

# Interactive Example Candidate Responses

## Paper 42 (May/June 2016), Question 5

### Cambridge International AS & A Level Chemistry 9701

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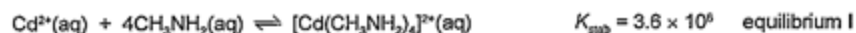
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5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.



(a) (i) Write an expression for the stability constant,  $K_{\text{stab}}$ , for equilibrium I, and state its units.

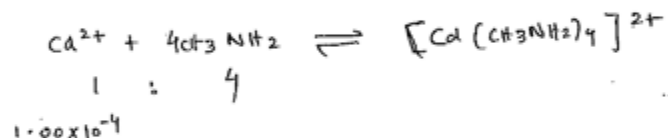
$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}}{[\text{CH}_3\text{NH}_2]^4 [\text{Cd}^{2+}]}$$

units  $\text{mol}^{-4} \text{dm}^{12}$  [2]

Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.

(ii) In a sample of ground water the concentration of  $\text{Cd}^{2+}(\text{aq})$  is  $1.00 \times 10^{-4} \text{mol dm}^{-3}$ .

Calculate the concentration of  $\text{CH}_3\text{NH}_2(\text{aq})$  needed to reduce the concentration of  $\text{Cd}^{2+}(\text{aq})$  in this dilute solution by a factor of one thousand.  $\times 1000 \rightarrow 1 \times 10^{-7}$



$$(1 \times 10^{-4}) - 4x = (1 \times 10^{-7}) =$$

$$4x = 9.99 \times 10^{-5}$$

$$x = 2.4975 \times 10^{-5}$$

$$= 2.50 \times 10^{-5} \text{mol dm}^{-3} \quad \text{concentration of } \text{CH}_3\text{NH}_2(\text{aq}) = 2.50 \text{ mol dm}^{-3} \quad [2]$$

Your  
Mark

5(a)(i)

5(a)(ii)

5(b)(i)

5(b)(ii)

5(b)(iii)

5(b)(iv)

Q5	Mark scheme
(a)(i)	$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$ <p>units: <math>\text{mol}^{-4} \text{dm}^{12}</math> [2]</p>
(a)(ii)	$\text{Cd}^{2+} + 4\text{CH}_3\text{NH}_2 \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ <p>at start: <math>1 \times 10^{-4}</math> <span style="margin-left: 100px;">0</span></p> <p>at eqm: <math>1 \times 10^{-7}</math> <span style="margin-left: 10px;">y</span> <span style="margin-left: 10px;"><math>1 \times 10^{-4} - 4y</math></span> <span style="margin-left: 10px;"><math>1 \times 10^{-7}</math></span></p> <p style="text-align: center;"><b>or <math>9.99 \times 10^{-5}</math> or <math>1.0 \times 10^{-4}</math></b></p> <p><math>9.99 \times 10^{-5} / (y^4 \times 10^{-7}) = 3.6 \times 10^6</math></p> <p>and <math>y = 4\sqrt[4]{(9.99 \times 10^{-5}) / (1 \times 10^{-7} \times 3.6 \times 10^6)} = \mathbf{0.129 / 0.13}</math> [2]</p>
(b)(i)	<p>(each complex is formed by) making (4 x) N-Cd bonds and breaking (6 x) O-Cd bonds</p> <p><b>or</b> same types of / similar bonds forming / breaking</p> <p><b>or</b> same number of bonds forming / breaking [1]</p>
(b)(ii)	$\Delta S = (\Delta H - \Delta G) / T = (60.7 - 56.5) \times 1000 / 298 = (+) \mathbf{14} / (+) \mathbf{14.1}$ [1]
(b)(iii)	<p>fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder)</p> <p><b>or</b> one en displaces two <math>\text{H}_2\text{O}</math> whereas one <math>\text{CH}_3\text{NH}_2</math> only displaces one <math>\text{H}_2\text{O}</math> [1]</p>
(b)(iv)	<p>The <math>[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}</math> / equilibrium 2 complex (is more stable) because:</p> <p><i>either</i> <math>K_{\text{stab}}</math> is greater <i>or</i> <math>\Delta G^\ominus</math> is more negative. [1]</p> <p style="text-align: right;"><b>[Total: 8]</b></p>

(b) Values for  $\Delta H^\circ$  and  $\Delta G^\circ$  for equilibria I and II, and the value of  $\Delta S^\circ$  for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

equilibrium	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$
I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

(i) Suggest a reason why the  $\Delta H^\circ$  values for the two equilibria are very similar.

In both complexes, 4 nitrogen atoms donate four lone pairs to make dative bonds with cadmium. So the energy released is very similar.

(ii) Calculate  $\Delta S^\circ$  for equilibrium II.

$$\Delta G = \Delta H - T\Delta S$$

$$(-60.7 \times 1000) = (-56.5 \times 1000) - (298)(\Delta S)$$

$$\Delta S = 14.09395$$

$$= 14.1 \text{ JK}^{-1} \text{mol}^{-1}$$

$$\Delta S^\circ = +14.1 \text{ JK}^{-1} \text{mol}^{-1} \quad [1]$$

(iii) Suggest a reason for the difference between the  $\Delta S^\circ$  you have calculated for equilibrium II and that for equilibrium I given in the table.

Increase in entropy for equilibrium 2 because fewer moles of reactant (2) converting to product (1). In equilibrium 1, a decrease in entropy because more moles of reactant (5) converting to product (1).

(iv) Which of the two complexes is the more stable? Give a reason for your answer.

The complex from equilibrium 2 because its formation is favored energetically ( $\Delta G$  is much more negative so reaction is more spontaneous in forward direction) and also because its  $K_{\text{stab}}$  value is higher. [Total: 8]

Your  
Mark

5(a)(i)

5(a)(ii)

5(b)(i)

5(b)(ii)

5(b)(iii)

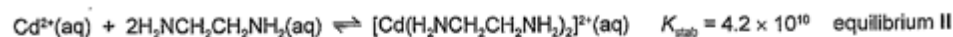
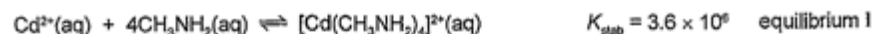
5(b)(iv)

## Q5 Mark scheme

(a)(i)	$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$ <p>units: <math>\text{mol}^{-4} \text{dm}^{12}</math></p>	[2]
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(b)(ii)	$\Delta S = (\Delta H - \Delta G) / T = (60.7 - 56.5) \times 1000 / 298 = (+)14 / (+)14.1$	[1]
(b)(iii)	<p>fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder)</p> <p><b>or</b> one en displaces two <math>\text{H}_2\text{O}</math> whereas one <math>\text{CH}_3\text{NH}_2</math> only displaces one <math>\text{H}_2\text{O}</math></p>	[1]
(b)(iv)	<p>The <math>[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}</math> / equilibrium 2 complex (is more stable) because:</p> <p><i>either</i> <math>K_{\text{stab}}</math> is greater <i>or</i> <math>\Delta G^\circ</math> is more negative.</p>	[1]

[Total: 8]

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$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$$

$\frac{(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^4} \Rightarrow \text{mol}^{-4} \text{ dm}^{12}$   
 units  $\text{mol}^{-4} \text{ dm}^{12}$  [2]

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(ii) In a sample of ground water the concentration of  $\text{Cd}^{2+}(\text{aq})$  is  $1.00 \times 10^{-4} \text{ mol dm}^{-3}$ .

Calculate the concentration of  $\text{CH}_3\text{NH}_2(\text{aq})$  needed to reduce the concentration of  $\text{Cd}^{2+}(\text{aq})$  in this dilute solution by a factor of one thousand.

$$\frac{1.00 \times 10^{-4} \times 4}{1000} \Rightarrow 4 \times 10^{-7}$$

concentration of  $\text{CH}_3\text{NH}_2(\text{aq}) = 4 \times 10^{-7} \text{ mol dm}^{-3}$  [2]

Your  
Mark

5(a)(i)

5(a)(ii)

5(b)(i)

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5(b)(iii)

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Q5	Mark scheme
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<b>[Total: 8]</b>	

(b) Values for  $\Delta H^\circ$  and  $\Delta G^\circ$  for equilibria I and II, and the value of  $\Delta S^\circ$  for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

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I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

(i) Suggest a reason why the  $\Delta H^\circ$  values for the two equilibria are very similar.

The values are very similar because the energy required by reactant to form a product for both equilibrium [1] is nearly same.

(ii) Calculate  $\Delta S^\circ$  for equilibrium II.

$$\Delta G = -T\Delta S$$

$$\Delta G = \Delta H_{\text{reaction}} - T\Delta S$$

$$-60.7 \times 1000 = -56.5 \times 1000 - 298 \Delta S$$

$$\Delta S = \frac{(-60.7 \times 1000) + (56.5 \times 1000)}{-298} = \Delta S$$

$$\Delta S = -14.1 \text{ JK}^{-1} \text{mol}^{-1} [1]$$

(iii) Suggest a reason for the difference between the  $\Delta S^\circ$  you have calculated for equilibrium II and that for equilibrium I given in the table.

=) The difference in equilibrium of II and equilibrium I is because equilibrium II is more random and spontaneous than that of equilibrium I. [1]

(iv) Which of the two complexes is the more stable? Give a reason for your answer.

=) Equilibrium II is more stable (1,2-diaminoethane) as  $K_{\text{stab}}$  is more and Gibbs energy also shows more energy [1] or work is to be done in experiment II.

[Total: 8]

Your  
Mark

5(a)(i)

5(a)(ii)

5(b)(i)

5(b)(ii)

5(b)(iii)

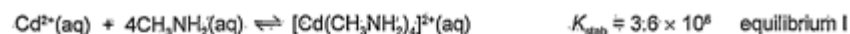
5(b)(iv)

### Q5 Mark scheme

(a)(i)	$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$ <p>units: <math>\text{mol}^{-4} \text{dm}^{12}</math></p>	[2]
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(b)(i)	<p>(each complex is formed by) making (4 x) N-Cd bonds and breaking (6 x) O-Cd bonds</p> <p>or same types of / similar bonds forming / breaking</p> <p>or same number of bonds forming / breaking</p>	[1]
(b)(ii)	$\Delta S = (\Delta H - \Delta G) / T = (60.7 - 56.5) \times 1000 / 298 = (+)14 / (+)14.1$	[1]
(b)(iii)	<p>fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder)</p> <p>or one en displaces two <math>\text{H}_2\text{O}</math> whereas one <math>\text{CH}_3\text{NH}_2</math> only displaces one <math>\text{H}_2\text{O}</math></p>	[1]
(b)(iv)	<p>The <math>[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}</math> / equilibrium 2 complex (is more stable) because:</p> <p>either <math>K_{\text{stab}}</math> is greater or <math>\Delta G^\circ</math> is more negative.</p>	[1]

[Total: 8]

5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.



(a) (i) Write an expression for the stability constant,  $K_{\text{stab}}$ , for equilibrium I, and state its units.

$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]}{[\text{Cd}][\text{CH}_3\text{NH}_2]^4}$$

units  $\text{mol}^{-4} \text{dm}^{12}$  [2]

Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.

(ii) In a sample of ground water the concentration of  $\text{Cd}^{2+}(\text{aq})$  is  $1.00 \times 10^{-4} \text{mol dm}^{-3}$ .

Calculate the concentration of  $\text{CH}_3\text{NH}_2(\text{aq})$  needed to reduce the concentration of  $\text{Cd}^{2+}(\text{aq})$  in this dilute solution by a factor of one thousand.

$$\frac{(4.2 \times 10^{10})}{1000} = \frac{1}{(1 \times 10^{-4})x^4}$$

$$\frac{(3.6 \times 10^6)}{1000} = \frac{1}{(1 \times 10^{-4})x}$$

concentration of  $\text{CH}_3\text{NH}_2(\text{aq}) = 0.36 \text{mol dm}^{-3}$  [2]

Your  
Mark

5(a)(i)

5(a)(ii)

5(b)(i)

5(b)(ii)

5(b)(iii)

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Q5	Mark scheme
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- (b) Values for  $\Delta H^\circ$  and  $\Delta G^\circ$  for equilibria I and II, and the value of  $\Delta S^\circ$  for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

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I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

- (i) Suggest a reason why the  $\Delta H^\circ$  values for the two equilibria are very similar.

Because it has the same transition metal involved. [1]

- (ii) Calculate  $\Delta S^\circ$  for equilibrium II.

$$\begin{aligned} \Delta S^\circ &= \frac{-\Delta G^\circ - \Delta H^\circ}{T} \\ &= \frac{-(-60.7) - (-56.5)}{298} \\ &= \frac{-60.7 + 56.5}{298} \\ &= \frac{-4.2}{298} \\ &= -14.1 \text{ JK}^{-1} \text{mol}^{-1} \end{aligned}$$

- (iii) Suggest a reason for the difference between the  $\Delta S^\circ$  you have calculated for equilibrium II and that for equilibrium I given in the table.

More Equilibrium I has more disorder ~~the~~ arrangement on its reactant side while 2 has more disorder on its product side. [1]

- (iv) Which of the two complexes is the more stable? Give a reason for your answer.

Equilibrium I  $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$  because of its higher  $K_{\text{stab}}$ . [1]

[Total: 8]

Your  
Mark

5(a)(i)

5(a)(ii)

5(b)(i)

5(b)(ii)

5(b)(iii)

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(b)(i)	<p>(each complex is formed by) making (4 x) N-Cd bonds and breaking (6 x) O-Cd bonds</p> <p><b>or</b> same types of / similar bonds forming / breaking</p> <p><b>or</b> same number of bonds forming / breaking</p>	[1]
(b)(ii)	$\Delta S = (\Delta H - \Delta G) / T = (60.7 - 56.5) \times 1000 / 298 = (+)14 / (+)14.1$	[1]
(b)(iii)	<p>fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder)</p> <p><b>or</b> one en displaces two <math>\text{H}_2\text{O}</math> whereas one <math>\text{CH}_3\text{NH}_2</math> only displaces one <math>\text{H}_2\text{O}</math></p>	[1]
(b)(iv)	<p>The <math>[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}</math> / equilibrium 2 complex (is more stable) because:</p> <p><i>either</i> <math>K_{\text{stab}}</math> is greater <i>or</i> <math>\Delta G^\circ</math> is more negative.</p>	[1]

[Total: 8]



Cambridge Assessment International Education  
The Triangle Building, Shaftesbury Road, Cambridge, CB2 8EA, United Kingdom  
t: +44 1223 553554 f: +44 1223 553558  
e: [info@cambridgeinternational.org](mailto:info@cambridgeinternational.org) [www.cambridgeinternational.org](http://www.cambridgeinternational.org)

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