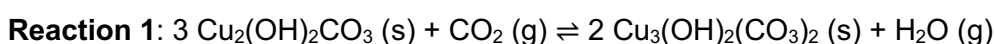


- 1 Malachite and azurite are copper-containing minerals found in damp environments. The following table shows some data for malachite and azurite, as well as some other compounds.

Substance	Standard enthalpy of formation / kJ mol <sup>-1</sup>
Malachite, Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub> (s)	-1046.5
Azurite, Cu <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> (s)	-1629.5
H <sub>2</sub> O (g)	-248.12
CO <sub>2</sub> (g)	-393.51

Malachite and azurite undergo an equilibrium reaction below:



- (a) At standard conditions, a sample of malachite and azurite is in *dynamic equilibrium*.

- (i) Define *dynamic equilibrium*. [1]

B1 for both points

- Where the rate of forward and backward reaction is the same and non-zero
- The composition of reactants and products has no net change

- (ii) Define *Le Chatelier's principle*. [1]

B1 – When a system at dynamic equilibrium encounters a change in conditions that shifts the position of equilibrium, the position of equilibrium will shift as to reduce that change.

- Try not to use 'eliminate', 'counteract' is fine.
- The best definition for this is one that's quoted in your school notes

- (iii) Explain changes to the composition of the sample of malachite and azurite when the following changes are applied separately:

- (1) an increase in partial pressure of CO<sub>2</sub> (g); and
- (2) an increase in the temperature such that malachite and azurite does not decompose.

[4]

For (1):

- B1 – Increase in partial pressure of carbon dioxide results in the position of equilibrium shifting right to reduce the initial increase in partial pressure of carbon dioxide, so more azurite will be formed, and less malachite is present in the sample

For (2):

- M1 – Calculates enthalpy change of forward reaction, with units

$$\Delta H = -1629.5 \times 2 - 248.12 + 1046.5 \times 3 + 393.51 = +25.89 \text{ kJ mol}^{-1}$$

3 s.f. not required, deduct 0.5 pts for wrong/no units

- B1 – Correct deduction of position of equilibrium with explanation  
The endothermic forward reaction is favoured to absorb the additional heat from the temperature increase, resulting in the position of equilibrium shifting right.
- B1 – Correct deduction of composition  
Hence, more azurite will be formed, and less malachite will be present in the sample.

(b) The equilibrium constant of **Reaction 1** is defined as

$$K = \frac{p_{\text{H}_2\text{O}} \times \chi_{\text{azurite}}^2}{p_{\text{CO}_2} \times \chi_{\text{malachite}}^3}$$

where  $\chi$  represents the mole fraction of a solid, with respect to the total number of moles of solid in the sample.

(i) Given that the standard entropy change of **Reaction 1** is  $-15.01 \text{ J mol}^{-1} \text{ K}^{-1}$ , what can you conclude about the position of equilibrium at 25 degrees Celsius? [2]

M1 – Calculates  $\Delta G$  (award ECF)

$$\Delta G = \Delta H - T\Delta S = +25.89(10^3) - 298(-15.01) = +30360 \text{ J mol}^{-1}$$

3 s.f. not required, deduct 0.5 pts for wrong/no units

A1 – Correct deduction (no ECF if M1 mark is not scored)

Hence, the position of equilibrium is (far) to the **left** at 25 degrees Celsius.

(ii) The following equation relates the standard change in Gibbs Free Energy of a reaction to its equilibrium constant.

$$\Delta G = -RT \ln K$$

50.00 g of pure malachite was left in the open at 25 degrees Celsius and atmospheric pressure. The atmosphere contains 0.04% carbon dioxide and 2.5% water vapour.

At equilibrium, it was found that there are  $b$  moles of azurite.

Show that  $b$  satisfies the equation below. [3]

$$\frac{b^2 \left(0.226 - \frac{1}{2}b\right)}{\left(0.226 - \frac{3}{2}b\right)^3} = X$$

where  $X$  is a constant to be determined.

Do **not** solve for  $b$ .

M1 – Able to derive the quantity 0.226 and  $\frac{3}{2}b$

$$n_{\text{malachite}} = \frac{50.00}{2(63.5) + 2(1.0 + 16.0) + 12.0 + 3(16.0)} = 0.2262 \text{ mol}$$

From Reaction 1

$$n_{\text{malachite}} (\text{end}) = \left(0.2262 - \frac{3}{2}b\right) \text{ mol}$$

M1 – Correct substitution and manipulation to derive the left-hand side expression

$$K = \frac{p_{\text{H}_2\text{O}} \times \chi_{\text{azurite}}^2}{p_{\text{CO}_2} \times \chi_{\text{malachite}}^3} = \frac{2.5 \times \left(\frac{b}{0.2262 - \frac{3}{2}b + b}\right)^2}{0.04 \times \left(\frac{0.226 - \frac{3}{2}b}{0.2262 - \frac{3}{2}b + b}\right)^3} = \frac{b^2 \left(0.2262 - \frac{1}{2}b\right)}{\left(0.2262 - \frac{3}{2}b\right)^3} \times 62.5$$

Do note that while the partial pressure can be explicitly computed, the ratio of the partial pressures is just needed here, hence the direct use of 2.5 and 0.04.

MA1 – Finds  $X$  and shows final expression, corrected to 3 s.f. (Award ECF)

$$\frac{b^2 \left(0.226 - \frac{1}{2}b\right)}{\left(0.226 - \frac{3}{2}b\right)^3} = X = \frac{e^{-\frac{\Delta G}{RT}}}{62.5} = \frac{e^{-\frac{30360}{8.31 \times (25+273)}}}{62.5} = 4.74 \times 10^{-6}$$

Candidates should have a rather good grasp of algebraic manipulation from O Level Mathematics as such basic knowledge is assumed in H2 Chemistry.

- (c) In reality, a sample containing malachite and azurite at equilibrium will contain mostly malachite. The mass of azurite can be considered as negligible compared to that of malachite.
- (i) A 100.00 g sample of pure azurite was left in an atmosphere that always contains the same percentage, by amount, of carbon dioxide and water vapour. Find the mass loss of the sample at equilibrium.

[2]

The way used here is less prone to errors

M1 – Calculates mass loss by proportion

Mass loss (by proportion of original mass)

$$\begin{aligned} &= \frac{12.0 + 2(16.0) - 16.0 - 2(1.0)}{3[2(63.5) + 2(1.0 + 16.0) + 12.0 + 3(16.0)] + 12.0 + 2(16.0)} \\ &= 0.036775 \end{aligned}$$

A1 – Correct answer

Since the sample contains mostly malachite instead of azurite, we can assume that the sample contains only malachite. Hence, the mass loss is 3.68 g.

(ii) Complete the graphs below in the scenario for (i).

[2]

At time  $t$ , the system was at equilibrium.

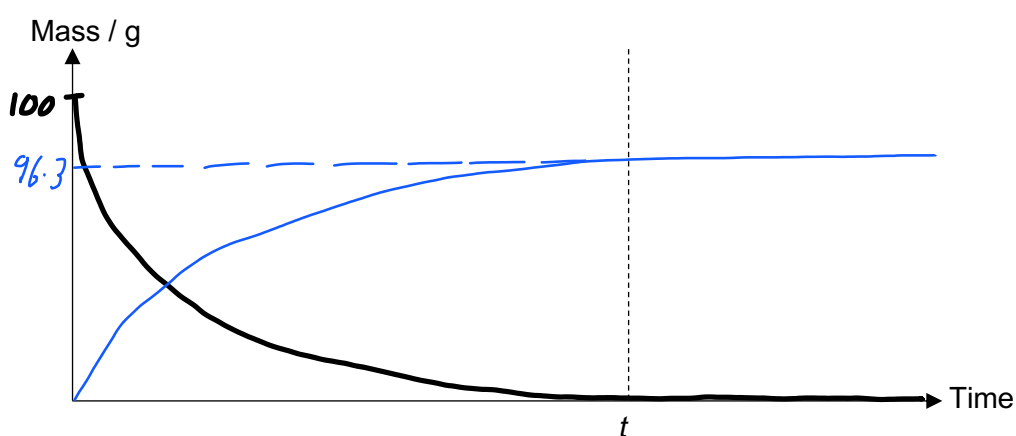
1. Draw 2 lines, one for the mass of azurite, one for the mass of malachite.

G1 – Correct trend and correct initial and final mass indicated

Blue: Malachite

Black: Azurite

Straight horizontal lines after  $t$



2. Draw 2 lines, one for the rate of forward reaction, one for the rate of backward reaction of **Reaction 1**.

G1 – Correct trend and final rates must be the same and constant

Blue: Backward

Red: Forward

