} ions while being oxidised to ethanal. The ethanal may be further oxidised to ethanoic acid.

1. $CH_3CHO(l) + 2H^+(aq) + 2e^- \rightarrow CH_3CH_2OH(g)$ $E^\ominus = -0.20\ V$

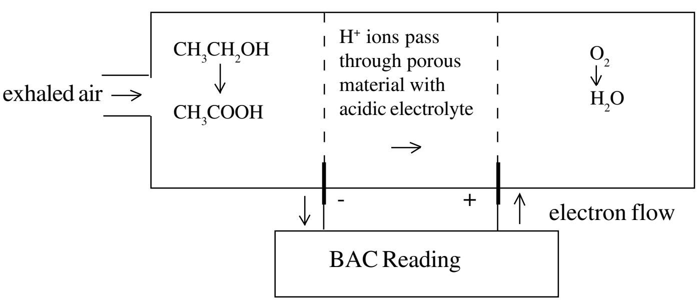
2. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\ominus = +1.33\ V$

The standard redox potentials show that the acidified dichromate ion is a better oxidant than ethanal since its $E^\ominus$ is more positive. Thus acidified dichromate will oxidize ethanol to ethanal. The cell voltage (emf) is + 1.53 V. The balanced equation is found by {(reversing 1) x 3} + 2:

$$3CH_3CH_2OH(aq) + Cr_2O_7^{2-}(s) + 8H^+(aq) \rightarrow 3CH_3CHO(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Type 2. The Fuel Cell (Electrochemical Cell) Breathalyser

A fuel cell is an electrochemical cell for converting chemical energy into electrical energy by a spontaneous redox reaction between a fuel and an oxidant. In a breathalyser the fuel is ethanol from a person's breath and the oxidant is oxygen from the air.



If the exhaled air contains ethanol (the fuel), the ethanol is oxidised at the platinum anode (negative) to ethanoic acid, hydrogen ions and electrons.

$$CH_3COOH(aq) + 4H^+(aq) + 4e^- \rightarrow CH_3CH_2OH(l) + H_2O(l) \quad E^\ominus = +0.06\ V. \quad \text{- - (1)}$$

These electrons pass externally to another platinum cathode (positive) and the hydrogen ions pass internally through a porous acid-electrolyte to the cathode. At the cathode oxygen is reduced to water.

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E^\ominus = +1.23\ V. \quad \text{- - (2)}$$

The overall cell reaction is:

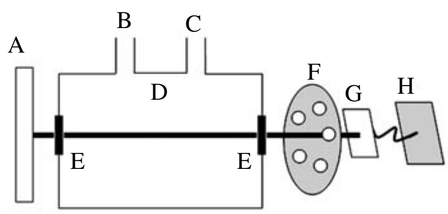
$$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(aq) + H_2O(l).$$
$$E^\ominus_{cell} = +1.23 - (+0.06) = +1.17\ V$$

Since $E^\ominus_{cell}$ is positive, the reaction is energetically feasible under standard conditions.

The more ethanol that is oxidized, the more electrons are produced. Hence, the greater the electrical current produced. A microprocessor measures the electrical current and calculates the blood alcohol concentration (BAC). The instrument is calibrated by using known concentrations of ethanol-air mixtures.

Most hand held breathalysers use fuel cell technology. They have the advantage in being highly sensitive and specific to ethanol and that the BAC reading is not influenced by other substances such as propanone, an organic chemical produced by some diabetics. It will however produce false BAC readings if the person being tested has any liquid ethanol trapped in their mouth, throat or stomach.

Type 3. Breathalyser that Uses Infrared (IR) Spectroscopy



A quartz lamp (IR source),
B breath input,
C breath outlet,
D sample chamber,
E lenses,
F filter wheel,
G photocell,
H microprocessor

Ethanol contains C-O, O-H, C-H, C-C covalent bonds. These absorb different parts of the IR spectrum. The different natural vibrational IR frequencies of these bonds differ from one another but they are in the same range as the frequencies of IR radiation. When ethanol molecules are exposed to a multi-frequency IR beam, each type of vibrating bond will absorb IR energy when the IR frequency and the natural vibrational bond frequency coincide.

A lamp produces a multi-frequency IR beam that passes through the sample chamber and is focused by a lens onto a spinning filter wheel.

The wheel contains filters that correspond to the natural vibrational and bending frequencies of the bonds in ethanol molecules. The IR radiation that passes through each filter is detected by a photocell. The electrical impulse produced is sent to a microprocessor which calculates and displays the BAC. Thus the instrument is specifically looking at the frequencies of the bonds in ethanol and the amount of ethanol is calculated from the amount of IR absorbed.

IR breathalysers, because of their larger size, are unsuitable for portable breath testing but they are extremely accurate and their BAC readings are used as evidence in court cases. They also have the advantage that the breath sample is deep lung air and they can detect the presence of mouth ethanol.

Practice Questions

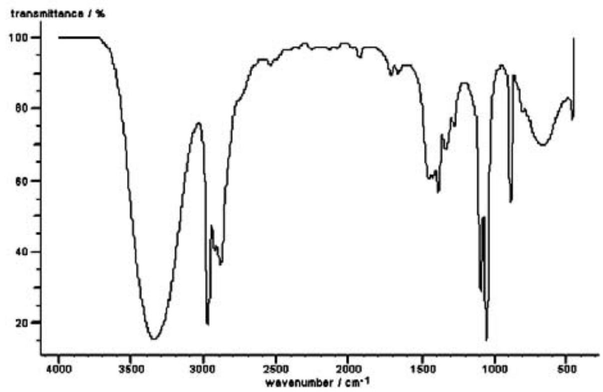
1. A motorist blew through a breathalyser consisting of a tube containing a mixture of sulfuric acid and potassium dichromate on silica gel.
   (a) State the colour change observed when ethanol is detected. [2]
   (b) Write an equation for the oxidation of ethanol to ethanal using [O] to represent the oxidising agent. [2]
   (c) If a suspect's breath contains 120 mg of ethanol per 100 cm^3, calculate the concentration of ethanol in mol dm^{-3}.[3]

2. The ionic equation for the reaction that occurs in a breathalyser using acidified potassium dichromate crystals is:

   $$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

   Write the two half-equations and, in terms of electrons, explain why this is a redox reaction. [5]

3. One type of breathalyser uses infrared spectroscopy to detect the quantity of ethanol vapour in the breath of a motorist at a police station. The infrared spectrum of ethanol liquid is shown below.



   (a) Use a Data Sheet to select two characteristic absorptions on the spectrum and state which bonds are responsible for these absorptions. [2]
   (b) Suggest which one of these absorptions is used for the detection and measurement of ethanol in a person's breath, giving reasons.[3]
   (c) Which organ of the body may be permanently affected by alcohol? [1]

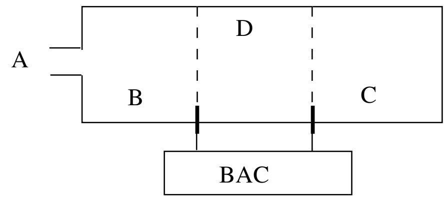
4. The relevant standard redox potentials for a breathalyser using acidified potassium dichromate are:

   1. $CH_3CHO(l) + 2H^+(aq) + 2e^- \rightarrow CH_3CH_2OH(g)$ $E^{\ominus} = -0.20$ V at pH = 7

   2. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E^{\ominus} = +1.33$ V at pH = 0

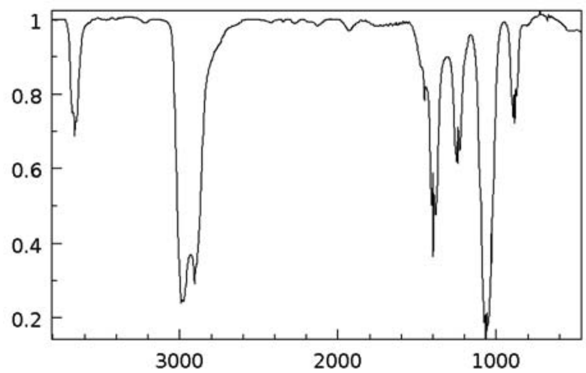
   (a) Write a balanced equation for the oxidation of ethanol to ethanal by acidified dichromate(VI) ions.
   (b) What are the oxidation numbers of chromium and of the carbon atom attached to the oxygen atom at the beginning and end of the reaction. (Assume the oxidation number of the methyl carbon is – 4) [4]
   (c) Use the standard redox potentials to calculate the cell voltage.[1]
   (d) Use Le Chatelier's principle to deduce the effect on the ethanal reduction potential as the pH decreases. [2]
   (e) Use your answer from d) to predict the effect on the cell voltage. Explain why it is very unlikely that the reaction will stop being feasible. [2]

5. The simplified diagram below is of a breathalyser based on an ethanol fuel cell. The motorist blows into the breathalyser through the tube at A.



   (a) Precisely what are B, C and D? [3]
   (b) Write the half-equations that occur at B and C. (Ethanol is converted into ethanoic acid.) [2]
   (c) Indicate on the diagram the flow of electrons and the movement of hydrogen ions. [2]
   (d) Where does oxidation occur and where does reduction occur?[2]

6. The IR spectrum of gaseous ethanol is shown below.



   The ethanol concentration in a person's breath is determined by measuring the intensity of the absorption band at 2950 cm^{-1}. The person's breath also contains water vapour which has several strong IR absorptions including bands at about 3600 cm^{-1} and 3800 cm^{-1}.
   (a) The labelling of the axes of the IR absorption spectrum has been omitted. How should both axes be labelled? [2]
   (b) Compare the positions of the above two bands due to water with those of ethanol in its spectrum above 3000 cm^{-1}. Which bond is responsible for the 2950 cm^{-1} absorption by ethanol and suggest why this 2950 cm^{-1} band is chosen for ethanol detection.[3]
   (c) Explain why ethanol and water both produce IR bands in the same region of spectrum. [1]
   (d) Diabetes sufferers often produce propanone vapour in their breath. Explain why a diabetic could give a positive result during a breath test even though they had not been drinking alcohol. [1]
   (e) Name another analytical technique that may be used to determine the ethanol content of blood. [1]

Answers

1. (a) Orange to green
   (b) $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$,
   (c) $120/46 \times 10^{-3} \times 10 = 0.026$ mol dm^{-3}

2. $CH_3CH_2OH + H_2O - 4e^- \rightarrow CH_3COOH + 4H^+$
   Ethanol is oxidised since electrons are lost.
   $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
   Dichromate is reduced since electrons are gained.
   Since both reduction and oxidation are occurring the reaction is redox.

3. (a) The (broad) absorption with peak at 3335 cm^{-1} is due to the O-H bond and that at 2960 cm^{-1} is due to a C-H bond. (or at 1050 cm^{-1} due to the C-O bond)
   (b) The C-H bond. A person's breath would contain water vapour and this also has an O-H bond. It is unlikely that there will be any other substances apart from ethanol in a person's breath that contain C-H bonds (or C-O bond).
   (c) The liver.

4. (a) See Type 1
   (b) Cr +6 to +3 and C zero to + 2,
   (c) $E^\ominus_{cell} = +1.33 - (-0.20) = +1.53$ V,
   (d) The pH decreases when [H$^+$] increases. Equilibrium 1 moves to the right and since this takes up electrons the redox potential becomes less negative / more positive.
   (e) Since $E^\ominus_{cell}$ is such a large positive value (+ 1.53 V) it is most unlike that the redox potential for ethanol/ethanal will ever exceed + 1.33 V and hence E_{cell} will never become negative to make the reaction not feasible.

5. (a) B: platinum anode. C: platinum cathode. D: (porous) acidic electrolyte.
   (b) At B: $CH_3CH_2OH + H_2O \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
   At C: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
   (c) See Type 2 diagram.
   (d) Oxidation occurs at B (anode) and reduction at C (cathode)

6. (a) Vertical axis: Transmission / %. Horizontal axis: Wavenumber / cm^{-1}.
   (b) Ethanol produces an absorption band at about 3750 cm^{-1} that is between those due to water at 3600 cm^{-1} and 3800 cm^{-1}. The 2950 cm^{-1} is chosen because it does not occur in water (or any other substance likely to be in a person's breath) and it is a strong absorption. The 2950 cm^{-1} band is due to the C-H bond.
   (c) They both have O-H groups.
   (d) Propanone has six C-H bonds and will also produce a strong absorption at about 2950 cm^{-1}.
   (e) e.g. Gas-liquid chromatography or HPLC followed by mass spectrometry.

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