Energy changes

Question Paper

Level	Pre U
Subject	Chemistry
Exam Board	Cambridge International Examinations
Topic	Energy changes- Physical Chemistry
Booklet	Question Paper

Time Allowed: **58 minutes**

Score: **/48**

Percentage: **/100**

Grade Boundaries:

1. *Aerozine 50* is a 50/50 mix of hydrazine, N_2H_4, and UDMH, $(CH_3)_2N_2H_2$. It is used as a rocket fuel, typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction of the UDMH with dinitrogen tetroxide is given in equation 2.1 and relevant thermodynamic data is in Table 2.1.

equation 2.1 $(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \rightarrow 2CO_2(g) + 4H_2O(g) + 3N_2(g)$

Table 2.1

substance	$\Delta_f H^{\ominus}(298\,K)\,/\,kJ\,mol^{-1}$	$S^{\ominus}(298\,K)\,/\,J\,K^{-1}\,mol^{-1}$
$(CH_3)_2N_2H_2(l)$	83.3	304.7
$N_2O_4(l)$	9.1	304.4
$CO_2(g)$	–393.5	213.8
$H_2O(g)$	–241.8	188.8
$N_2(g)$	0.0	191.6

(a) Suggest an equation for the reaction between hydrazine, N_2H_4, and dinitrogen tetroxide, N_2O_4.

.... [1]

(b) Define the term *standard enthalpy change of formation*.

....

.... [2]

(c) **(i)** Calculate the enthalpy change, $\Delta_r H^{\ominus}(298\,K)$, for the reaction in equation 2.1, giving your answer to one decimal place.

$\Delta_r H^{\ominus}(298\,K)$ .... $kJ\,mol^{-1}$ [3]

(ii) The entropy change, $\Delta_r S^{\ominus}(298\,K)$, for the reaction in equation 2.1 is $+844.1\,J\,K^{-1}\,mol^{-1}$.

Explain, without calculation, why this entropy change has such a large, positive value.

....

....

.... [2]

(iii) Calculate the free energy change, $\Delta_r G^{\ominus}(298\,K)$, for the reaction in equation 2.1, giving your answer to one decimal place.

$\Delta_r G^{\ominus}(298\,K)$ .... $kJ\,mol^{-1}$ [2]

(d) Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4, together) used in the thruster rockets in the ascent stage of a lunar module was 244 kg.

Assume that the UDMH and dinitrogen tetroxide were mixed in the molar ratio 1:2.

(i) Calculate the mass of UDMH in the propellant mixture.

mass of UDMH = ... kg [1]

(ii) Calculate the total number of moles of gas produced from the complete reaction of this mass of UDMH with dinitrogen tetroxide, as in equation 2.1.

moles of gas = ... [2]

(iii) Calculate the total volume of product gases formed from the reaction of this mass of UDMH with dinitrogen tetroxide, as in equation 2.1, at a temperature of –10.0 °C and a pressure of 600 Pa.

Give your answer to three significant figures and **include the units**.

volume of gas = ... [3]

(e) Dinitrogen tetroxide, N_2O_4, exists in equilibrium with nitrogen dioxide, NO_2, which itself can be decomposed into nitrogen monoxide, NO, and oxygen, as shown in equation 2.2.

equation 2.2 $$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

The rate equation for this thermal decomposition is as follows.

$$\text{rate} = k[NO_2]^2$$

The rate constant, *k*, for the thermal decomposition of nitrogen dioxide was measured at five different temperatures and the results were used to plot the graph in Fig. 2.1.

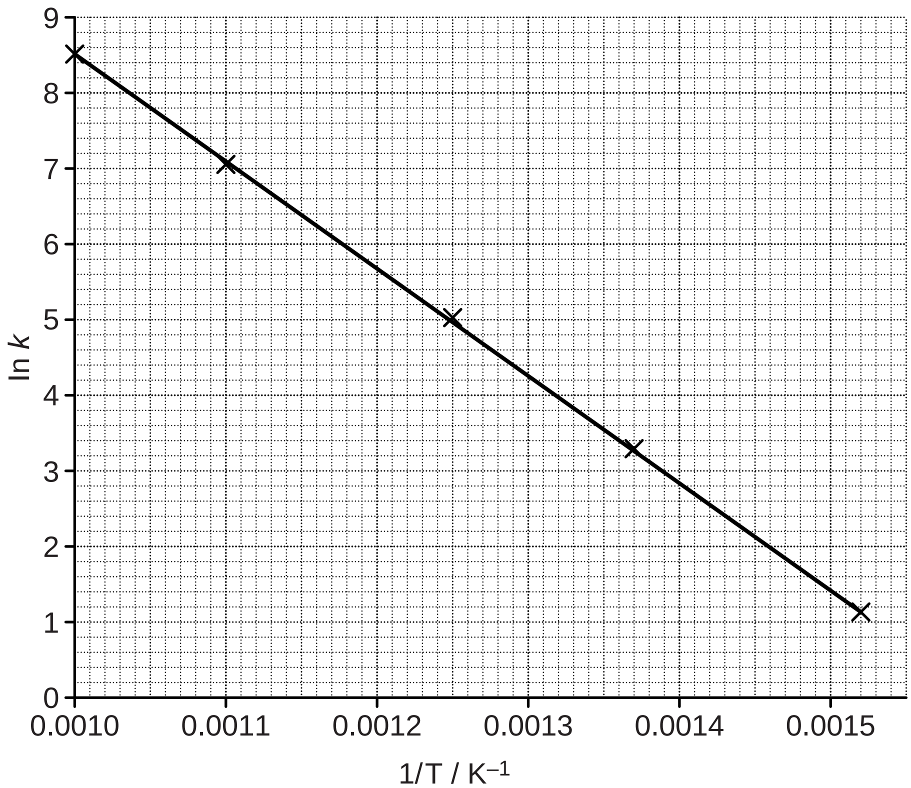


Fig. 2.1

(i) Equation 7 in the data booklet can be rewritten in the form $y = mx + c$, as follows.

$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$

Use the graph to calculate the activation energy, E_a, for the reaction in equation 2.2.

E_a = ... kJ mol^{-1} [2]

(ii) A vessel with a volume of 2.00 dm^3 is filled with 4.00 mol of NO_2 at a temperature of 650 K.

The rate constant, *k*, at this temperature is 3.16 $dm^3\,mol^{-1}\,s^{-1}$.

Calculate the initial rate of decomposition at this temperature for the reaction in equation 2.2 and **include the units**.

initial rate = ... [2]

(iii) A mechanism suggested for the thermal decomposition of nitrogen dioxide is shown.

step one $NO_2 + NO_2 \rightarrow NO + NO_3$ *slow*

step two $NO_3 \rightarrow NO + O_2$ *fast*

Explain whether or not this mechanism is consistent with the rate equation given.

....

....

.... [1]

[Total: 21]

2. The light blue colour of aqueous copper(II) sulfate is due to the presence of the hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}(aq)$.

Equations 4.1 and 4.2 show two different partial ligand substitution reactions of the hexaaquacopper(II) ion. In equation 4.1 'en' represents 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$.

equation 4.1 $[Cu(H_2O)_6]^{2+}(aq) + en(aq) \longrightarrow [Cu(en)(H_2O)_4]^{2+}(aq) + 2H_2O(l)$

$\Delta_r H^{\ominus} = -54\ kJ\ mol^{-1}$;

$\Delta_r S^{\ominus} = +23\ J\ K^{-1}\ mol^{-1}$

equation 4.2 $[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \longrightarrow [Cu(NH_3)_2(H_2O)_4]^{2+}(aq) + 2H_2O(l)$

$\Delta_r H^{\ominus} = -46\ kJ\ mol^{-1}$;

$\Delta_r S^{\ominus} = -8.4\ J\ K^{-1}\ mol^{-1}$

(a) Explain why the enthalpy changes, $\Delta_r H^{\ominus}$, of the reactions shown in equations 4.1 and 4.2 are so similar.

....

....

....

.... [2]

(b) Comment on the values of the entropy changes, $\Delta_r S^{\ominus}$, of the reactions shown in equations 4.1 and 4.2 and explain why they are different.

....

....

....

.... [2]

(c) The cation produced in the reaction shown in equation 4.2 can exist as two different isomers.

(i) State the type of isomerism exhibited by this cation.

.... [1]

(ii) Draw and label the two different isomers of this cation.

[2]

(d) Further ligand substitution leads to the production of the complex ion $[Cu(en)_3]^{2+}$, which also exhibits isomerism.

(i) State the type of isomerism exhibited by $[Cu(en)_3]^{2+}$.

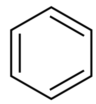
.... [1]

(ii) Draw 3-D representations of the two isomers of $[Cu(en)_3]^{2+}$.

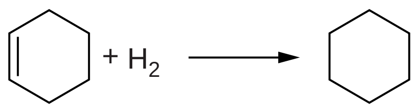
[2]

[Total: 10]

3. Kekulé proposed the following structure for benzene.



(a) The enthalpy of hydrogenation of cyclohexene, as shown, is $-121\,kJ\,mol^{-1}$.



Based on this value for cyclohexene it is possible to calculate that the enthalpy of hydrogenation of benzene, based on Kekulé's structure, should be $-363\,kJ\,mol^{-1}$.

Explain the difference between this calculated value and the actual value for the enthalpy of hydrogenation of benzene of $-209\,kJ\,mol^{-1}$.

....

....

....

.... [2]

(b) Benzene undergoes electrophilic substitution reactions.

(i) What is meant by the term *electrophile*?

....

.... [1]

(ii) Nitrobenzene, $C_6H_5NO_2$, can be formed from benzene. Give the reagents and conditions necessary for this process and identify the electrophile.

reagents ....

conditions ....

electrophile .... [3]

(c) Fig. 5.1 shows a reaction sequence starting from nitrobenzene.

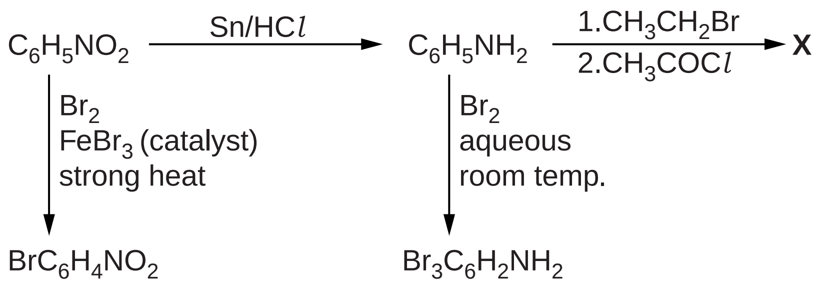


Fig. 5.1

(i) Explain why the bromination of phenylamine, $C_6H_5NH_2$, is possible with the mild conditions shown in Fig. 5.1.

....

....

....

....

....

.... [3]

(ii) Give the equation for the reaction between nitrobenzene and the reducing mixture, Sn/HC*l*. You should use [H] to represent the reducing agent in your equation.

.... [1]

(d) **(i)** Compound **X**, in Fig. 5.1, has the composition by mass:

carbon, 73.59%; hydrogen, 8.03%; nitrogen, 8.58%; oxygen, 9.80%.

It has a relative molecular mass of 163.

Calculate the molecular formula of **X**.

[3]

(ii) The ^{1}H NMR of **X** has a complex signal between 7.00 ppm and 7.55 ppm because of the five protons on its benzene ring, and three other signals as partly detailed in Table 5.1.

Table 5.1

δ / ppm	integration ratio	splitting pattern
1.12	3	
1.83		singlet
3.75	2	

Complete Table 5.1, give the structure of **X**, and explain the origin of the ^{1}H NMR signals.

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....[4]

[Total: 17]