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Candle Calorimetry

A Level

A giant candle of paraffin wax, weighing $1377\,\mathrm{pounds}$ ($1\,\mathrm{pound} = 0.454\,\mathrm{kg}$), was placed in a calorimeter and melted. Paraffin wax is a mixture of different long-chain hydrocarbons and so it does not have well-defined thermodynamic properties, because these depend on the relative proportions of components.

The melting point of wax is between $44\,^{\circ}\mathrm{C}$ and $60\,^{\circ}\mathrm{C}$, with an average of $52\,^{\circ}\mathrm{C}$.

The average heat capacity is $2.5\,\mathrm{J\,K^{-1}\,g^{-1}}$ (between $2.1\,\mathrm{J\,K^{-1}\,g^{-1}}$ and $2.9\,\mathrm{J\,K^{-1}\,g^{-1}}$) and a typical average enthalpy of fusion is $200\,\mathrm{J\,g^{-1}}$.

Part A Energy for heating

Calculate the energy needed to heat the candle from room temperature ($25\,^{\circ}\mathrm{C}$) to its melting point at $52\,^{\circ}\mathrm{C}$, assuming the average values apply exactly for this candle. Give your answer to two significant figures.

Part B Energy for melting

Calculate the heat needed to melt the candle, once it has reached its melting temperature. Again assume the average values apply, and give your answer to 3 significant figures

Used with permission from the Cambridge Chemistry Challenge: C3L6

A Rusty Carillon

A Level

An excavated Chinese ancient bronze musical instrument, carillon, was covered entirely by rust. Chemical analysis showed that the rust contains CuCl, $\mathrm{Cu_2O}$ and $\mathrm{Cu_2(OH)_3Cl}$. Simulation experiments showed that CuCl was formed first under the action of both air and Cl containing aqueous solution and then $\mathrm{Cu_2(OH)_3Cl}$ produced in the following way:

$$\mathrm{Cu} \longrightarrow \mathrm{CuCl} \longrightarrow \mathrm{Cu_2(OH)_3Cl}$$

Rate constants k_c for this reaction were measured at various temperatures in a simulation experiment in order to obtain its kinetic parameters. The results of the experiment are given below.

Temperature / $^\circ\mathrm{C}$	k_c / $\mathrm{mol\,dm^{-3}\,s^{-1}}$
25	1.29×10^{-4}
40	2.50×10^{-4}

Part A Activation energy

Find the value of the activation energy of this reaction.

Adapted from the International Chemistry Olympiad, Beijing 1995, Problem 1.2

Discovering Phosphorus

A Level

White phosphorus is an allotrope of phosphorus which burns very easily. This makes it useful in smoke grenades and in other smoke producing applications.

White phosphorus is burned in a sufficient supply of oxygen to give product X in the unbalanced equation below.

$$\mathrm{P}_{(s)} + \mathrm{O}_{2\,(g)} \longrightarrow \mathrm{X}_{(s)}$$

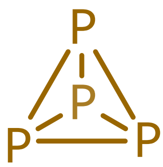

Figure 1: Diagram of the bonding in white phosphorus. The phosphorus atoms are arranged in a tetrahedron.

Part A Empirical formula

In a sample of $22\,\mathrm{g}$ of X, there is $9.6\,\mathrm{g}$ of phosphorus.

The empirical formula for X is of the form $\mathrm{P}_a\mathrm{O}_b$. Type your answer in the form ab, such that if $\mathrm{a} = 3$ and $\mathrm{b} = 2$ the answer would be 32.

Part B Molecular formula

It is found that there is approximately $0.26\,\mathrm{mol}$ of X in $73\,\mathrm{g}$. What is the molecular formula for X?

The molecular formula for X is of the form $\mathrm{P}_a\mathrm{O}_b$. Type your answer in the form ab, such that if $\mathrm{a} = 3$ and $\mathrm{b} = 2$ the answer would be 32.

Part C Enthalpy change of formation

Given that the standard state of P is P_4 (white phosphorus), and using the bond enthalpy data given in the table below, calculate the enthalpy change of formation of compound X?

The enthalpy of vaporisation of P_4 is $51.9\,\mathrm{kJ\,mol^{-1}}$ and that of X is $93.52\,\mathrm{kJ\,mol^{-1}}$.

Bond	**Bond dissociation enthalpy** $/\mathrm{kJmol^{-1}}$
$\mathrm{P{-}P}$	$+201$
$\mathrm{P{-}O}$	$+376$
$\mathrm{P{=}O}$	$+460$
$\mathrm{O{=}O}$	$+495$

Part D Red phosphorus

Figure 3: The structure for Red Phosphorus

Red phosphorus burns less easily in air and is has a less exothermic combustion enthalpy.

Why does red phosphorus have a less exothermic combustion enthalpy than white phosphorus?

- Extra bonds in red phosphorus which need to be broken
- More intermolecular forces which needs to be overcome
- Less bond strain in red phosphorus
- Higher rate constant for red phosphorus burning
- Lower activation energy for white phosphorus burning

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Chlorate Decomposition

A Level

$10\,\mathrm{g}$ of $\mathrm{KClO_3}$ decomposes by the following reaction:

$$2\,\mathrm{KClO_3\,(s)} \longrightarrow 2\,\mathrm{KCl\,(s)} + 3\,\mathrm{O_2\,(g)}$$

Part A Enthalpy change

The enthalpies of formation at $298\,\mathrm{K}$ of the species involved in the reaction are:

$\Delta_\mathsf{f} H^{\circ}(\mathrm{KCl\,(s)}) = -437\,\mathrm{kJ\,mol^{-1}}$

$\Delta_\mathsf{f} H^{\circ}(\mathrm{KClO_3\,(s)}) = -391\,\mathrm{kJ\,mol^{-1}}$

What is the enthalpy change in the reaction of the $10\,\mathrm{g}$ of potassium chlorate above, to appropriate precision?

Part B Final volume

The pressure, temperature and volume of a number of moles of gas are related by the ideal gas law, $pV = nRT$.

The reaction above takes place in a constant pressure calorimeter with an initial volume of $1.0\,\mathrm{dm^3}$ air at atmospheric pressure.

If the heat evolved by the reaction is used to heat up the products and the calorimeter and the air it contains, from a starting temperature of $298\,\mathrm{K}$, what will be the final volume of the enclosed gases?

The constant pressure molar heat capacity of oxygen is $\frac{7}{2}R$. The heat capacity of the calorimeter is $50.0\,\mathrm{J\,K^{-1}}$ and the molar heat capacity of KCl is $51.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

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Baffling Benzene

A Level

Substance	$\Delta H^{\circ}\,(\text{combustion})\,/\,\text{kJ mol}^{-1}$
Benzene	-3268
Cyclohexane	-3920
Cyclohexene	-3754
Hydrogen	-286

Part A Hydrogenation of cyclohexene

Calculate the enthalpy change of hydrogenation of cyclohexene using the data in the table.

Part B Hydrogenation of benzene

Calculate the enthalpy change of hydrogenation of benzene, assuming it is hydrogenated all the way to cyclohexane.

Part C Predicted ratio

Using the Kekule structure for Benzene, what is the predicted ratio of the hydrogenation enthalpy for benzene to that for cyclohexene?

- 0.50
- 3
- 2
- 0.33
- 1

Adapted with permission from UCLES, A Level Chemistry, June 1989, Paper 1, Question 2.

Fireworks!

A Level

C C C

Alongside being used in weaponry, gunpowder is also the most important component of fireworks.

It is a mixture of an oxidizing agent, KNO_3 and fuel, C and S. The most effective ratio of potassium nitrate to carbon to sulfur is $75 : 15 : 10$ by mass (not the stoichiometric ratio for the reaction below).

The reaction between these components forms a mixture of products, the most important being the gaseous ones, N_2 and CO_2. Assume these can be treated as ideal gases. One simplified form of the reaction can be written as:

$$10\,KNO_3 + 8\,C + 3\,S \longrightarrow 2\,K_2CO_3 + 3\,K_2SO_4 + 6\,CO_2 + 5\,N_2$$

Part A Limiting reagent

Assuming this is the only reaction that takes place, what is the limiting reagent in gunpowder?

- C
- S
- KNO_3

Part B Pressure reached

This reaction can heat up to temperatures as high as $1000\,^\circ C$. How high would the pressure in a firework container (cylinder of diameter $d = 7.0\,cm$ and height $h = 50\,cm$) with $100\,g$ of gunpowder become, if it did not explode?

Glass Calorimeter

A Level

C C C

$500\,\mathrm{g}$ of ice at $-20\,^{\circ}\mathrm{C}$ is placed in a glass calorimeter (which is at the same temperature as the ice) of mass of $1.2\,\mathrm{kg}$. The whole system (including the calorimeter) is heated up to $20\,^{\circ}\mathrm{C}$.

The specific heat capacity of ice is $2.1\,\mathrm{J\,K^{-1}\,g^{-1}}$, while that of water is $4.2\,\mathrm{J\,K^{-1}\,g^{-1}}$. The enthalpy of fusion of water is $335\,\mathrm{J\,g^{-1}}$.

The molar heat capacity of $\mathrm{SiO_2}$ is $42\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Part A Moles of glass

The molar mass of silicon, Si, is $28\,\mathrm{g\,mol^{-1}}$ and the molar mass of oxygen, O, is $16\,\mathrm{g\,mol^{-1}}$.

Assuming the glass is made out of pure silicon dioxide, how many moles of $\mathrm{SiO_2}$ are there in the calorimeter? Give your answer to 2 significant figures.

Part B Energy input

How much energy is necessary for the heating to occur? Give your answer to 2 significant figures.

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Temperature Variation

A Level

Two substances, X and Y, react in an inert solvent according to the following equation:

$$\mathrm{X} + 2\,\mathrm{Y} \longrightarrow \mathrm{XY_2}.$$

The following experiments were run to determine the order of the reaction between X and Y, at $20\,^{\circ}\mathrm{C}$.

Experiment number	**Initial concentration of** $\mathrm{X/mol\,dm^{-3}}$	**Initial concentration of** $\mathrm{Y/mol\,dm^{-3}}$	**Initial rate of formation of** $\mathrm{XY_2/mol\,dm^{-3}\,min^{-1}}$
1	0.10	0.10	0.0010
2	0.10	0.20	0.0040
3	0.10	0.30	0.0090
4	0.15	0.10	0.0010
5	0.20	0.20	$?$

Part A Order of the reaction

What is the order of the reaction with respect to X and Y, respectively?

- 2; 1
- -1; -1
- 1; 0
- 1; 2
- 0; 2
- 0; 1

Part B Rate constant

Calculate the numerical value for the rate constant k.

Part C Initial rate of experiment 5

Predict the rate of formation of $\mathrm{XY_2}$ in experiment 5.

Part D Greatest reaction rate

The rate constant has an Arrhenius dependence on temperature. Knowing that the activation energy for the reaction is $53\,\mathrm{kJ\,mol^{-1}}$, which of the following sets of conditions will give the greatest rate of reaction?

- $[X] = 0.1\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.2\,\mathrm{mol\,dm^{-3}}$, $T = 40\,°\mathrm{C}$.
- $[X] = 0.1\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.3\,\mathrm{mol\,dm^{-3}}$, $T = 30\,°\mathrm{C}$.
- $[X] = 0.2\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.2\,\mathrm{mol\,dm^{-3}}$, $T = 30\,°\mathrm{C}$.
- $[X] = 0.3\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.1\,\mathrm{mol\,dm^{-3}}$, $T = 30\,°\mathrm{C}$.
- $[X] = 0.3\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.1\,\mathrm{mol\,dm^{-3}}$, $T = 20\,°\mathrm{C}$.

Adapted with permission from UCLES, A Level Chemistry, June 1988, Paper 3, Question 12 and A Level Chemistry, June 1986, Paper 2, Question 2.

Ceriously Cringeworthy

A Level

Cr and Ce undergo the following redox reaction:

$$\mathrm{Cr(III)} + 3\,\mathrm{Ce(IV)} \longrightarrow \mathrm{Cr(VI)} + 3\,\mathrm{Ce(III)}$$

The rate of this reaction varies as follows:

$[\mathrm{Cr(III)}]$ $/\mathrm{mol\,dm^{-3}}$	$[\mathrm{Ce(IV)}]$ $/\mathrm{mol\,dm^{-3}}$	$[\mathrm{Cr(VI)}]$ $/\mathrm{mol\,dm^{-3}}$	$[\mathrm{Ce(III)}]$ $/\mathrm{mol\,dm^{-3}}$	Rate $/\mathrm{mol\,dm^{-3}\,s^{-1}}$
0.050	0.020	0.040	0.025	1.0×10^{-6}
0.100	0.020	0.040	0.025	2.0×10^{-6}
0.050	0.040	0.040	0.025	4.0×10^{-6}
0.050	0.020	0.020	0.025	1.0×10^{-6}
0.050	0.020	0.020	0.050	5.0×10^{-7}

Part A Partial reaction orders

What are the partial reaction orders with respect to $\mathrm{Cr(III)}$, $\mathrm{Ce(IV)}$, $\mathrm{Cr(VI)}$ and $\mathrm{Ce(III)}$?

- $1,\ 3,\ -1,\ -3$
- $1,\ 2,\ 0,\ 0$
- $1,\ 3,\ 0,\ 0$
- $1,\ 1,\ 0,\ 0$
- $1,\ 2,\ 0,\ -1$

Part B Overall order of reaction

What is the overall reaction order?

Part C Rate constant

Calculate the rate constant for the reaction.

Adapted with permission from Oxford and Cambridge School Examination Board, Chemistry, June 1989, Question 4