Past-paper walk-through

Bond Enthalpies ▪ 6.7

eXercise

Questions in this set

- 2019 Q2
- 2017 Q2

Reading the mark scheme

- **B1** a mark that stands on its own – the point is either made or not.
- **M1** a *method* mark: the right approach, even if the number is wrong.
- **A1** an *answer* mark, and it usually needs its M mark first.
- **C1** a working mark on the way to the answer.
- // separates answers the examiner accepts equally.
- **ecf** = error carried forward: a later part is marked on your own earlier answer.
- **owtte** = "or words to that effect" – the wording need not match.

Question 2

2019 ▪ Q2

Answer the following questions relating to the chemistry of the halogens.
(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

$$Br_2 \qquad Cl_2 \qquad F_2 \qquad I_2$$

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: $NaBr(aq)$, $Cl_2(g)$, and $I_2(s)$.
| Half-Reaction | E° at 25°C (V) | |—|—| | $Br_2 + 2\,e^- \rightarrow 2\,Br^-$ | 1.07 | | $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$ | 1.36 | | $I_2 + 2\,e^- \rightarrow 2\,I^-$ | 0.53 |

Question 2

Half-Reaction	$E°$ at 25°C (V)
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$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	0.53

Question 2

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

Question 2

2019 ▪ Q2

Answer the following questions relating to the chemistry of the halogens.

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of E° for the reaction.

Br_2 and Cl_2 can react to form the compound BrCl.

Question 2

2019 ▪ Q2

Answer the following questions relating to the chemistry of the halogens.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of each substance.

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\,\mathrm{BrCl}(g) \rightleftharpoons \mathrm{Br_2}(g) + \mathrm{Cl_2}(g) \qquad \Delta H^\circ = 1.6\ \mathrm{kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $\mathrm{BrCl}(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

Question 2

2019 ▪ Q2

Answer the following questions relating to the chemistry of the halogens.

(d) Calculate the pressure in the container before equilibrium is established.

Question 2

2019 ▪ Q2

Answer the following questions relating to the chemistry of the halogens.

(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

Question 2

2019 ▪ Q2

Answer the following questions relating to the chemistry of the halogens.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.

Question 2

2019 ▪ Q2

Answer the following questions relating to the chemistry of the halogens.

(g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using ΔH° for the reaction (1.6 kJ/mol_{rxn}) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

Solution 2

(a)

Mark scheme

- I2 (circled). I2 has the longest bond length because the atomic radius of I is greater than the radii of the other halogen atoms (Br, Cl, F), so the internuclear distance between the two bonded I atoms is greater than in the other diatomic halogens. 1 point for circling I2 with a valid atomic-structure justification.

Solution 2

(b)

Mark scheme

- Balanced equation ($Cl2$ is a strong enough oxidizer to oxidize Br since E°(Cl2/Cl)=1.36 V > E°(Br2/Br)=1.07 V, whereas I2 cannot): 2 Br (aq) + Cl2(g) $\rightarrow$ Br2 + 2 Cl (aq). 1 point for the correct balanced equation. $E^\circ =$ E°(reduced species) $-$ E°(oxidized species) $= 1.36$ V $- 1.07$ V $= +0.29$ V; a positive E° confirms the reaction is thermodynamically favorable. 1 point for the correct E° calculation.

Solution 2

(c)

Mark scheme

- Br2(l) has only London dispersion forces between its nonpolar molecules. BrCl(l) is polar, so it has both London forces and dipole-dipole forces. 1 point for correctly identifying the IMFs present in each substance. However, Br2 has a larger, more polarizable electron cloud than BrCl, so the London forces in Br2(l) are stronger than the combined (London + dipole-dipole) forces in BrCl(l); this is why Br2's boiling point (332 K) is higher than BrCl's (278 K) despite BrCl being polar. 1 point for this valid explanation invoking polarizability.

Solution 2

(d)

Mark scheme

- $P = nRT/V = (0.100\ \text{mol})(0.08206\ \text{L} \cdot \text{atm} \cdot \text{mol}^{\ 1} \cdot \text{K}^{\ 1})(298\ \text{K})\ /\ (2.00\ \text{L}) = 1.22\ \text{atm}$. 1 point for the correct pressure with consistent units.

Solution 2

(e)

Mark scheme

- Keq = $[Br2][Cl2]$ / $[BrCl]^2$ (equivalently, in terms of partial pressures: Keq = $P(Br2) \cdot P(Cl2) / P(BrCl)^2$). 1 point for a correct equilibrium expression.

Solution 2

(f)

Mark scheme

- ICE table (partial pressures, atm) for 2 BrCl(g)   Br2(g) + Cl2(g): Initial 1.22, 0, 0; Change $-2x$, $+x$, $+x$; Equilibrium 0.71, 0.26, 0.26. Since 42% of BrCl decomposed, P(BrCl decomposed) = (0.42)(1.22 atm) = 0.51 atm = 2x, so x = 0.26 atm. 1 point for the correct stoichiometric (ICE) values at equilibrium. Keq = $(0.26)(0.26)/(0.71)^2 = 0.13$. 1 point for a Keq value consistent with the student's ICE table (a molar-concentration-based solution also earns full credit).

Solution 2

(g)

Mark scheme

- $\Delta H^\circ = \Sigma$(bond energies)broken $- \Sigma$(bond energies)formed. 1.6 kJ/mol $=$ 2(Br—Cl bond energy) $-$ (193 kJ/mol $+$ 243 kJ/mol); (436 $+$ 1.6) kJ/mol $=$ 2(Br—Cl bond energy); Br—Cl bond energy $=$ 219 kJ/mol. 1 point for the correct calculation.

Question 2

2017 ▪ Q2

Answer the following questions about the isomers fulminic acid and isocyanic acid.
Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.
[Two Lewis structures side by side: Left: H–C N–Ö: (H bonded to C by a single bond, C triple-bonded to N, N bonded to O by a single bond, O has two lone pairs) Right: H–C̈=N=Ö: (H bonded to C by a single bond, C double-bonded to N, N double-bonded to O, C has one lone pair, O has two lone pairs)]
Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftharpoons HNCO(g)$$

fulminic acid   *isocyanic acid*

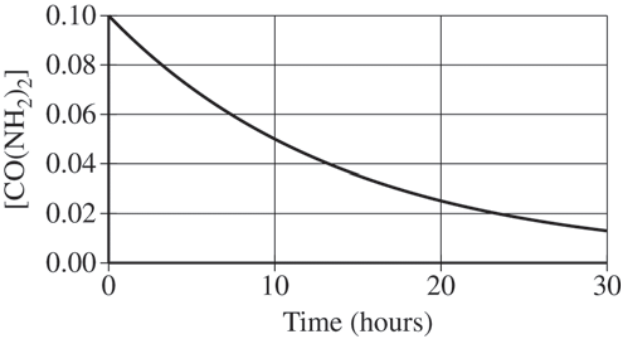
Question 2

| Fulminic Acid | Isocyanic Acid | |—|—| | H–C N–Ö: (O has two lone pairs) | H–N̈=C=Ö: (N has one lone pair, O has two lone pairs) |

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Question 2

Time (hours)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



Question 2

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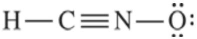	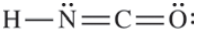

Question 2

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N−O	201	C=N	615	H−C	413
C=O	745	C≡N	891	H−N	391

Question 2

2017 ▪ Q2

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Question 2

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of HCNO(g) to form HNCO(g).

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2017 ▪ Q2

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Question 2

(c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.

Question 2

2017 ▪ Q2

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Question 2

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

Question 2

2017 ▪ Q2

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Question 2

(e)(i) The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftharpoons NH_4^+(aq) + OCN^-(aq)$$

A student studying the decomposition reaction runs the reaction at $90°C$. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125

[Graph: y-axis $[CO(NH_2)_2]$ from 0.00 to 0.10 in increments of 0.02; x-axis "Time (hours)" from 0 to 30; a smooth exponential-decay curve starting at $(0, 0.10)$ and decreasing to approximately $(30, 0.0125)$, consistent with the data table above.]

Question 2

The student proposes that the rate law is $\textit{rate} = k[CO(NH_2)_2]$.
Explain how the data support the student's proposed rate law.
(e)(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

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2017 ▪ Q2

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Question 2

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^{-}(aq)$.

Solution 2

(a)

Mark scheme

- In the left diagram (H-C triple-bond N-O: with O having 3 lone pairs... i.e. H-C#N-O:), the C atom has a formal charge of 0 and the O atom has a formal charge of -1. In the right diagram (H-C(double bond)N(double bond)O:), the C atom has a formal charge of -1 and the O atom has a formal charge of 0. The diagram on the left is the better representation because it puts the negative formal charge on oxygen, which is more electronegative than carbon. 1 point earned for a correct assignment of formal charges in the two diagrams; 1 point earned for a correct explanation.

Solution 2

(b)

Mark scheme

- Sum bond enthalpies from each Lewis structure. HCNO (bonds broken): H-C (413) + C#N triple bond (891) + N-O (201) = 1505 kJ/mol. HNCO (bonds formed): H-N (391) + C=N (615) + C=O (745) = 1751 kJ/mol. delta H (standard) = sum(enthalpies of bonds broken) - sum(enthalpies of bonds formed) = 1505 kJ/mol - 1751 kJ/mol = -246 kJ/mol_rxn. 1 point earned for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken; 1 point earned for the correct determination of delta H (standard).

Solution 2

(c)

Mark scheme

- The change from fulminic acid to isocyanic acid is a rearrangement of atoms (isomerization) with no change in phase and no change in the number of molecules, so there is essentially no change in the number of accessible microstates and delta S (standard) is close to zero. 1 point earned for a correct explanation.

Solution 2

(d) Mark scheme

- Isocyanic acid (HNCO) is present in higher concentration at equilibrium. Delta G (standard) is essentially equal to delta H (standard) because delta S (standard) is essentially zero, so delta G (standard) is approximately -246 kJ/mol_rxn, indicating the forward reaction (HCNO -> HNCO) is thermodynamically favorable. Since delta G (standard) is negative, K > 1 (delta G standard = -RT ln K), resulting in a higher equilibrium concentration of product (HNCO) than reactant (HCNO). 1 point earned for the correct choice WITH a valid justification (calculation of delta G standard is sufficient justification); 1 point earned for correctly connecting thermodynamic favorability to the equilibrium constant K.

Solution 2

(e)(i)

Mark scheme

- From inspecting the data table or the graph, the decomposition reaction has a constant half-life (the urea concentration approximately halves every 10 hours: 0.1000 to 0.0500 over the first 10 h, 0.0500 to 0.0250 over the next 10 h, etc.), which indicates the reaction is first order. 1 point earned for a correct explanation.

Solution 2

(e)(ii)

Mark scheme

- Since the reaction is first order: k = 0.693 / t(1/2) = 0.693 / 10. h = 0.069 h^-1 (equivalently k = (ln[A]0 - ln[A]t)/t = (ln 0.1000 - ln 0.0500) / 10. h = 0.069 h^-1). 1 point earned for the correct value of k with correct units.

Solution 2

(f)

Mark scheme

- Perform the experiment again starting at a different initial concentration of OH-(aq) (changing only [OH-], holding other variables such as temperature and initial urea concentration constant), and measure how the concentration of CO(NH2)2 changes over time; compare the resulting rate/rate constant to that obtained at pH 13. 1 point earned for the description of a valid experiment (correct changed initial condition and data to be gathered).