

Past-paper walk-through

Absolute Entropy and Entropy Change ■ 9.2

eXercise

Questions in this set

- 2025 Q3
- 2022 Q2
- 2021 Q2
- 2019 Q1
- 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 3

2025 ■ Q3

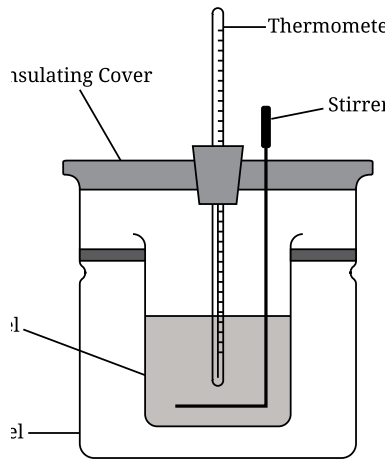
White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

[Left: a ball-and-stick tetrahedral structure of P_4 , showing four P atoms (spheres) at the vertices of a tetrahedron connected by bonds (sticks).]

[Right: an incomplete Lewis diagram showing four P atoms arranged in a tetrahedral projection (one P at top, one P in the middle/front, two P at the bottom left and right), connected by single bonds forming the P_4 skeleton, with no lone pairs drawn yet.]

(a) In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.

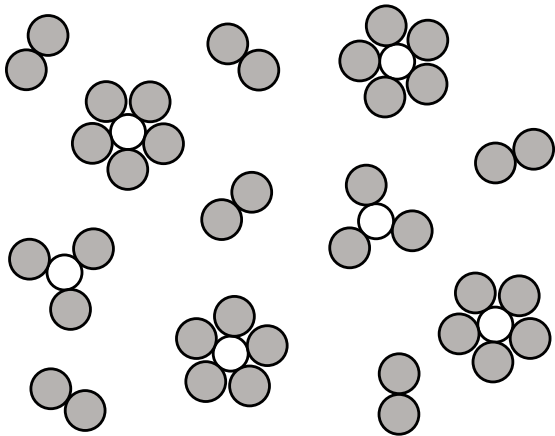
Question 3



Question 3

Mass of P_4O_{10}	0.100 g
Mass of H_2O	100.0 g
Initial temperature	22.00° C
Final temperature	22.38° C
Molar mass of P_4O_{10}	283.9 g/mol
Specific heat of H_2O	4.18 J/(g·°C)

Question 3



Question 3

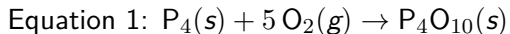
2025 ■ Q3

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(b) The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.



Question 3

(b)(i) The entropy change of the reaction, ΔS° , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

(b)(ii) The enthalpy change of the reaction, ΔH° , is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not** by entropy. Is the student's claim correct? Justify your answer by using the relationship between ΔG° , ΔH° , and ΔS° .

Question 3

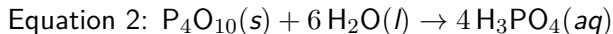
2025 ■ Q3

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(c) $P_4O_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.



Question 3

A chemist uses a calorimetry experiment to determine the enthalpy change for the reaction, as represented by the following diagram.

[Calorimeter diagram: a coffee-cup-style calorimeter labeled "Thermometer" (inserted through the insulating cover), "Stirrer" (inserted alongside the thermometer), "Insulating Cover" (the lid), "Inner Vessel" (the cup holding the solution, shaded), and "Outer Vessel" (the outer supporting cup).]

The chemist carries out the calorimetry experiment and records the following information.

Quantity	Value	—	—	Mass of P_4O_{10}	0.100 g	Mass of H_2O	100.0 g
Initial temperature	22.00°C	Final temperature	22.38°C	Molar mass of P_4O_{10}	283.9 g/mol	Specific heat of H_2O	4.18 J/(g · °C)

(c)(i) Calculate the amount of heat, q , released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.

Question 3

(c)(ii) Calculate the value of $\Delta H_{\text{rxn}}^{\circ}$ for equation 2 in $\text{kJ/mol}_{\text{rxn}}$. Include the sign in your answer.

Question 3

2025 ■ Q3

White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

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[Right: an incomplete Lewis diagram showing four P atoms arranged in a tetrahedral projection (one P at top, one P in the middle/front, two P at the bottom left and right), connected by single bonds forming the P_4 skeleton, with no lone pairs drawn yet.]

(d) The chemist weighed out 0.100 g P_4O_{10} of and 100.0 g of H_2O to perform a second trial. In the second trial, some of the solid P_4O_{10} stuck to the weighing paper and was not transferred to the calorimeter. Given that P_4O_{10} is the limiting reactant,

Question 3

would ΔT for the second trial be greater than, less than, or equal to the value in the first trial? Justify your answer.

$\text{P}_4(\text{s})$ also reacts readily with $\text{Cl}_2(\text{g})$ to produce phosphorus trichloride, $\text{PCl}_3(\text{g})$, which in turn reacts with $\text{Cl}_2(\text{g})$ in an equilibrium process to produce $\text{PCl}_5(\text{g})$. The reactions are represented by equations 3 and 4.



Question 3

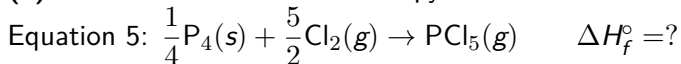
2025 ■ Q3

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(e) Calculate the standard enthalpy of formation of $PCl_5(g)$ represented by equation 5.



The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.

Question 3

[Particle diagram: a box containing multiple particles at random positions representing an equilibrium mixture; a key indicates two-atom particles (grey-grey) = Cl_2 , four-atom tetrahedral-looking particles (grey with three white) = PCl_3 , and six-atom particles (grey with five white) = PCl_5 . The box shows several Cl_2 particles (pairs of grey circles), several PCl_3 particles (grey center with three white circles), and several PCl_5 particles (grey center with five white circles) scattered throughout.]

Question 3

2025 ■ Q3

White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

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(f) Equation 4 for the reaction that occurs is shown.



(f)(i) If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?

Question 3

(f)(ii) Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2° .

Solution 3

(a)

Mark scheme

- Complete Lewis diagram for P_4 : the four P atoms form a tetrahedron, each bonded to the other three P atoms by single bonds, and each P atom bears one lone (nonbonding) pair of electrons — giving each P three bonding pairs plus one lone pair, satisfying the octet rule.

Solution 3

(b)

Mark scheme

- No separate response required — this is the context/stem presenting equation 1 ($\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$), thermodynamically favorable at 298 K, that parts (i) and (ii) below refer to.

(b)(i)

Mark scheme

- Because gas particles are more dispersed (have more accessible microstates) than solids, the entropy decreases as the reactants (which include a gas, O_2) convert into the solid product (P_4O_{10}).

Solution 3

(b)(ii)

Mark scheme

- Yes, the student's claim is correct. Given $\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$, the reaction must have $\Delta G_{rxn}^{\circ} < 0$ to be favorable. Because the reaction is exothermic, $\Delta H_{rxn}^{\circ} < 0$ and enthalpy contributes to favorability. $\Delta S_{rxn}^{\circ} < 0$, so entropy does NOT contribute to favorability — i.e., enthalpy alone drives it.

Solution 3

(c)

Mark scheme

- No separate response required — this is the context/stem describing the calorimetry experiment for the exothermic reaction of $\text{P}_4\text{O}_{10}(\text{s})$ with water (equation 2: $\text{P}_4\text{O}_{10}(\text{s}) + 6 \text{H}_2\text{O}(\text{l}) \rightarrow 4 \text{H}_3\text{PO}_4(\text{aq})$) that parts (i) and (ii) below use.

Solution 3

(c)(i)

Mark scheme

- $q = mc\Delta T = (100.1 \text{ g})(4.18 \text{ J/(g}\cdot^{\circ}\text{C)})(22.38^{\circ}\text{C} - 22.00^{\circ}\text{C}) = 160 \text{ J} = 0.16 \text{ kJ}$
(reported to the correct number of significant figures).

Solution 3

(c)(ii)

Mark scheme

$$\blacksquare q_{rxn} = -q_{surr} = -0.16 \text{ kJ.}$$

$$\Delta H_{rxn}^{\circ} = \frac{-0.16 \text{ kJ}}{0.100 \text{ g P}_4\text{O}_{10}} \times \frac{283.9 \text{ g P}_4\text{O}_{10}}{1 \text{ mol P}_4\text{O}_{10}} \times \frac{1 \text{ mol P}_4\text{O}_{10}}{1 \text{ mol}_{rxn}} = -450 \text{ kJ/mol}_{rxn}.$$

The correct (negative) sign must be included.

Solution 3

(d)

Mark scheme

- Less than. If less P_4O_{10} is present (some stuck to the weighing paper), less thermal energy will be transferred to the water during the reaction, causing the temperature increase (ΔT) to be less than it was with the full 0.100 g of P_4O_{10} .

Solution 3

(e)

Mark scheme

- Using Hess's law:

$$\Delta H_{f,\text{PCl}_5(g)}^\circ = \frac{1}{4}\Delta H_1^\circ + \Delta H_2^\circ = \frac{1}{4}(-1148) + (-88) = -375 \text{ kJ/mol.}$$

Solution 3

(f)

Mark scheme

- No separate response required — this is the context/stem presenting equation 4 ($\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$, $\Delta H_2^\circ = -88 \text{ kJ/mol}_{\text{rxn}}$) that parts (i) and (ii) below refer to.

Solution 3

(f)(i)

Mark scheme

- Reading partial pressures of 1.00 atm per particle from the diagram (4 PCl_5 , 2 PCl_3 , 6 Cl_2 particles): $K_p = \frac{P_{\text{PCl}_5}}{(P_{\text{PCl}_3})(P_{\text{Cl}_2})} = \frac{4.00}{(2.00)(6.00)} = \frac{1}{3} = 0.333$.

Solution 3

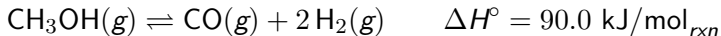
(f)(ii)

Mark scheme

- Decrease. The negative value of ΔH_2° indicates the reaction is exothermic. Because exothermic reactions favor reactant formation at higher temperature (the equilibrium shifts toward reactants as heat is added), the value of K_p decreases.

Question 2

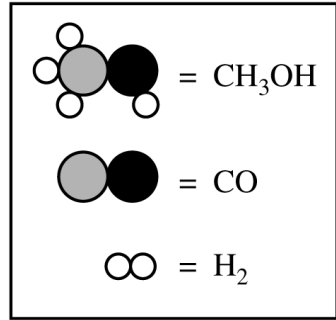
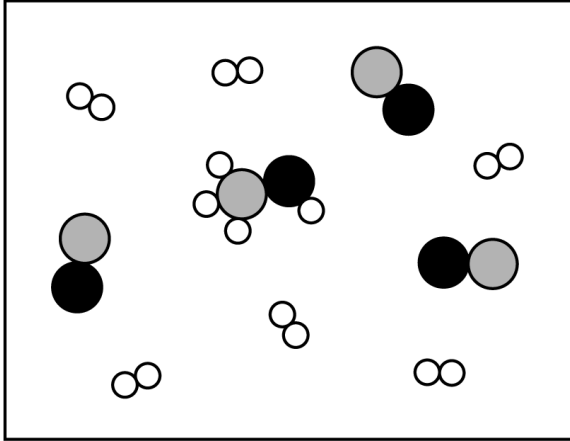
2022 ■ Q2



Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

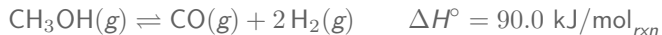
(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

Question 2



Question 2

2022 ■ Q2



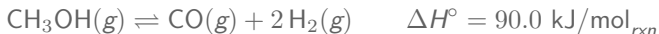
Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.

[A blank box is provided containing the unconnected atomic symbols “C” and “O”, for the student to complete into a full Lewis structure.]

Question 2

2022 ■ Q2



Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(c)(i) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	S° (J/(K · mol))	CH ₃ OH(<i>g</i>)	240.	CO(<i>g</i>)	198	H ₂ (<i>g</i>)
			131			

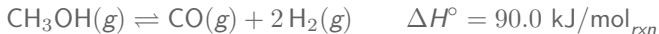
Use the data in the table to calculate the value of the standard entropy change, ΔS° , in J/(K · mol_{rxn}), for the reaction.

Question 2

(c)(ii) Calculate the value of ΔG° , in $\text{kJ/mol}_{\text{rxn}}$, for the reaction at 375 K. Assume that ΔH° and ΔS° are independent of temperature.

Question 2

2022 ■ Q2



Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(d) The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.

[A rectangular box (the "container") contains a mixture of particles at equilibrium: several two-linked-open-circle pairs (H₂), and several three-part particles each made of one gray sphere + one black sphere + one small open circle (CO), plus one larger cluster shown as CH₃OH. A key box beside it identifies: a cluster of one gray sphere +

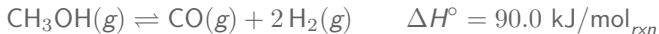
Question 2

one black sphere + three small open circles = CH_3OH ; one gray sphere + one black sphere = CO ; two small open circles joined = H_2 . Counting the container: there appear to be 1 CH_3OH particle, 4 CO particles, and 8 H_2 particles.]

Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

Question 2

2022 ■ Q2

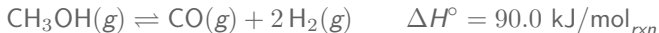


Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(e) Write the expression for the equilibrium constant, K_p , for the reaction.

Question 2

2022 ■ Q2



Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(f)



The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

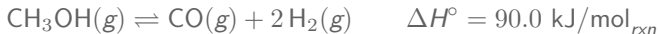
Question 2

Substance	Partial Pressure at Different Temperature		CH ₃ OH(<i>g</i>)	2.7 atm
CO(<i>g</i>)	4.2 atm	H ₂ (<i>g</i>)	8.4 atm	

Use the information in the table to calculate the value of the equilibrium constant, K_p , at the new temperature.

Question 2

2022 ■ Q2



Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $\text{CH}_3\text{OH}(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q , with the value of the equilibrium constant, K_p .

Solution 2

(a)

Mark scheme

- The H atoms are reduced because they change from an oxidation number of +1 (in CH_3OH) to 0 (in H_2) in the forward reaction.

Solution 2

(b)

Mark scheme

- Complete Lewis electron-dot diagram for CO obeying the octet rule: a carbon–oxygen triple bond ($\text{:C}\equiv\text{O:}$) with one lone pair on carbon and one lone pair on oxygen, giving each atom an octet (triple bond = 6 shared electrons + 1 lone pair = 8 electrons around each atom).

Solution 2

(c)(i)

Mark scheme

- $\Delta S^{\circ}_{\text{rxn}} = \Sigma \Delta S^{\circ}_{\text{products}} - \Sigma \Delta S^{\circ}_{\text{reactants}} = (\Delta S^{\circ}_{\text{CO(g)}} + 2\Delta S^{\circ}_{\text{H}_2\text{(g)}}) - \Delta S^{\circ}_{\text{CH}_3\text{OH(g)}}$ (1 point for correct stoichiometry, may be implicit). Using the table values (S° : $\text{CH}_3\text{OH(g)} = 240. \text{ J/(K} \cdot \text{mol)}$, $\text{CO(g)} = 198 \text{ J/(K} \cdot \text{mol)}$, $\text{H}_2\text{(g)} = 131 \text{ J/(K} \cdot \text{mol)}$): $\Delta S^{\circ}_{\text{rxn}} = 198 + 2(131) - 240. = 220. \text{ J/(K} \cdot \text{mol}_{\text{rxn}})$ (1 point for the correct calculated value).

Solution 2

(c)(ii)

Mark scheme

- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.0 \text{ kJ/mol}_{\text{rxn}} - (375 \text{ K})(0.220 \text{ kJ/(K} \cdot \text{mol}_{\text{rxn}})) = +7.5 \text{ kJ/mol}_{\text{rxn}}$ (assuming ΔH° and ΔS° are independent of temperature).

Solution 2

(d)

Mark scheme

- From the particle-level diagram, CO particles make up 3 of the 10 total gas particles shown in the container. With a total pressure of 12.0 atm: $P_{\text{CO}} = (3/10)(12.0 \text{ atm}) = 3.6 \text{ atm}$.

Solution 2

(e)

Mark scheme

- $K_p = (P_{\text{CO}})(P_{\text{H}_2})^2 / (P_{\text{CH}_3\text{OH}})$.

Solution 2

(f)

Mark scheme

- Using the partial pressures at the new equilibrium temperature ($\text{CH}_3\text{OH} = 2.7$ atm, $\text{CO} = 4.2$ atm, $\text{H}_2 = 8.4$ atm): $K_p = (P_{\text{CO}})(P_{\text{H}_2})^2 / (P_{\text{CH}_3\text{OH}}) = (4.2)(8.4)^2 / (2.7) = 110$.

Solution 2

(g) Mark scheme

- Comparison of Q and K (1 point): doubling the container volume causes the partial pressure of each species to decrease by a factor of two; because there are more moles of gaseous products than reactants, the resulting decrease in the numerator of Q is larger (raised to a higher net power) than the decrease in the denominator, making $Q_p < K_p$ — explicitly $Q_p = [(P_{\text{CO}}/2)(P_{\text{H}_2}/2)^2] / (P_{\text{CH}_3\text{OH}}/2) = K_p/4 \approx 27 < K_p$. Answer and justification (1 point): the number of moles of $\text{CH}_3\text{OH}(\text{g})$ will decrease. Since $Q_p < K_p$, the reaction proceeds forward as equilibrium re-establishes, increasing the partial pressures (moles) of the products and decreasing the moles of CH_3OH .

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

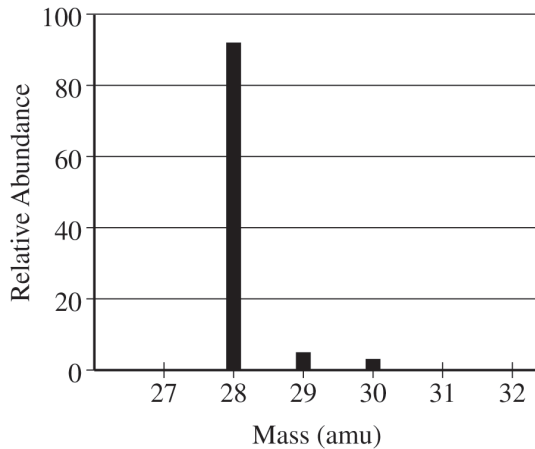
(a)(i) The mass spectrum of a pure sample of Si is shown below.

[Bar graph: Relative Abundance (y-axis, 0 to 100) vs. Mass (amu) (x-axis, 27 to 32).
A tall bar of relative abundance ~ 92 at mass 28; a very small bar at mass 29 (~ 3); a very small bar at mass 30 (~ 4); negligible/no bars at 27, 31, 32.]

How many protons and how many neutrons are in the nucleus of an atom of the most abundant isotope of Si?

(a)(ii) Write the ground-state electron configuration of Si.

Question 2



Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

(b) Two compounds that contain Si are SiO_2 and SiH_4 .

At 161 K, SiH_4 boils but SiO_2 remains as a solid. Using principles of interparticle forces, explain the difference in boiling points.

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

(c) At high temperatures, SiH_4 decomposes to form solid silicon and hydrogen gas.
Write a balanced equation for the reaction.

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

(d) A table of absolute entropies of some substances is given below.

Substance	S° (J/(mol · K))
$\text{H}_2(g)$	131
$\text{Si}(s)$	18
$\text{SiH}_4(g)$	205

Explain why the absolute molar entropy of $\text{Si}(s)$ is less than that of $\text{H}_2(g)$.

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

(e) Calculate the value, in $\text{J}/(\text{mol} \cdot \text{K})$, of ΔS° for the reaction.

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

(f) The reaction is thermodynamically favorable at all temperatures. Explain why the reaction occurs only at high temperatures.

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

(g) A partial photoelectron spectrum of pure Si is shown below. On the spectrum, draw the missing peak that corresponds to the electrons in the $3p$ sublevel.

[Photoelectron spectrum: Relative Number of Electrons (y-axis) vs. Binding Energy (MJ/mol) (x-axis, logarithmic scale decreasing left to right: 1,000, 100, 10, 1, 0.1). Peaks shown (from left to right, i.e. highest to lowest binding energy): a small peak near ~ 180 (between 1,000 and 100), a small peak near ~ 20 (between 100 and 10), a tall peak near ~ 10 , and a small peak near ~ 1.5 (between 1 and 0.1). No peak is shown corresponding to the $3p$ sublevel — the student must draw it in at the appropriate position and relative height.]

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

(h) Using principles of atomic structure, explain why the first ionization energy of Ge is lower than that of Si.

Question 2

2021 ■ Q2

Answer the following questions about the element Si and some of its compounds.

- (i)** A single photon with a wavelength of $4.00 \times 10^{-7} \text{ m}$ is absorbed by the Si sample. Calculate the energy of the photon in joules.

Solution 2

(a)(i)

Mark scheme

- The mass spectrum's tallest peak (highest relative abundance, ~92%) is at mass 28, so Si-28 is the most abundant isotope. Silicon's atomic number is 14, so this isotope has 14 protons and $(28 - 14 =)$ 14 neutrons.

(a)(ii)

Mark scheme

- Accept either equivalent form of the ground-state electron configuration of Si: $1s^2 2s^2 2p^6 3s^2 3p^2$, or the noble-gas-core notation $[\text{Ne}]3s^2 3p^2$.

Solution 2

(b)

Mark scheme

- SiH_4 is composed of discrete molecules, so the only intermolecular forces between SiH_4 molecules are (relatively weak) London dispersion forces. SiO_2 , by contrast, is a network covalent solid with strong covalent Si–O bonds extending throughout the entire structure. Because London dispersion forces are much weaker than covalent bonds, SiH_4 boils at a much lower temperature (it is already a gas at 161 K) while SiO_2 remains solid.

Solution 2

(c)

Mark scheme

- $\text{SiH}_4(g) \rightarrow \text{Si}(s) + 2 \text{H}_2(g)$ (state symbols not required; equation is already balanced).

Solution 2

(d)

Mark scheme

- $\text{H}_2(\text{g})$ molecules are more highly dispersed (able to move freely and occupy a much larger volume) than $\text{Si}(\text{s})$ atoms, and therefore have higher absolute molar entropy. Silicon is a solid, so its atoms are held in fixed positions within the lattice, are far less dispersed, and consequently have lower absolute molar entropy than $\text{H}_2(\text{g})$.

Solution 2

(e)

Mark scheme

- $\Delta S_{rxn}^{\circ} = S_{\text{products}}^{\circ} - S_{\text{reactants}}^{\circ} = [18 + 2(131)] - 205 = +75 \text{ J}/(\text{mol}_{rxn} \cdot \text{K})$,
using S° : Si(s)=18, H₂(g)=131 ($\times 2$ mol), SiH₄(g)=205, all in J/(mol · K).

Solution 2

(f)

Mark scheme

- High temperature is required so the reactant SiH_4 molecules have sufficient thermal (kinetic) energy to overcome the activation energy barrier of the reaction. A negative ΔG° (thermodynamic favorability) only indicates the reaction is spontaneous, not that it proceeds at an appreciable rate at low temperature — reaction rate is a kinetic property governed separately by activation energy.

Solution 2

(g)

Mark scheme

- The missing peak (representing the Si 3p electrons) should be drawn as the rightmost peak on the spectrum — i.e., at the lowest binding energy (below the existing 1 MJ/mol region), since 3p electrons are Si's outermost/valence electrons and thus the most weakly bound. Its height should reach the second gridline above the horizontal axis, reflecting that the 3p sublevel holds 2 electrons.

Solution 2

(h)

Mark scheme

- The valence electrons of a Ge atom occupy a higher principal energy level/shell ($n=4$) than those of a Si atom ($n=3$), so the average distance between the nucleus and the valence electrons is greater in Ge than in Si. This greater separation results in weaker Coulombic attraction between the Ge nucleus and its valence electrons, making them less tightly bound and therefore easier to remove — giving Ge a lower first ionization energy than Si.

Solution 2

(i)

Mark scheme

$$\blacksquare E = h\nu = h\frac{c}{\lambda} = (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \left(\frac{2.998 \times 10^8 \text{ m/s}}{4.00 \times 10^{-7} \text{ m}} \right) = 4.97 \times 10^{-19} \text{ J}.$$

Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H}-\text{N}(\text{H})-\text{C}(=\text{O})-\text{N}(\text{H})-\text{H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.

Question 1



Polystyrene
Cup



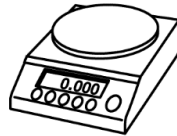
Thermometer



Stirring
Rod



Bottle of
Urea

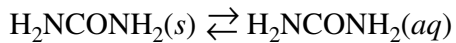
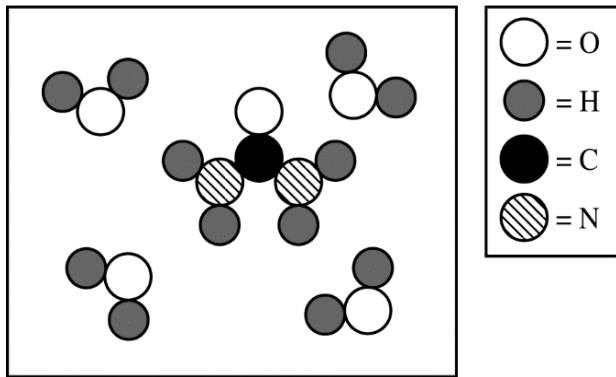


Balance



Distilled
Water

Question 1



Question 1

	S° (J/(mol·K))
$\text{H}_2\text{NCONH}_2(s)$	104.6
$\text{H}_2\text{NCONH}_2(aq)$	?

Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H}-\text{N}(\text{H})-\text{C}(=\text{O})-\text{N}(\text{H})-\text{H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

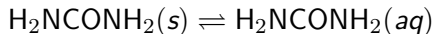
The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (—) to indicate a possible location of a hydrogen bond between a water molecule and the urea molecule.

[Diagram: a box containing one urea molecule (drawn with spheres: white = O, gray = H, black = C, hatched = N) surrounded by four separate water molecules, each

Question 1

water molecule drawn as one white (O) sphere bonded to two gray (H) spheres;
legend: white circle = O, gray circle = H, black circle = C, hatched circle = N]



The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at $20.^\circ\text{C}$.

Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H}-\text{N}(\text{H})-\text{C}(=\text{O})-\text{N}(\text{H})-\text{H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(c) Calculate the concentration of urea, in mol/L, in the saturated solution at $20.^{\circ}\text{C}$.

Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H}-\text{N}(\text{H})-\text{C}(=\text{O})-\text{N}(\text{H})-\text{H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 M . Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.

[Diagram: row of laboratory equipment icons, labelled left to right: Polystyrene Cup, Thermometer, Stirring Rod, Bottle of Urea, Balance, Distilled Water]

Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H—N(H)—C(=O)—N(H)—H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is $4.18 \text{ J}/(\text{g}\cdot^\circ\text{C})$, list the specific measurements that are required to be made during the experiment.

$S^\circ \text{ (J/(mol}\cdot\text{K))}$	—	—	$\text{H}_2\text{NCONH}_2(\text{s})$	104.6	$\text{H}_2\text{NCONH}_2(\text{aq})$	?
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Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H—N(H)—C(=O)—N(H)—H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(f) The entropy change for the dissolution of urea, $\Delta S_{\text{soln}}^\circ$, is $70.1 \text{ J}/(\text{mol}\cdot\text{K})$ at 25°C . Using the information in the table above, calculate the absolute molar entropy, S° , of aqueous urea.

Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H}-\text{N}(\text{H})-\text{C}(=\text{O})-\text{N}(\text{H})-\text{H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(g) Using particle-level reasoning, explain why $\Delta S_{\text{soln}}^\circ$ is positive for the dissolution of urea in water.

Question 1

2019 ■ Q1

[Complete Lewis electron-dot diagram of urea: $\text{H}-\text{N}(\text{H})-\text{C}(=\text{O})-\text{N}(\text{H})-\text{H}$, with the carbon double-bonded to oxygen (two lone pairs on O), and each nitrogen bonded to two H atoms and bearing one lone pair, and the central carbon bonded to both nitrogens]

The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(h) The student claims that ΔS° for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C . Use the thermodynamic information above to support the student's claim.

Solution 1

(a)

Mark scheme

- sp^2 . The carbon atom in urea is bonded to three groups (two N atoms and one O atom, one bond of which is a double bond) with no lone pairs, giving trigonal-planar sp^2 hybridization. 1 point for stating sp^2 .

Solution 1

(b)

Mark scheme

- A dashed line should connect a hydrogen atom of a water molecule to a nitrogen or oxygen atom of urea, OR an oxygen atom of a water molecule to a hydrogen atom of urea (an H-bond donor H drawn near an H-bond acceptor lone pair). 1 point is earned for any correctly placed dashed line matching this pattern.

Solution 1

(c)

Mark scheme

- Moles of urea: $5.39 \text{ g H}_2\text{NCONH}_2 \times (1 \text{ mol} / 60.06 \text{ g}) = 0.0897 \text{ mol}$ (1 point, may be implicit). Molarity: $0.0897 \text{ mol} / 0.00500 \text{ L} = 17.9 \text{ M}$ (1 point for the correct molarity).

Solution 1

(d)

Mark scheme

- Endothermic. The increased solubility at the higher temperature (19.8 M at 25°C vs. 17.9 M at 20.°C) implies the dissolution of urea is endothermic. By Le Chatelier's principle: heating a saturated solution stresses the equilibrium, and that stress is counteracted by more urea dissolving (the endothermic direction is favored). 1 point for the correct answer (endothermic) with this justification.

Solution 1

(e)

Mark scheme

- To determine the molar heat of solution calorimetrically, the student must measure: the mass of urea and the mass of water used (1 point); and the initial temperature of the water and the final temperature of the resulting solution (1 point). With the given specific heat $4.18 \text{ J}/(\text{g} \cdot ^\circ\text{C})$, these give $q = mc\Delta T$, which is then divided by moles of urea for the molar heat of solution.

Solution 1

(f)

Mark scheme

- $\Delta S^{\circ}_{\text{soln}} = S^{\circ}(\text{H}_2\text{NCONH}_2(\text{aq})) - S^{\circ}(\text{H}_2\text{NCONH}_2(\text{s})); 70.1 \text{ J}/(\text{mol} \cdot \text{K}) = S^{\circ}(\text{aq}) - 104.6 \text{ J}/(\text{mol} \cdot \text{K}); S^{\circ}(\text{H}_2\text{NCONH}_2(\text{aq})) = 174.7 \text{ J}/(\text{mol} \cdot \text{K}).$ 1 point for the correct answer.

Solution 1

(g)

Mark scheme

- Urea molecules in aqueous solution have a much greater number of possible arrangements/microstates (free to move and interact throughout the solution) than in the ordered solid, so dissolution increases the number of accessible microstates, giving a positive $\Delta S^{\circ}_{\text{soln}}$. 1 point for a correct particle-level explanation along these lines.

Solution 1

(h)

Mark scheme

- Thermodynamic favorability at standard conditions is determined by the sign of ΔG° , where $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Since ΔS° is positive, the $-T\Delta S^\circ$ term is negative, making ΔG° smaller (more negative) and thus making the dissolution more thermodynamically favorable — supporting the student's claim. 1 point for this reasoning.

Question 2

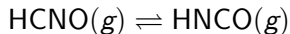
2017 ■ Q2

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: $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (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: $\text{H}-\text{C}=\text{N}=\ddot{\text{O}}:$ (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.



fulminic acid

isocyanic acid

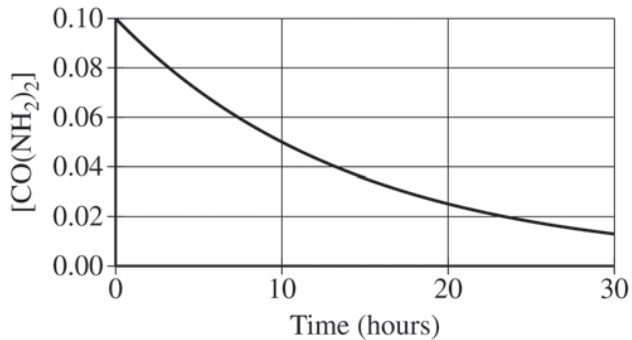
Question 2

| Fulminic Acid | Isocyanic Acid | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) |
 $\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$ (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)	$[\text{CO}(\text{NH}_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



Question 2

Fulminic Acid	Isocyanic Acid
$\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$	$\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$

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

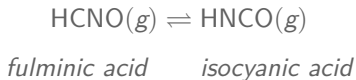
2017 ■ Q2

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Fulminic acid can convert to isocyanic acid according to the equation below.



| Fulminic Acid | Isocyanic Acid | $|\text{—}| \text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

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 $\text{HCNO}(g)$ to form $\text{HNCO}(g)$.

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

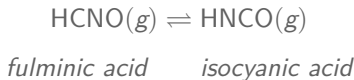
2017 ■ Q2

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| Fulminic Acid | Isocyanic Acid | $|\text{—}|\text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

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

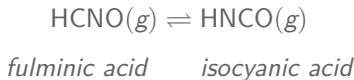
2017 ■ Q2

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Fulminic acid can convert to isocyanic acid according to the equation below.



| Fulminic Acid | Isocyanic Acid | $|\text{—}|\text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

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

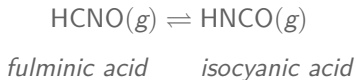
2017 ■ Q2

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| Fulminic Acid | Isocyanic Acid | $|\text{---}|\text{---}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

Question 2

(e)(i) The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\text{CO}(\text{NH}_2)_2$, represented below.



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(NH₂)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 $rate = k[CO(NH_2)_2]$.

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.

Question 2

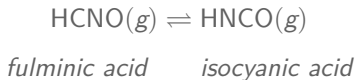
2017 ■ Q2

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: $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (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: $\text{H}-\text{C}=\text{N}=\ddot{\text{O}}:$ (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.



| Fulminic Acid | Isocyanic Acid | $|\text{—}| \text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

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 $\text{OH}^{-}(\text{aq})$.

Solution 2

(a)

Mark scheme

- In the left diagram ($\text{H-C triple-bond N-O:}$ with O having 3 lone pairs... i.e. $\text{H-C}\equiv\text{N-O:}$), the C atom has a formal charge of 0 and the O atom has a formal charge of -1. In the right diagram ($\text{H-C(double bond)N(double bond)O:}$), 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 $\equiv$ 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. ΔH (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 ΔH (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 ΔS (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 $\rightarrow$ 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: $k = 0.693 / t(1/2) = 0.693 / 10. \text{ h} = 0.069 \text{ h}^{-1}$ (equivalently $k = (\ln[A]_0 - \ln[A]_t)/t = (\ln 0.1000 - \ln 0.0500) / 10. \text{ h} = 0.069 \text{ h}^{-1}$). 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 $\text{OH}^-(\text{aq})$ (changing only $[\text{OH}^-]$, holding other variables such as temperature and initial urea concentration constant), and measure how the concentration of $\text{CO}(\text{NH}_2)_2$ 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).