

## Past-paper walk-through

Gibbs Free Energy and Thermodynamic Favorability ■ 9.3

eXercise

## Questions in this set

- 2026 Q4
- 2025 Q3
- 2024 Q2
- 2023 Q1
- 2022 Q2
- 2019 Q1
- 2016 Q2
- 2015 Q2

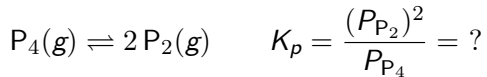
## Reading the mark scheme

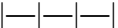
- **B1** a mark that stands on its own – the point is either made or not.
- **M1** a *method* mark: the right approach, even if the number is wrong.
- **A1** an *answer* mark, and it usually needs its M mark first.
- **C1** a working mark on the way to the answer.
- **//** separates answers the examiner 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 4

2026 ■ Q4

White phosphorus,  $P_4(g)$ , can decompose into  $P_2(g)$  at elevated temperatures. A balanced chemical equation,  $K_p$  expression, and Lewis diagrams for the chemical species involved in the reaction are given.

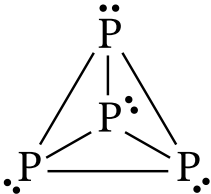


| Compound |  $P_4$  |  $P_2$  |  | Lewis diagram | [Tetrahedral arrangement of 4 P atoms, each bonded to the other three by single bonds, each P atom bearing one lone pair] | [ $: P \equiv P :$  — a P atom triple-bonded to another P atom, each bearing one lone pair] |

## Question 4

**(a)** The average bond length in  $P_4$  molecules is 221 pm, whereas the average bond length in  $P_2$  molecules is 189 pm. **\*\*Explain\*\*** why the average bond length in  $P_4$  is greater than the average bond length in  $P_2$ .

# Question 4

| Compound      | $P_4$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | $P_2$          |
|---------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| Lewis diagram |  <p>The diagram shows a tetrahedral arrangement of four phosphorus (P) atoms. Each P atom is connected to three other P atoms by single bonds, forming a tetrahedron. Each P atom has one lone pair of electrons, represented by two dots. The lone pairs are located at the top (for the top atom), bottom-left (for the bottom-left atom), and bottom-right (for the bottom-right atom). The bottom-center atom has its lone pair to its right.</p> | $:P \equiv P:$ |

## Question 4

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| Compound |  $P_4$  |  $P_2$  |  $|\text{---}|\text{---}|\text{---}|$  | Lewis diagram | [Tetrahedral arrangement of 4 P atoms, each bonded to the other three by single bonds, each P atom bearing one lone pair] | [ $: P \equiv P :$  — a P atom triple-bonded to another P atom, each bearing one lone pair] |

**(b)** A sample of  $P_4(s)$  is placed in a sealed rigid container and heated to 1600. K, at which point the initial partial pressure of  $P_4(g)$  is 0.470 atm. Some of the  $P_4(g)$

## Question 4

decomposes into  $\text{P}_2(g)$  as the system reaches equilibrium. At equilibrium, the partial pressure of  $\text{P}_2(g)$  is determined to be 0.630 atm.

**\*\*Calculate\*\*** the value of the equilibrium constant,  $K_p$ , for the reaction at 1600. K. Show the work that leads to your answer.



## Question 4

2026 ■ Q4

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| Compound |  $P_4$  |  $P_2$  |  $|\text{---}|\text{---}|\text{---}|$  | Lewis diagram | [Tetrahedral arrangement of 4 P atoms, each bonded to the other three by single bonds, each P atom bearing one lone pair] | [ $: P \equiv P :$  — a P atom triple-bonded to another P atom, each bearing one lone pair] |

**(c)** The reaction is thermodynamically favorable under standard conditions only at temperatures above 1500 K. A student claims that the reaction must be endothermic

## Question 4

because it is favorable only at high temperatures. Do you agree or disagree?

**\*\*Justify\*\*** your answer using  $\Delta S^\circ_{rxn}$  and  $\Delta G^\circ_{rxn}$ .

## Question 3

2025 ■ Q3

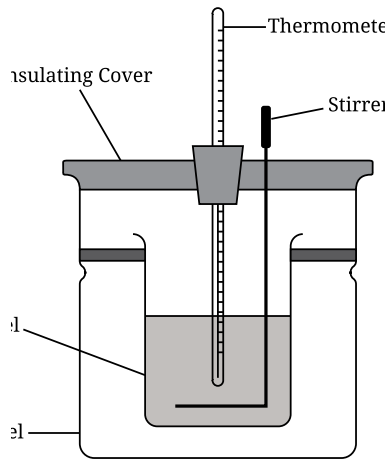
White phosphorus is composed of  $P_4$  molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

[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.

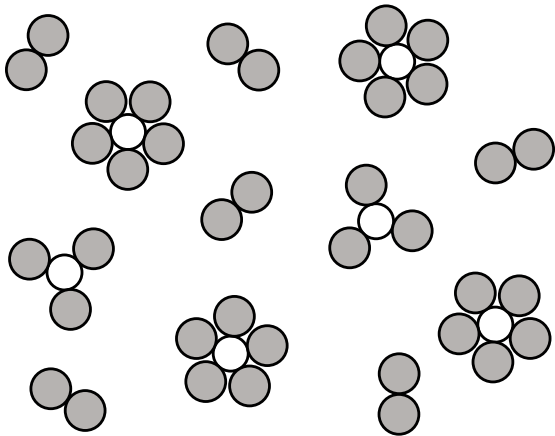
## Question 3



## Question 3

|                                         |               |
|-----------------------------------------|---------------|
| Mass of $\text{P}_4\text{O}_{10}$       | 0.100 g       |
| Mass of $\text{H}_2\text{O}$            | 100.0 g       |
| Initial temperature                     | 22.00° C      |
| Final temperature                       | 22.38° C      |
| Molar mass of $\text{P}_4\text{O}_{10}$ | 283.9 g/mol   |
| Specific heat of $\text{H}_2\text{O}$   | 4.18 J/(g·°C) |

## Question 3



## Question 3

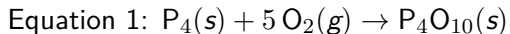
2025 ■ Q3

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.]

**(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,  $\Delta S^\circ$ , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

**(b)(ii)** The enthalpy change of the reaction,  $\Delta H^\circ$ , 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  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ .



## Question 3

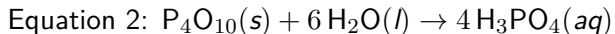
2025 ■ Q3

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.]

**(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 $\text{P}_4\text{O}_{10}$       | 0.100 g     | Mass of $\text{H}_2\text{O}$          | 100.0 g         |
| Initial temperature | 22.00°C | Final temperature | 22.38°C | Molar mass of $\text{P}_4\text{O}_{10}$ | 283.9 g/mol | Specific heat of $\text{H}_2\text{O}$ | 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  $\Delta H_{rxn}^{\circ}$  for equation 2 in  $\text{kJ/mol}_{rxn}$ . Include the sign in your answer.

## Question 3

2025 ■ Q3

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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  $\Delta T$  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

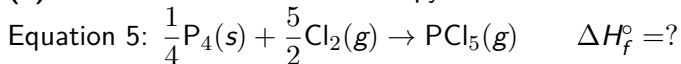
2025 ■ Q3

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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) =  $\text{Cl}_2$ , four-atom tetrahedral-looking particles (grey with three white) =  $\text{PCl}_3$ , and six-atom particles (grey with five white) =  $\text{PCl}_5$ . The box shows several  $\text{Cl}_2$  particles (pairs of grey circles), several  $\text{PCl}_3$  particles (grey center with three white circles), and several  $\text{PCl}_5$  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  $\Delta H_2^\circ$ .

## Solution 3

(a)

### Mark scheme

- Complete Lewis diagram for  $\text{P}_4$ : 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,  $\text{O}_2$ ) convert into the solid product ( $\text{P}_4\text{O}_{10}$ ).

## 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

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

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

The correct (negative) sign must be included.

## Solution 3

(d)

### Mark scheme

- Less than. If less  $\text{P}_4\text{O}_{10}$  is present (some stuck to the weighing paper), less thermal energy will be transferred to the water during the reaction, causing the temperature increase ( $\Delta T$ ) to be less than it was with the full 0.100 g of  $\text{P}_4\text{O}_{10}$ .



## 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  $\text{PCl}_5$ , 2  $\text{PCl}_3$ , 6  $\text{Cl}_2$  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

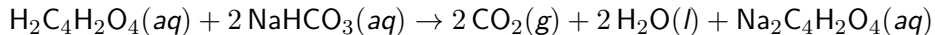
(f)(ii)

## Mark scheme

- Decrease. The negative value of  $\Delta H_2^\circ$  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

2024 ■ Q2



2. A chemical reaction between maleic acid ( $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) occurs in the presence of water to produce carbon dioxide and sodium maleate ( $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ ), as represented by the following equation.

**(a)(i)** A student combines equal masses of  $\text{H}_2\text{C}_4\text{H}_2\text{O}_4(s)$  chunks and  $\text{NaHCO}_3(s)$  chunks with sufficient water at  $20.0^\circ\text{C}$ . The student determines that  $0.0114 \text{ mol}$  of  $\text{CO}_2(g)$  is produced after the reaction goes to completion.

Calculate the number of grams of  $\text{CO}_2(g)$  produced.

**(a)(ii)** The  $\text{CO}_2(g)$  produced from the reaction at  $20.0^\circ\text{C}$  was collected and found to have a pressure of  $1.25 \text{ atm}$ . Calculate the volume of  $\text{CO}_2(g)$ , in liters.

## Question 2

2024 ■ Q2



2. A chemical reaction between maleic acid ( $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) occurs in the presence of water to produce carbon dioxide and sodium maleate ( $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ ), as represented by the following equation.

**(b)(i)** The student performs a second experiment that is identical to the first except that the student grinds the chunks of  $\text{H}_2\text{C}_4\text{H}_2\text{O}_4(s)$  and  $\text{NaHCO}_3(s)$  into powder before combining the powder with water.

What happens to the surface area of the reactants when the student grinds the chunks into powder?

## Question 2

**(b)(ii)** The rate-determining step for the overall reaction is the dissolving of the solids. Would the time required for the dissolving of the solids in the second experiment be longer than, shorter than, or the same as the time required in the first experiment?

Justify your answer based on the collisions between particles.

**(b)(iii)** When the reaction is complete, will the volume of  $\text{CO}_2(g)$  at the end of the second experiment be greater than, less than, or equal to the volume at the end of the first experiment? Justify your answer.

## Question 2

2024 ■ Q2



2. A chemical reaction between maleic acid ( $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) occurs in the presence of water to produce carbon dioxide and sodium maleate ( $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ ), as represented by the following equation.

**(c)** The student conducts additional trials of the experiment and produces the following data table.

| Trial | Mass of $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ (grams) | Mass of $\text{NaHCO}_3$ (grams) | Moles of $\text{CO}_2$ Produced (mol) |
|-------|------------------------------------------------------------|----------------------------------|---------------------------------------|
| 3     | 1.543                                                      | 1.251                            | 0.01489                               |
| 4     | 1.543                                                      | 1.686                            | 0.02007                               |

Based on the student's data, identify the limiting reactant in trial 3. Justify your answer.



## Question 2

2024 ■ Q2



2. A chemical reaction between maleic acid ( $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) occurs in the presence of water to produce carbon dioxide and sodium maleate ( $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ ), as represented by the following equation.

**(d)** The reaction has a value of  $\Delta S^\circ$  greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

## Question 2

2024 ■ Q2



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**(e)** The student notices that the temperature of the reaction mixture decreases as the reaction takes place and correctly determines that the reaction is endothermic.

The student claims that the reaction is thermodynamically favorable at all temperatures because  $\Delta S_{\text{rxn}}^{\circ} > 0$  and the reaction is endothermic. Do you agree or disagree with the student's claim? Justify your answer.

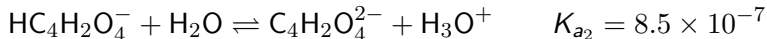
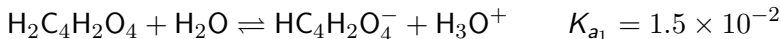
## Question 2

2024 ■ Q2



2. A chemical reaction between maleic acid ( $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) occurs in the presence of water to produce carbon dioxide and sodium maleate ( $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ ), as represented by the following equation.

**(f)** Next, the student investigates the acid-base behavior of maleic acid. The student notes that maleic acid is a diprotic acid. The two acid dissociation processes that occur are represented by the following equations.



## Question 2

Calculate the  $\text{p}K_{\text{a}2}$  value for the  $\text{HC}_4\text{H}_2\text{O}_4^-$  ion.

## Question 2

2024 ■ Q2



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**(g)** A buffer solution with a pH of 7.00 is prepared using  $\text{C}_4\text{H}_2\text{O}_4^{2-}$  and  $\text{HC}_4\text{H}_2\text{O}_4^-$ . Calculate the ratio

$$\frac{[\text{C}_4\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_4\text{H}_2\text{O}_4^-]}$$

in this solution.

## Solution 2

**(a)(i)****Mark scheme**

$$\blacksquare 0.0114 \text{ mol CO}_2 \times \frac{44.01 \text{ g}}{1 \text{ mol}} = 0.502 \text{ g CO}_2.$$

## Solution 2

(a)(ii)

## Mark scheme

- Using  $PV = nRT$ :

$$V = \frac{nRT}{P} = \frac{(0.0114 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K}))(293 \text{ K})}{1.25 \text{ atm}} = 0.219 \text{ L.}$$

## Solution 2

**(b)(i)**

### Mark scheme

- Claim: the surface area of the solid reactants increases when the chunks are ground into powder.

**(b)(ii)**

### Mark scheme

- Shorter than. The powdered solids have a larger surface area than the solid chunks, so collisions between water molecules and the solid surface particles occur more frequently, resulting in a faster rate of dissolution and a shorter time to dissolve the solids.



## Solution 2

(b)(iii)

### Mark scheme

- Equal to. Both experiments begin with the same amount (mass) of reactants, so they produce the same number of moles of  $\text{CO}_2(g)$  under the same conditions of pressure and temperature; therefore the final volume of  $\text{CO}_2$  will be the same regardless of particle size (rate changes, but the final amount/volume does not).

## Solution 2

### (c) Mark scheme

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- $\text{NaHCO}_3$  is the limiting reactant (accept either justification): changing the mass of  $\text{NaHCO}_3$  alters the amount of  $\text{CO}_2$  produced, OR  $\text{NaHCO}_3$  has the smaller theoretical yield of  $\text{CO}_2$ :

$$1.543 \text{ g H}_2\text{C}_4\text{H}_2\text{O}_4 \times \frac{1 \text{ mol}}{116.07 \text{ g}} \times \frac{2 \text{ mol CO}_2}{1 \text{ mol acid}} = 0.02659 \text{ mol CO}_2 \text{ (if acid were limiting)}$$

$$\text{vs. } 1.251 \text{ g NaHCO}_3 \times \frac{1 \text{ mol}}{84.01 \text{ g}} \times \frac{2 \text{ mol CO}_2}{2 \text{ mol NaHCO}_3} = 0.01489 \text{ mol CO}_2$$

(if  $\text{NaHCO}_3$  limiting) — the smaller value ( $\text{NaHCO}_3$ ) is the actual limiting reactant, matching the trial's observed  $0.01489 \text{ mol CO}_2$ .

## Solution 2

(d)

### Mark scheme

- The entropy change is positive because the aqueous/solid reactants produce 2 moles of gas ( $\text{CO}_2$ ) particles, according to the balanced equation. Gases are far more dispersed (occupy many more microstates) than condensed (solid/aqueous) phases, so the entropy of the products is greater than that of the reactants.

## Solution 2

(e)

## Mark scheme

- Disagree. Accept either justification: (1) The reaction is endothermic ( $\Delta H > 0$ ) with a positive entropy change ( $\Delta S > 0$ ), so it is only thermodynamically favorable at a high enough temperature where the magnitude of  $-T\Delta S$  exceeds  $\Delta H$  — NOT at all temperatures. (2) For a reaction to be thermodynamically favorable ( $\Delta G < 0$ ) at ALL temperatures, it must be exothermic ( $\Delta H < 0$ ) AND have  $\Delta S > 0$  — this reaction is endothermic, so it fails that requirement.

## Solution 2

(f)

## Mark scheme

- Given  $K_{a_2} = 8.5 \times 10^{-7}$  for the second dissociation of maleic acid:  
 $\text{p}K_{a_2} = -\log(8.5 \times 10^{-7}) = 6.07.$

## Solution 2

(g)

## Mark scheme

- Using the Henderson–Hasselbalch equation:  $\text{pH} = \text{p}K_{a_2} + \log \frac{[\text{C}_4\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_4\text{H}_2\text{O}_4^-]}$ .

Solving:  $\frac{[\text{C}_4\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_4\text{H}_2\text{O}_4^-]} = 10^{(\text{pH} - \text{p}K_{a_2})} = 10^{(7.00 - 6.07)} = 8.5.$

## Question 1

2023 ■ Q1

Answer the following questions related to manganese compounds.

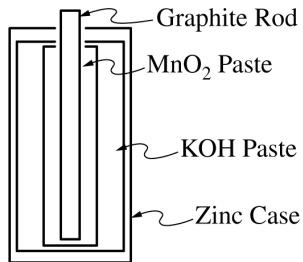
**(a)(i)** Manganese has several common oxidation states.

Write the complete electron configuration for an Mn atom in the ground state.

**(a)(ii)** When manganese forms cations, electrons are lost from which subshell first?

Identify both the number and letter associated with the subshell.

# Question 1



| Reduction Half-Reaction                                                                                      | $E^\circ$ (V) |
|--------------------------------------------------------------------------------------------------------------|---------------|
| $\text{Zn}^{2+}(aq) + 2 e^- \rightarrow \text{Zn}(s)$                                                        | -0.76         |
| $\text{ZnO}(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Zn}(s) + 2 \text{OH}^-(aq)$                 | -1.28         |
| $2 \text{MnO}_2(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2 \text{OH}^-(aq)$ | 0.15          |

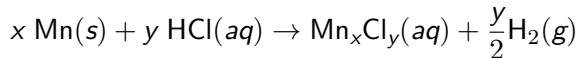


## Question 1

2023 ■ Q1

Answer the following questions related to manganese compounds.

**(b)** A student performs an experiment to produce a manganese salt of unknown composition,  $\text{Mn}_x\text{Cl}_y(\text{aq})$ , and determine its empirical formula. The student places a sample of  $\text{Mn}(\text{s})$  in a beaker containing excess  $\text{HCl}(\text{aq})$ , as represented by the following equation.



The student heats the resulting mixture until only  $\text{Mn}_x\text{Cl}_y(\text{s})$  remains in the beaker. The data are given in the following table.

## Question 1

| Quantity                                                                   | Value    |
|----------------------------------------------------------------------------|----------|
| Mass of empty beaker                                                       | 60.169 g |
| Mass of beaker and Mn(s)                                                   | 61.262 g |
| Mass of beaker and $\text{Mn}_x\text{Cl}_y$ after heating to constant mass | 62.673 g |

Calculate the mass of Cl in the sample of  $\text{Mn}_x\text{Cl}_y(s)$  remaining in the beaker.

# Question 1

2023 ■ Q1

Answer the following questions related to manganese compounds.

**(c)** Calculate the number of moles of Cl in the sample of  $\text{Mn}_x\text{Cl}_y(\text{s})$  remaining in the beaker.

## Question 1

2023 ■ Q1

Answer the following questions related to manganese compounds.

**(d)** The student determines that 0.0199 mol of Mn was used in the experiment. Use the data to determine the empirical formula of the  $\text{Mn}_x\text{Cl}_y(\text{s})$ .

## Question 1

2023 ■ Q1

Answer the following questions related to manganese compounds.

**(e)** The student repeats the experiment using the same amounts of Mn and HCl and notices that some of the  $\text{Mn}_x\text{Cl}_y$  splatters out of the beaker as it is heated to dryness. Will the number of moles of Cl calculated for this trial be greater than, less than, or equal to the number calculated in part (c)? Justify your answer.

## Question 1

Answer the following questions related to manganese compounds.

[Diagram of an alkaline battery: a graphite rod runs through the center, surrounded by  $\text{MnO}_2$  paste, then  $\text{KOH}$  paste, enclosed by a zinc case.]

Some half-reactions are given in the table.

| Reduction Half-Reaction                                                                                                                      | $E^\circ$ (V) |
|----------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$                                                                    | -0.76         |
| $\text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq})$                | -1.28         |
| $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq})$ | 0.15          |

**(f)(i)** Based on the half-reactions given in the table, write the balanced net ionic equation for the reaction that has the greatest thermodynamic favorability.

**(f)(ii)** Calculate the value of  $E_{cell}^{\circ}$  for the overall reaction.

## Question 1

**(f)(iii)** Calculate the value of  $\Delta G^\circ$  in  $\text{kJ/mol}_{\text{rxn}}$ .

**(f)(iv)** A student claims that the total mass of an alkaline battery decreases as the battery operates because the anode loses mass. Do you agree with the student's claim? Justify your answer.

# Solution 1

## (a)(i)

### Mark scheme

- Ground-state Mn ( $Z=25$ ) electron configuration:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$  (equivalently  $[\text{Ar}]4s^2 3d^5$ ). Either full or noble-gas-core notation is accepted.

## (a)(ii)

### Mark scheme

- Electrons are lost first from the 4s subshell (number = 4, letter = s) when Mn forms cations, consistent with the configuration in part (a)(i) — the 4s electrons are removed before the 3d electrons.



## Solution 1

(b)

## Mark scheme

- Mass of Cl in the sample = mass of dry beaker +  $\text{Mn}_x\text{Cl}_y$  minus mass of the empty beaker:  $62.673 \text{ g} - 61.262 \text{ g} = 1.411 \text{ g Cl}$ .

## Solution 1

(c)

## Mark scheme

- Convert mass of Cl to moles:  $1.411 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 0.03980 \text{ mol Cl}.$

## Solution 1

(d)

## Mark scheme

- Mole ratio Cl:Mn =  $\frac{0.03980 \text{ mol Cl}}{0.0199 \text{ mol Mn}} = \frac{2 \text{ mol Cl}}{1 \text{ mol Mn}}$ , so the empirical formula is  $\text{MnCl}_2$ .

## Solution 1

(e)

## Mark scheme

- Less than. If some of the mass of aqueous  $\text{Mn}_x\text{Cl}_y$  is lost due to splattering, the final mass of the dry beaker and  $\text{Mn}_x\text{Cl}_y$  will be decreased, which will decrease the calculated mass and number of moles of chlorine in the dry solid.

# Solution 1

(f)

## Mark scheme

- This is introductory/stem text describing the alkaline battery ( $\text{MnO}_2/\text{Zn}$  cell) and giving the reduction half-reaction table; it poses no separate question of its own. The scoring guidelines award all 4 points for this context across parts (f)(i)–(f)(iv) below, so no points are attached to this stem leaf.

## Solution 1

(f)(i)

## Mark scheme

- Combine the  $\text{MnO}_2$  reduction half-reaction with the reverse of the less-favorable  $\text{Zn}/\text{ZnO}$  half-reaction:  
 $2\text{MnO}_2(s) + \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{OH}^-(aq)$  and  
 $\text{Zn}(s) + 2\text{OH}^-(aq) \rightarrow \text{ZnO}(s) + \text{H}_2\text{O}(l) + 2e^-$ . Adding gives the overall balanced net ionic equation:  $2\text{MnO}_2(s) + \text{Zn}(s) \rightarrow \text{Mn}_2\text{O}_3(s) + \text{ZnO}(s)$ .

## Solution 1

(f)(ii)

## Mark scheme

$$\blacksquare E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.15 \text{ V} - (-1.28 \text{ V}) = 1.43 \text{ V}.$$

## Solution 1

(f)(iii)

Mark scheme

$$\blacksquare \Delta G^\circ = -nFE^\circ = -\frac{2 \text{ mol } e^-}{1 \text{ mol}_{rxn}} \times 96,485 \text{ C} \times \frac{1.43 \text{ J}}{1 \text{ C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -276 \text{ kJ/mol}_{rxn}.$$



# Solution 1

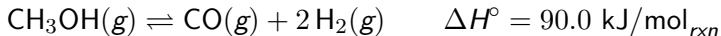
(f)(iv)

## Mark scheme

- Disagree. The battery is enclosed (sealed), so no mass enters or leaves the system — no change in total mass will occur. (Also accept: all reactants and products are in the solid phase, so with no gases entering or exiting the sealed battery, the total mass stays the same.)

## Question 2

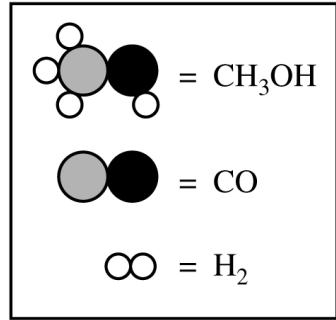
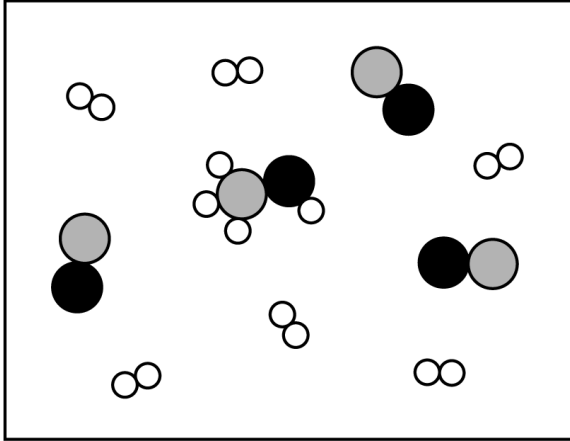
2022 ■ Q2



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.

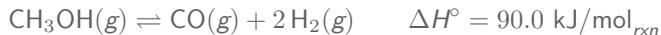
**(a)** Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

## Question 2



## Question 2

2022 ■ Q2



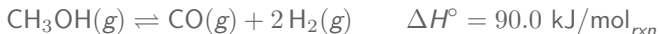
Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

**(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 | $S^\circ$ (J/(K · mol)) | CH <sub>3</sub> OH( <i>g</i> ) | 240. | CO( <i>g</i> ) | 198 | H <sub>2</sub> ( <i>g</i> ) |
|           |                         |                                | 131  |                |     |                             |

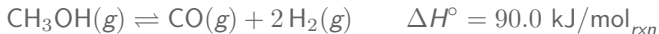
Use the data in the table to calculate the value of the standard entropy change,  $\Delta S^\circ$ , in J/(K · mol<sub>rxn</sub>), for the reaction.

## Question 2

**(c)(ii)** Calculate the value of  $\Delta G^\circ$ , in  $\text{kJ/mol}_{\text{rxn}}$ , for the reaction at 375 K. Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  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 (H<sub>2</sub>), 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 CH<sub>3</sub>OH. A key box beside it identifies: a cluster of one gray sphere +

## Question 2

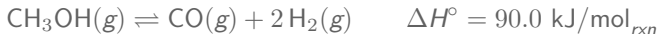
one black sphere + three small open circles =  $\text{CH}_3\text{OH}$ ; one gray sphere + one black sphere =  $\text{CO}$ ; two small open circles joined =  $\text{H}_2$ . Counting the container: there appear to be 1  $\text{CH}_3\text{OH}$  particle, 4  $\text{CO}$  particles, and 8  $\text{H}_2$  particles.]

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



## Question 2

2022 ■ Q2

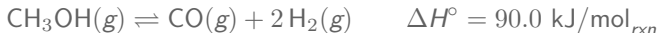


Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

**(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.

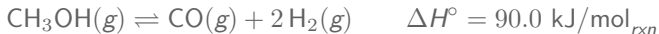
## Question 2

|                |                                           |                             |                                |         |
|----------------|-------------------------------------------|-----------------------------|--------------------------------|---------|
| Substance      | Partial Pressure at Different Temperature |                             | CH <sub>3</sub> OH( <i>g</i> ) | 2.7 atm |
| CO( <i>g</i> ) | 4.2 atm                                   | H <sub>2</sub> ( <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  $\text{CH}_3\text{OH}$ ) to 0 (in  $\text{H}_2$ ) 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 ( $S^{\circ}$ :  $\text{CH}_3\text{OH(g)} = 240. \text{ J/(K} \cdot \text{mol)}$ ,  $\text{CO(g)} = 198 \text{ J/(K} \cdot \text{mol)}$ ,  $\text{H}_2\text{(g)} = 131 \text{ J/(K} \cdot \text{mol)}$ ):  $\Delta S^{\circ}_{\text{rxn}} = 198 + 2(131) - 240. = 220. \text{ J/(K} \cdot \text{mol}_{\text{rxn}})$  (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  $\Delta H^\circ$  and  $\Delta S^\circ$  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  $\text{CH}_3\text{OH}$ .

## 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,  $\text{H}_2\text{NCONH}_2$ , 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

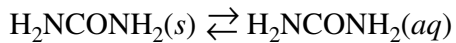
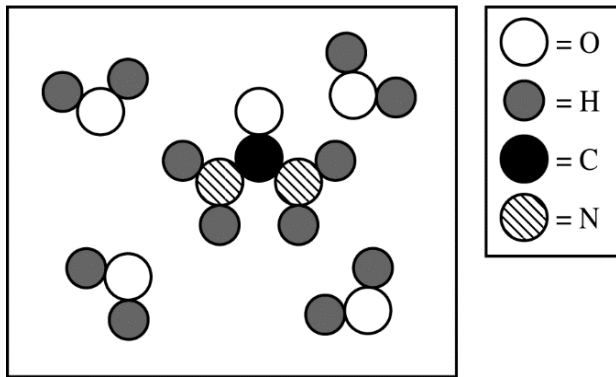


Balance



Distilled  
Water

## Question 1



## Question 1

|                                | $S^\circ$ (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]

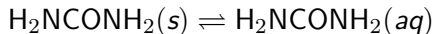
The compound urea,  $\text{H}_2\text{NCONH}_2$ , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

**(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  $\text{H}_2\text{NCONH}_2$  (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,  $\text{H}_2\text{NCONH}_2$ , 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,  $\text{H}_2\text{NCONH}_2$ , 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  $25^\circ\text{C}$  is  $19.8\text{ M}$ . 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,  $\text{H}_2\text{NCONH}_2$ , 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  $4.18 \text{ J/(g}\cdot^\circ\text{C)}$ , 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 | $\text{H}_2\text{NCONH}_2(\text{aq})$ | ? |
|------------------------------------------|---|---|--------------------------------------|-------|---------------------------------------|---|

# 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,  $\text{H}_2\text{NCONH}_2$ , 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  $25^\circ\text{C}$ . Using the information in the table above, calculate the absolute molar entropy,  $S^\circ$ , 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,  $\text{H}_2\text{NCONH}_2$ , 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,  $\text{H}_2\text{NCONH}_2$ , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

**(h)** The student claims that  $\Delta S^\circ$  for the process contributes to the thermodynamic favorability of the dissolution of urea at  $25^\circ\text{C}$ . 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)

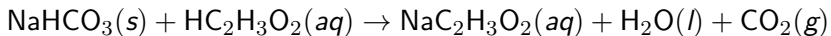
## Mark scheme

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



## Question 2

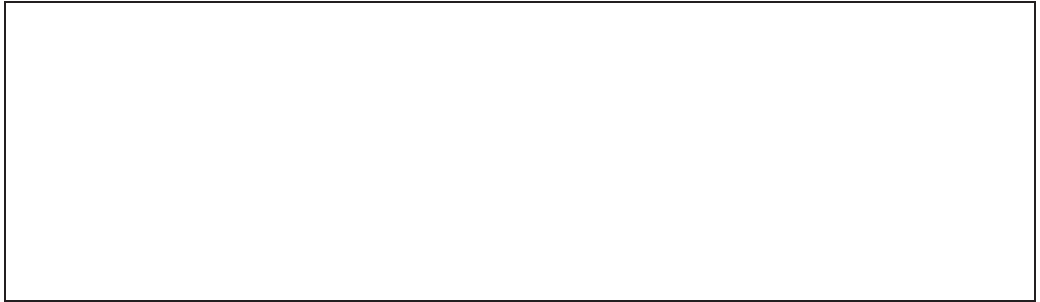
2016 ■ Q2



A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

**(a)** Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

## Question 2

A large, empty rectangular box with a thin black border, intended for the user to provide their answer to the question.

## Question 2

2016 ■ Q2



A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

**(b)** Based on the information above, identify the limiting reactant. Justify your answer with calculations.

## Question 2

2016 ■ Q2



A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

**(c)** The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

## Question 2

2016 ■ Q2



A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

**(d)(i)** In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both. Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between  $\text{NaHCO}_3(s)$  and  $\text{HC}_2\text{H}_3\text{O}_2(aq)$ ? Answer by drawing a circle around one of the choices below.

Enthalpy only   Entropy only   Both enthalpy and entropy

**(d)(ii)** Justify your selection in part (d)(i) in terms of  $\Delta G^\circ$ .

## Question 2

2016 ■ Q2



A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

**(e)** The  $\text{HCO}_3^-$  ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the  $\text{HCO}_3^-$  ion that is (are) consistent with the given information.

[Empty box provided for the student to draw the Lewis electron-dot diagram(s).]

## Question 2

2016 ■ Q2



A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

**(f)** A student prepares a solution containing equimolar amounts of  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaC}_2\text{H}_3\text{O}_2$ . The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M  $\text{HNO}_3(aq)$  and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between  $\text{HNO}_3(aq)$  and the chemical species in the sample that is responsible for the pH remaining at 4.7.

## Solution 2

(a)

### Mark scheme

- It is an acid-base reaction: the weak acid  $\text{HC}_2\text{H}_3\text{O}_2$  reacts with the weak base  $\text{HCO}_3^-$ , with  $\text{HC}_2\text{H}_3\text{O}_2$  donating a proton. (Equivalently: no solid precipitates, so it is not a precipitation reaction; no oxidation numbers change, so it is not a redox reaction.) 1 point for identifying the reaction as acid-base, 1 point for a valid justification.



## Solution 2

(b)

### Mark scheme

- $2.24 \text{ g NaHCO}_3 \times (1 \text{ mol} / 84.0 \text{ g}) = 0.0267 \text{ mol NaHCO}_3$ .  $60.0 \text{ mL} \times (0.875 \text{ mol HC}_2\text{H}_3\text{O}_2 / 1000 \text{ mL}) = 0.0525 \text{ mol HC}_2\text{H}_3\text{O}_2$ .  $\text{NaHCO}_3(\text{s})$  and  $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$  react in a 1:1 ratio, so the smaller mole amount,  $\text{NaHCO}_3(\text{s})$ , is the limiting reactant. 1 point for calculating the number of moles of each reactant, 1 point for correctly identifying  $\text{NaHCO}_3$  as the limiting reactant, consistent with the calculation.

## Solution 2

(c)

### Mark scheme

- As the reaction proceeds, both reactants are consumed and their concentrations decrease; collisions between reactant particles become less frequent as concentrations decrease, so the reaction rate slows. 1 point for a valid explanation in terms of collision frequency between reactant particles.

## Solution 2

(d)(i)

### Mark scheme

- 'Entropy only' should be circled. Because the flask gets cooler as the reaction proceeds, the reaction is endothermic and cannot be driven by a favorable enthalpy change — it must be driven by entropy. 1 point for circling 'Entropy only'.

## Solution 2

(d)(ii)

### Mark scheme

- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ; a reaction is thermodynamically favorable when  $\Delta G^\circ$  is negative. Since the reaction is endothermic (flask gets cooler,  $\Delta H^\circ$  is positive), enthalpy does not help make  $\Delta G^\circ$  negative, so the reaction is not driven by enthalpy. Because the reactants contain no gas while one product ( $\text{CO}_2$ ) is a gas,  $\Delta S^\circ$  must be positive, which helps make  $\Delta G^\circ$  negative — so the reaction is entropy-driven. 1 point for a valid justification referencing the signs of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ .

## Solution 2

### (e) Mark scheme

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- A correct Lewis structure for  $\text{HCO}_3^-$  has a central C bonded to three O atoms: one  $\text{C}=\text{O}$  double bond, one  $\text{C}-\text{O}$  single bond to an O bearing three lone pairs (charge  $-1$  on that O), and one  $\text{C}-\text{O}$  single bond to the  $\text{O}-\text{H}$  oxygen (two lone pairs on that O), with the H attached to that same oxygen. Because two C-to-O bonds are equal length and the third ( $\text{C}-\text{OH}$ ) is longer, resonance exists between the two equivalent non-OH oxygens — shown either as two resonance structures or as one structure with a double-headed resonance arrow between those two oxygens. 1 point for a correct Lewis structure of  $\text{HCO}_3^-$ , 1 point for indicating resonance between the two equivalent (non-OH) oxygens.

## Solution 2

(f)

## Mark scheme

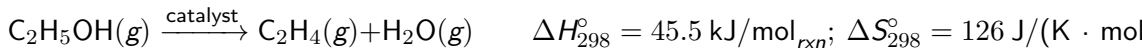
- $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$  (equivalently:  $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2$ ). 1 point for a correct, balanced net-ionic equation showing the acetate ion neutralizing the added  $\text{H}_3\text{O}^+/\text{H}^+$ , which is why the pH remains at 4.7 (buffer action).

## Question 2

2015 ■ Q2

Ethene,  $\text{C}_2\text{H}_4(g)$  (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol,  $\text{C}_2\text{H}_5\text{OH}(g)$  (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram above. The equation for the dehydration reaction is given below.

[Diagram of the lab synthesis setup: on the left, a test tube labeled "Test Tube" contains "Glass Wool with Ethanol" and "Solid Catalyst", heated from below by a "Bunsen Burner", both mounted on a stand. A delivery tube leads from the test tube on the right to a second, inverted test tube labeled "Ethene" that is collecting gas over water in a basin, also mounted on a stand.]



## Question 2

ethanol

ethene   water

A student added a 0.200 g sample of  $\text{C}_2\text{H}_5\text{OH}(l)$  to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the  $\text{C}_2\text{H}_5\text{OH}(l)$  evaporated and gas generation stopped. When the reaction stopped, the volume of collected gas was 0.0854 L at 0.822 atm and 305 K. (The vapor pressure of water at 305 K is 35.7 torr.)

**(a)(i)** Calculate the number of moles of  $\text{C}_2\text{H}_4(g)$  that are actually produced in the experiment and measured in the gas collection tube.

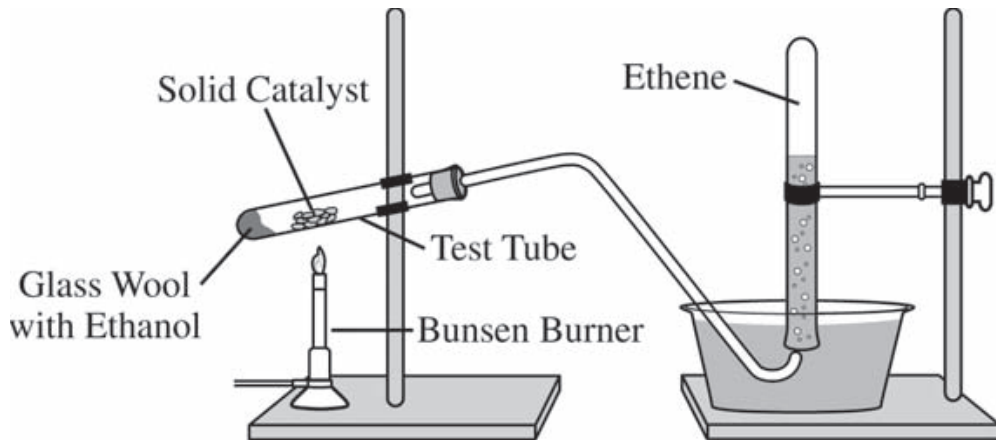
**(a)(ii)** Calculate the number of moles of  $\text{C}_2\text{H}_4(g)$  that would be produced if the dehydration reaction went to completion.



## Question 2



## Question 2

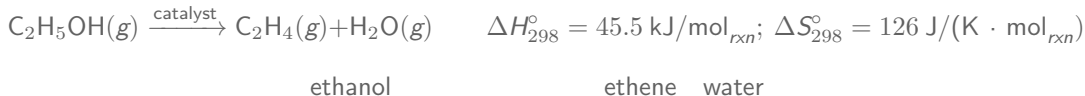


## Question 2

2015 ■ Q2

Ethene,  $\text{C}_2\text{H}_4(g)$  (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol,  $\text{C}_2\text{H}_5\text{OH}(g)$  (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram above. The equation for the dehydration reaction is given below.

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## Question 2

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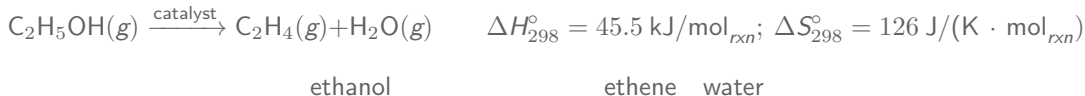
**(b)** Calculate the percent yield of  $\text{C}_2\text{H}_4(g)$  in the experiment.

## Question 2

2015 ■ Q2

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## Question 2

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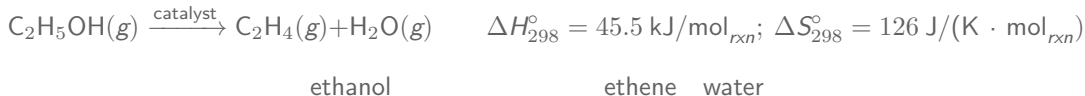
**(c)** Because the dehydration reaction is not observed to occur at 298 K, the student claims that the reaction has an equilibrium constant less than 1.00 at 298 K. Do the thermodynamic data for the reaction support the student's claim? Justify your answer, including a calculation of  $\Delta G_{298}^\circ$  for the reaction.

## Question 2

2015 ■ Q2

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**(d)** The Lewis electron-dot diagram for  $\text{C}_2\text{H}_4$  is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for  $\text{C}_2\text{H}_5\text{OH}$  by drawing in all of the electron pairs.

[Two boxes side by side. Left box: the completed Lewis structure of  $\text{C}_2\text{H}_4$  — two carbon atoms double-bonded to each other, each carbon also bonded to two hydrogen atoms (H H above, H H below), with all lone pairs and bonding pairs shown as dots. Right box: the skeletal (bonds-only, no lone pairs drawn) atom arrangement for  $\text{C}_2\text{H}_5\text{OH}$  — H H above the two carbons, "H C C O H" in a row, and H H below the first carbon — for the student to complete with electron pairs.]

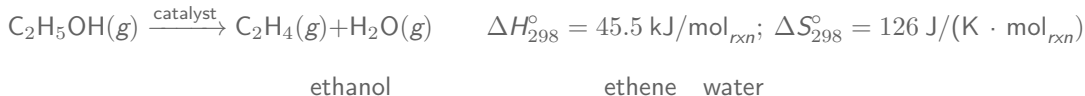


## Question 2

2015 ■ Q2

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## Question 2

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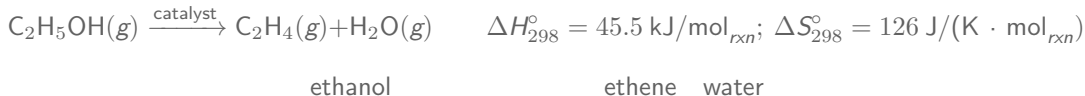
**(e)** What is the approximate value of the C–O–H bond angle in the ethanol molecule?

## Question 2

2015 ■ Q2

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**(f)** During the dehydration experiment,  $\text{C}_2\text{H}_4(g)$  and unreacted  $\text{C}_2\text{H}_5\text{OH}(g)$  passed through the tube into the water. The  $\text{C}_2\text{H}_4$  was quantitatively collected as a gas, but the unreacted  $\text{C}_2\text{H}_5\text{OH}$  was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

## Solution 2

(a)(i)

### Mark scheme

- First find the partial pressure of dry ethene by subtracting water's vapor pressure at 305 K from the total pressure:  $35.7 \text{ torr} \times (1 \text{ atm} / 760 \text{ torr}) = 0.0470 \text{ atm}$ ;  $P_{\text{ethene}} = P_{\text{total}} - P_{\text{water}} = 0.822 \text{ atm} - 0.0470 \text{ atm} = 0.775 \text{ atm}$  (1 point for this pressure calculation). Then apply the ideal gas law:  $n = PV/RT = (0.775 \text{ atm})(0.0854 \text{ L}) / [(0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(305 \text{ K})] = 0.00264 \text{ mol C}_2\text{H}_4$  actually produced and collected (1 point for the correct number of moles of ethene gas).

## Solution 2

(a)(ii)

### Mark scheme

- $0.200 \text{ g C}_2\text{H}_5\text{OH} \times (1 \text{ mol C}_2\text{H}_5\text{OH} / 46.1 \text{ g C}_2\text{H}_5\text{OH}) \times (1 \text{ mol C}_2\text{H}_4 / 1 \text{ mol C}_2\text{H}_5\text{OH}) = 0.00434 \text{ mol C}_2\text{H}_4$  would be produced if the dehydration reaction went to completion. 1 point for the correct number of moles of ethene produced.

## Solution 2

(b)

### Mark scheme

- Percent yield = (actual yield / maximum possible yield)  $\times$  100 = (0.00264 mol / 0.00434 mol)  $\times$  100 = 60.8%. 1 point for the correct percent yield.

## Solution 2

(c)

## Mark scheme

- Yes, the thermodynamic data support the student's claim.  $\Delta G_{298} = \Delta H - T \cdot \Delta S = 45.5 \text{ kJ/mol}_{\text{rxn}} - (298 \text{ K})(0.126 \text{ kJ/(K} \cdot \text{mol}_{\text{rxn}})) = 8.0 \text{ kJ/mol}_{\text{rxn}}$  (1 point for the correct calculation of  $\Delta G$ ). Because  $\Delta G_{298} > 0$ ,  $K_p = e^{(-\Delta G/RT)} < 1.00$ , which confirms the equilibrium constant is less than 1.00 at 298 K, supporting the student's claim (1 point for a valid justification linking a positive  $\Delta G$  to  $K < 1$ ).



## Solution 2

(d)

### Mark scheme

- The completed Lewis structure of  $\text{C}_2\text{H}_5\text{OH}$  (ethanol) must show all bonding pairs (the C-C bond, four C-H bonds, one C-O bond, and the O-H bond) plus the two nonbonding (lone) electron pairs on the oxygen atom; a line may be used in place of a dot pair. 1 point for a correct, complete diagram.

## Solution 2

(e)

### Mark scheme

- The C-O-H bond angle in ethanol is approximately 109 degrees, since the oxygen atom is roughly  $sp^3$ -hybridized (bent/tetrahedral electron geometry) with two lone pairs. 1 point is earned for any answer from 100 degrees to 115 degrees.

## Solution 2

### (f) Mark scheme

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- Ethene ( $\text{C}_2\text{H}_4$ ) is nonpolar, so it can only interact with polar water molecules through weak dipole/induced-dipole forces, making it only slightly soluble in water (1 point for comparing the solubility of ethene in water with the solubility of ethanol in water in terms of their difference in polarity). Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is polar and its  $-\text{OH}$  group can form hydrogen bonds with water molecules as it dissolves, making ethanol much more soluble in water; this is why the  $\text{C}_2\text{H}_4(\text{g})$  passing through the tube was quantitatively collected as a gas while the unreacted  $\text{C}_2\text{H}_5\text{OH}(\text{g})$  was not (1 point for describing the intermolecular forces between ethene and water as weak dipole/induced-dipole forces AND attributing ethanol's

## Solution 2

solubility in water to the hydrogen bonds formed between ethanol and water molecules).