

1. NO(g), H<sub>2</sub>(g), N<sub>2</sub>(g) and H<sub>2</sub>O(g) exist in equilibrium:



At room temperature and pressure, the equilibrium lies well to the right-hand side.

Which of the following could be the equilibrium constant for this equilibrium?

- A  $1.54 \times 10^{-3} \text{ mol dm}^{-3}$   
 \* B  $6.50 \times 10^2 \text{ mol dm}^{-3}$   
 C  $1.54 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$   
 \* D  $6.50 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$

$$K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]^2}$$

Your answer

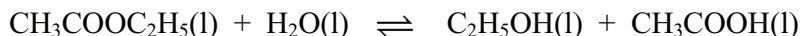
A  B  C  D



[1]

units =  $\frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3} \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \frac{1}{\text{mol dm}^{-3}} = \text{mol}^{-1} \text{ dm}^3$

2. Two students set up the **equilibrium** system below.



The students **titrated** samples of the **equilibrium mixture with sodium hydroxide, NaOH(aq)**, to determine the **concentration** of **CH<sub>3</sub>COOH**.

The students used their results to calculate a **value for K<sub>c</sub>**.

The students' values for **K<sub>c</sub>** were different.

Which of the reason(s) below could explain **why** the calculated values for **K<sub>c</sub>** were different?

SAME RATIOS  
↑↑

- ✓ 1: Each student carried out their experiment at a **different temperature**.
- ✗ 2: Each student used a **different concentration of NaOH(aq)** in their titration.
- ✗ 3: Each student titrated a **different volume** of the **equilibrium mixture**.

would need ↑ / ↓ volume of NaOH so some moles would react.

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

K<sub>c</sub> is only affected by changes in temperature (affects ⇌ ratios that don't restore).

Your answer

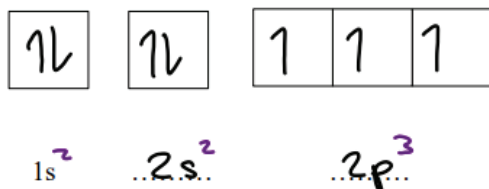
would need ↑ / ↓ volume of NaOH but same moles would react ⇒ SAME RATIOS

[1]

3. Ammonia is a gas with covalently-bonded molecules consisting of nitrogen and hydrogen atoms.

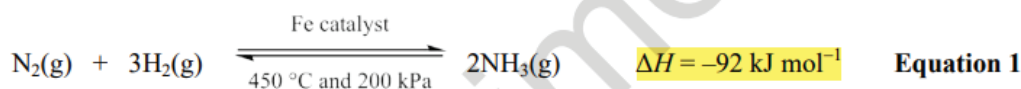
(a) Show the electron configuration of a nitrogen atom using 'electron-in-box' diagrams.

Label each sub-shell.



Hund's Rule  
fill each orbital  
singularly before  
filling an orbital  
with 2 electrons [2]

(b) Ammonia can be made from the reaction of nitrogen and hydrogen in the Haber process.



What effect will increasing the temperature have on the composition of the equilibrium mixture and on the value of the equilibrium constant?

Explain your answer.

The forward reaction is exothermic so increasing temperature favours the backwards reaction, so more  $\text{N}_2$  and  $\text{H}_2$  produced so the value of the equilibrium constant will decrease. [2]

- (c) A chemist mixes together 0.450 mol  $N_2$  with 0.450 mol  $H_2$  in a sealed container.

The mixture is heated and allowed to reach equilibrium.

At equilibrium, the mixture contains 0.400 mol  $N_2$  and the total pressure is 500 kPa.

Calculate  $K_p$ .

Show all your working.

Include units in your answer.

$N_2$	$H_2$	$NH_3$
I 0.450	0.450	0
C -0.050	-0.150	+0.100
E 0.400	0.300	0.100

$$P(N_2) = \frac{0.400}{0.800} \times 500 = 250 \text{ kPa}$$

$$P(H_2) = \frac{0.300}{0.800} \times 500 = 187.5 \text{ kPa}$$

*Partial pressure = mol fraction × total pressure*

$$P(NH_3) = \frac{0.100}{0.800} \times 500 = 62.5 \text{ kPa}$$

$$K_p = \frac{P(NH_3)^2}{P(N_2) \times P(H_2)^3} = \frac{62.5^2}{250 \times 187.5^3} = 2.37 \times 10^{-6} \text{ kPa}^{-2}$$

$$\frac{\text{kPa}^2}{\text{kPa} \times \text{kPa}^3} = \frac{\text{kPa}^2}{\text{kPa}^4} = \frac{1}{\text{kPa}^2}$$

$$K_p = 2.37 \times 10^{-6} \text{ units } \text{kPa}^{-2} \quad [5]$$

- (d) A chemical company receives an order to supply  $1.96 \times 10^{10} \text{ dm}^3$  of ammonia at room temperature and pressure. The Haber process produces a 95.0% yield.

$$n = \frac{\text{volume (dm}^3\text{)}}{24}$$

Calculate the mass of hydrogen, in tonnes, required to produce the ammonia.

Give your answer to three significant figures.

$$n(\text{NH}_3) = \frac{1.96 \times 10^{10}}{24} = 8.167 \times 10^8 \text{ mol}$$



$$n(\text{H}_2) = \frac{8.167 \times 10^8}{2} \times 3 = 1.225 \times 10^9 \text{ mol}$$

$$2 \times 1.225 \times 10^9 = 2.450 \times 10^9 \text{ g}$$

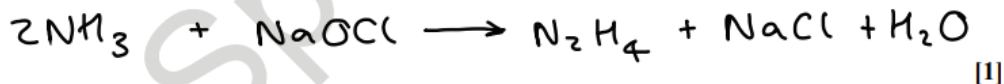
$$\text{mass of H}_2 = \frac{2.450 \times 10^9}{1 \times 10^6} = 2450 \text{ tonnes}$$

$$\frac{2450 \times 100}{95} = 2580 \text{ tonnes}$$

required mass of hydrogen = ..... 2580 ..... tonnes [3]

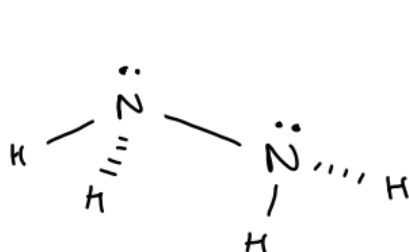
- (e) (i) Hydrazine,  $\text{N}_2\text{H}_4$ , is used as a rocket fuel. Hydrazine can be prepared from the reaction of ammonia with sodium chlorate(I). There are two other products in the reaction.

Write an equation for this reaction.



- (ii) Using the electron pair repulsion theory, draw a 3-D diagram of a molecule of hydrazine.

Predict the H-N-H bond angle around each nitrogen atom.



3bp: 1 lp pyramidal  
107°

H-N-H bond angle: ..... 107° ..... [2]

4. A mixture of  $N_2$  and  $O_2$  gases has a total pressure of 1.42 atm.  
The mole fraction of  $N_2$  is 0.700.

What is the partial pressure, in atm, of  $O_2$  in the mixture?

- A 0.211  
B 0.426  
C 0.493  
D 0.994

$$1 - 0.7 = 0.3 \text{ mole fraction of } O_2$$

$$0.3 \times 1.42 = 0.426 \text{ atm}$$

Your answer

B

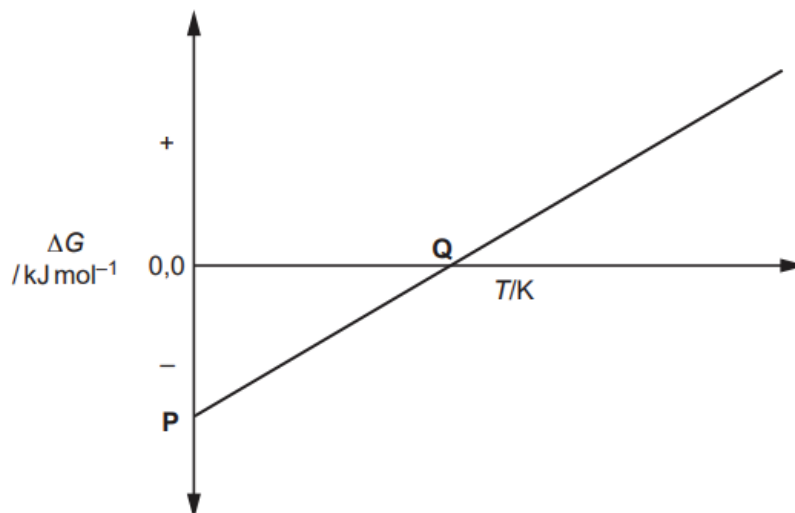
[1]

5. This question is about free energy changes,  $\Delta G$ , enthalpy changes,  $\Delta H$ , and temperature,  $T$ .

(a) The Gibbs' equation is shown below.

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

A chemist investigates a reaction to determine how  $\Delta G$  varies with  $T$ . The results are shown in **Fig. 18.1**.



**Fig. 18.1**

What is significant about the gradient of the line and the values **P** and **Q** shown in **Fig. 18.1**? Explain your reasoning.

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

$$y = c + mx$$

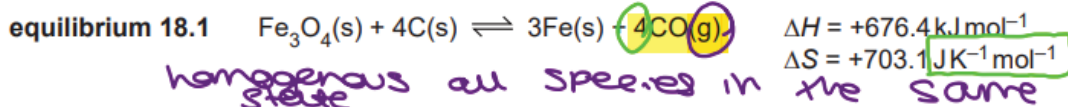
$$\text{gradient} = -\Delta S$$

$$P \text{ (y intercept)} = \Delta H$$

Q = Temperature where feasibility changed

[4]

- (b) Iron can be extracted from its ore  $\text{Fe}_3\text{O}_4$  using carbon. Several equilibria are involved including **equilibrium 18.1**, shown below.



- (i) Why is **equilibrium 18.1** a **heterogeneous** equilibrium?

*species in different states/phases*

..... [1]

- (ii) Write the expression for  $K_p$  for **equilibrium 18.1**.

$$K_p = P(\text{CO}(\text{g}))^4 \leftarrow \text{stoichiometry}$$

[1]

- (iii) The forward reaction in **equilibrium 18.1** is only feasible at high temperatures.

- Show that the forward reaction is **not** feasible at  $25^\circ\text{C}$ .  $\leftarrow +273 = 298 \text{ K}$
- Calculate the **minimum temperature**, in K, for the forward reaction to be feasible.

$$\uparrow$$

$$\frac{\Delta H}{\Delta S}$$

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

$$\Delta G = 676.4 - 298 \times 0.7031 = 467 \text{ kJ mol}^{-1}$$

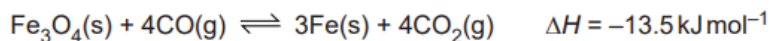
$$\Delta G > 0 \quad \text{so not feasible}$$

$$\text{min. temp} = \frac{676.4}{0.7031} = 962 \text{ K}$$

minimum temperature = 962 ..... K [3]



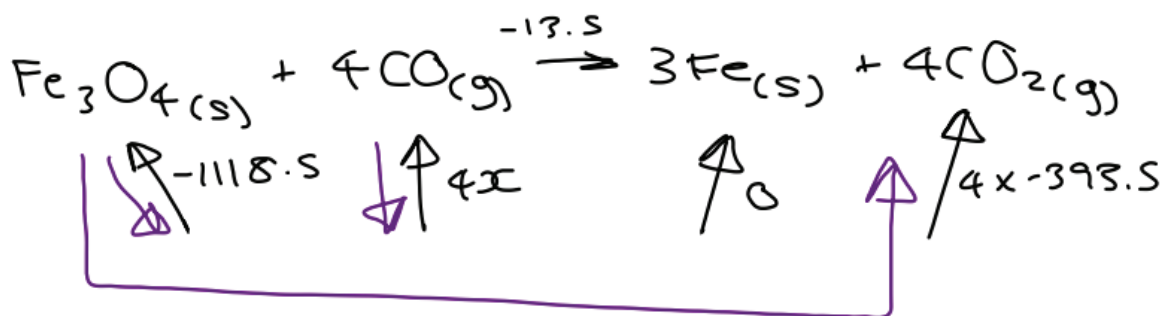
(iv) Another equilibrium involved in the extraction of iron from  $\text{Fe}_3\text{O}_4$  is shown below.



Enthalpy changes of formation,  $\Delta_f H$ , for  $\text{Fe}_3\text{O}_4(\text{s})$  and  $\text{CO}_2(\text{g})$  are shown in the table.

Compound	$\Delta_f H / \text{kJ mol}^{-1}$
$\text{Fe}_3\text{O}_4(\text{s})$	-1118.5
$\text{CO}_2(\text{g})$	-393.5

Calculate the enthalpy change of formation,  $\Delta_f H$ , for  $\text{CO}(\text{g})$ .



$$(1118.5 - 4x) + (0 + (4x - 393.5)) = -13.5$$

$$1118.5 - 4x = 1560.5$$

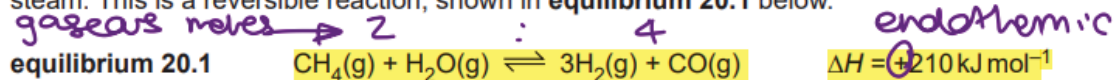
$$-4x = 442$$

$$x = -110.5 \text{ kJ mol}^{-1}$$

$$\Delta_f H, \text{ for CO}(\text{g}) = \dots -110.5 \dots \text{ kJ mol}^{-1} \text{ [3]}$$

6. This question is about equilibrium reactions.

- (a) Hydrogen gas is manufactured by the chemical industry using the reaction of methane and steam. This is a reversible reaction, shown in **equilibrium 20.1** below.



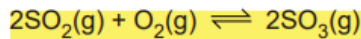
Explain, in terms of le Chatelier's principle, the conditions of pressure and temperature for a maximum yield of hydrogen from **equilibrium 20.1**, and explain why the operational conditions used by the chemical industry may be different.

forward reaction is endothermic  
 so increase temperature

right has more gaseous moles  
 so low pressure conditions

low pressure = slow rate  
 high temperature = uses lots of  
 energy / fuel [4]

- (b) A chemist investigates the equilibrium reaction between sulfur dioxide, oxygen, and sulfur trioxide, shown below.



$$\frac{1000}{400} = 2.5$$

- The chemist mixes together  $\text{SO}_2$  and  $\text{O}_2$  with a catalyst.
- The chemist compresses the gas mixture to a volume of  $400 \text{ cm}^3$ .
- The mixture is heated to a constant temperature and is allowed to reach equilibrium without changing the total gas volume.

The equilibrium mixture contains  $0.0540 \text{ mol SO}_2$  and  $0.0270 \text{ mol O}_2$ .

At the temperature used, the numerical value for  $K_c$  is  $3.045 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ .

- (i) Write the expression for  $K_c$  and the units of  $K_c$  for this equilibrium.

$$K_c = \frac{[\text{SO}_3]^2 \text{ mol}^2 \text{ dm}^{-6}}{[\text{SO}_2]^2 [\text{O}_2] \text{ mol}^3 \text{ dm}^3} \quad \text{units: mol}^{-1} \text{ dm}^3 \quad [2]$$

- (ii) Determine the amount, in mol, of  $\text{SO}_3$  in the equilibrium mixture at this temperature.

Give your final answer to an **appropriate number of significant figures**.

Show all your working.

$$[\text{SO}_2] = 0.054 \times 2.5 = 0.135 \text{ mol dm}^{-3}$$

$$[\text{O}_2] = 0.027 \times 2.5 = 0.0675 \text{ mol dm}^{-3}$$

$$3.045 \times 10^4 = \frac{[\text{SO}_3]^2}{[0.135]^2 [0.0675]}$$

$$[\text{SO}_3] = \sqrt{3.045 \times 10^4 \times ([0.135]^2 [0.0675])}$$

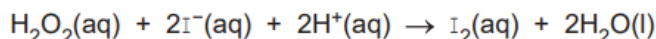
$$[\text{SO}_3] = 6.12 \text{ mol dm}^{-3}$$

$$\frac{6.12}{2.5} = 2.45 \text{ mol (3sf.)}$$

equilibrium amount of  $\text{SO}_3 = \dots\dots\dots 2.45 \dots\dots\dots \text{ mol [4]}$

7. This question is about reactions of hydrogen peroxide,  $\text{H}_2\text{O}_2$ .

(a) Hydrogen peroxide,  $\text{H}_2\text{O}_2$ , iodide ions,  $\text{I}^-$ , and acid,  $\text{H}^+$ , react as shown in the equation below.



A student carries out several experiments at the same temperature, using the initial rates method, to determine the rate constant,  $k$ , for this reaction.

The results are shown below.

Experiment	Initial concentrations			Rate / $10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$
	$[\text{H}_2\text{O}_2(\text{aq})]$ / $\text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})]$ / $\text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})]$ / $\text{mol dm}^{-3}$	
1	0.0100	0.0100	0.100	2.00
2	0.0100	0.0200	0.100	4.00
3	0.0200	0.0100	0.100	4.00
4	0.0200	0.0100	0.200	4.00

*Handwritten notes: 1st order (pointing to [H2O2] and [I-]), 0th order (pointing to [H+]).*

(i) Determine the rate equation and calculate the rate constant,  $k$ , including units.

$$\text{rate} = k [\text{H}_2\text{O}_2]^1 [\text{I}^-]^1 [\text{H}^+]^0$$

$$\text{rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

$$\frac{2 \times 10^{-6}}{0.01 \times 0.01} = 0.02$$

$$\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$$

↑

$$k = 0.02 \text{ units mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

(ii) The rate constant,  $k$ , for this reaction is determined at different temperatures,  $T$ .

Explain how the student could determine the activation energy,  $E_a$ , for the reaction graphically using values of  $k$  and  $T$ .

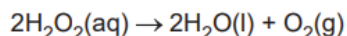
plot a graph of  $\ln k$  against  
 $1/T$  and measure the  
gradient.

$$E_a = \text{gradient} \times R$$

$$\ln k = \frac{-E_a}{RT} + \ln A$$

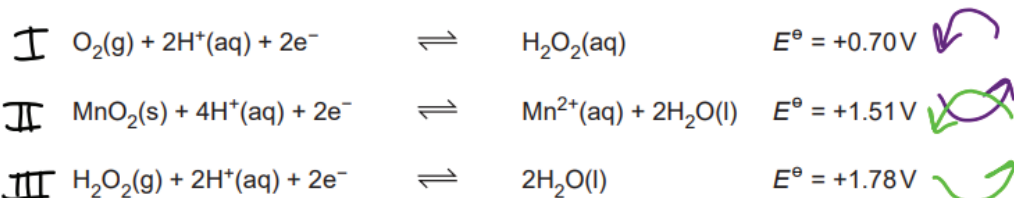
[3]

(b) Solutions of hydrogen peroxide decompose slowly into water and oxygen:



This reaction is catalysed by manganese dioxide,  $\text{MnO}_2(\text{s})$ .

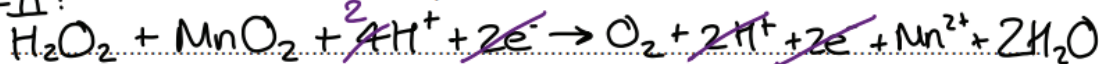
Standard electrode potentials are shown below.



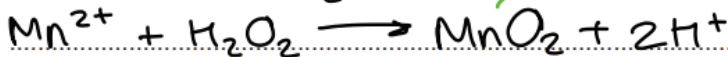
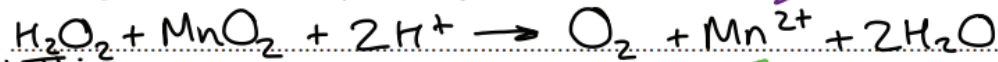
Using the electrode potentials, explain how  $\text{MnO}_2$  is able to act as a catalyst for the decomposition of hydrogen peroxide.

You answer should include relevant equations.

I+II:



II+III:



I more -ve E than II so I moves

left. II more -ve E than III moves left.

$\text{MnO}_2$  is regenerated so acts  
as a catalyst.

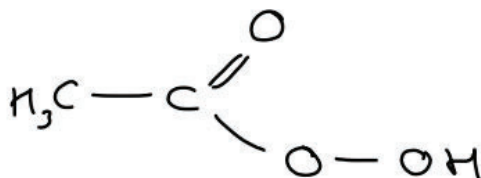
[4]

(c) Peroxycarboxylic acids are organic compounds with the COOOH functional group.

Peroxyethanoic acid, CH<sub>3</sub>COOOH, is used as a disinfectant.

(i) Suggest the structure for CH<sub>3</sub>COOOH.

The COOOH functional group must be clearly displayed.



[1]

(ii) Peroxyethanoic acid can be prepared by reacting hydrogen peroxide with ethanoic acid. This is a **heterogeneous** equilibrium.



A 250 cm<sup>3</sup> equilibrium mixture contains concentrations of 0.500 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>(aq) and 0.500 mol dm<sup>-3</sup> CH<sub>3</sub>COOH(aq).

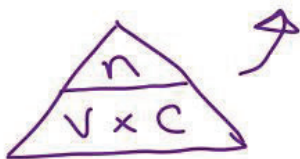
Calculate the amount, in mol, of peroxyethanoic acid in the equilibrium mixture.

*squares brackets means concentration*

$$0.37 = K_c = \frac{[\text{CH}_3\text{COOOH}]}{[\text{H}_2\text{O}_2][\text{CH}_3\text{COOH}]} = \frac{[\text{CH}_3\text{COOOH}]}{[0.5][0.5]}$$

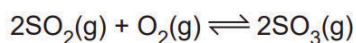
$$0.37 \times [0.5][0.5] = [\text{CH}_3\text{COOOH}] = 0.0925 \text{ mol dm}^{-3}$$

$$0.0925 \times 250 \times 10^{-3} = 0.023125 \text{ mol}$$



amount = ..... 0.023 ..... mol [3]

8. The reversible reaction of sulfur dioxide and oxygen to form sulfur trioxide is shown below.



An equilibrium mixture contains 2.4 mol  $\text{SO}_2$ , 1.2 mol  $\text{O}_2$  and 0.4 mol  $\text{SO}_3$ .  
The total pressure is 250 atm.

What is the partial pressure of  $\text{SO}_3$ ?

A 15 atm

B 25 atm

C 100 atm

D 200 atm

↳ mole fraction  $\times$  total pressure

$$\frac{0.4}{2.4 + 1.2 + 0.4} = 0.1 = \text{mole fraction}$$

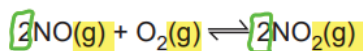
$$0.1 \times 250 = 25 \text{ atm}$$

Your answer

B

[1]

9. Nitrogen monoxide, NO, and oxygen, O<sub>2</sub>, react to form nitrogen dioxide, NO<sub>2</sub>, in the reversible reaction shown in **equilibrium 18.1**.



Equilibrium 18.1

- (a) Write an expression for  $K_c$  for this equilibrium and state the units. *all parts in same state included*

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}$$

*molar ratio in question*

*[ ] = concentration (mol dm<sup>-3</sup>)<sup>2</sup>*

$$\text{Units} = \frac{\text{mol}^{-1} \text{dm}^3}{(\text{mol dm}^{-3})^3} = \frac{1}{\text{mol dm}^{-3}} \quad [2]$$

- (b) A chemist mixes together nitrogen and oxygen and pressurises the gases so that their total gas volume is 4.0 dm<sup>3</sup>.

- The mixture is allowed to reach equilibrium at constant temperature and volume.
- The equilibrium mixture contains 0.40 mol NO and 0.80 mol O<sub>2</sub>.
- Under these conditions, the numerical value of  $K_c$  is 45.

Calculate the amount, in mol, of NO<sub>2</sub> in the equilibrium mixture.



$$\frac{0.4}{4} = 0.1 \text{ mol dm}^{-3} = [\text{NO}]$$

$$\frac{0.8}{4} = 0.2 \text{ mol dm}^{-3} = [\text{O}_2]$$

$$45 = \frac{[\text{NO}_2]^2}{[0.1]^2 [0.2]}$$

$$[\text{NO}_2]^2 = 45 \times 0.1^2 \times 0.2 = 0.09$$

$$[\text{NO}_2] = \sqrt{0.09} = 0.3 \text{ mol dm}^{-3}$$

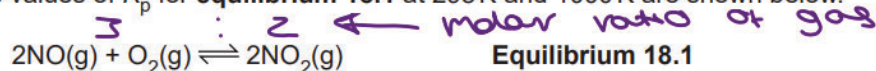
$$0.3 \times 4 = 1.2 \text{ mol}$$

*opposite of first step*

amount of NO<sub>2</sub> = 1.2 mol [4]



(c) The values of  $K_p$  for **equilibrium 18.1** at 298 K and 1000 K are shown below.



Temperature / K	$K_p / \text{atm}^{-1}$
298	$K_p = 2.19 \times 10^{12}$
1000	$K_p = 2.03 \times 10^{-1}$

(i) Predict, with a reason, whether the forward reaction is exothermic or endothermic.

$K_p$  decreases as temperature increases so exothermic [1]

(ii) The chemist **increases the pressure** of the equilibrium mixture at the same temperature. State, and explain in terms of  $K_p$ , how you would expect the equilibrium position to change.

equilibrium shifts to side with fewer moles of gas

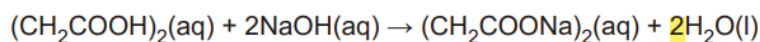
Equilibrium position will shift to the right so ratio in  $K_p$  expression decreases so ratio increases to restore  $K_p$ .

denominator increases more than numerator

[3]

10. A student carries out two experiments in the laboratory based on succinic acid (butanedioic acid),  $(\text{CH}_2\text{COOH})_2$ .

(a) Aqueous succinic acid can be neutralised by aqueous sodium hydroxide,  $\text{NaOH}(\text{aq})$ :



This reaction can be used to determine a value for the **enthalpy change of neutralisation**,  $\Delta_{\text{neut}}H$ .

The student follows this method:

- Add  $50.0 \text{ cm}^3$  of  $0.400 \text{ mol dm}^{-3}$  succinic acid to a polystyrene cup.
- Measure out  $50.0 \text{ cm}^3$  of  $1.00 \text{ mol dm}^{-3}$   $\text{NaOH}(\text{aq})$ , which is in excess.
- Measure the temperature of both solutions.
- Add the  $\text{NaOH}(\text{aq})$  to the aqueous succinic acid in the polystyrene cup, stir the mixture, and record the maximum temperature.

energy released to produce 1 mol of water there are 2 so ÷ by 2 at the end of the calculation

### Temperature readings

Maximum temperature of mixture/ $^{\circ}\text{C}$	26.5
Initial temperature of both solutions/ $^{\circ}\text{C}$	21.5

Calculate a value for the enthalpy change of neutralisation,  $\Delta_{\text{neut}}H$ , in  $\text{kJ mol}^{-1}$ .

Assume that the density of all solutions and the specific heat capacity,  $c$ , of the reaction mixture are the same as for water.



$$50 \times 10^{-3} \times 0.4 = 0.02 \text{ mol}$$

$$Q = mc\Delta T \quad \leftarrow \quad 26.5 - 21.5 = 5^{\circ}\text{C}$$

$\uparrow$   $\uparrow$   $\uparrow$   
 $100 \text{ cm}^3$   $4.18$

$$100 \times 4.18 \times 5 = 2090 \text{ J} = 2.090 \text{ kJ}$$

$$\frac{2.090}{0.02} = \pm 104.5 \text{ kJ mol}^{-1}$$

$$\frac{104.5}{2} = \pm 52.3 \text{ kJ mol}^{-1}$$

enthalpy change of neutralisation is -ve

$$\Delta_{\text{neut}}H = \dots - 52.3 \dots \text{ kJ mol}^{-1} \quad [4]$$

- (b) Succinic acid is esterified by ethanol,  $C_2H_5OH$ , in the presence of an acid catalyst to form an equilibrium mixture.

The equilibrium constant,  $K_c$ , for this equilibrium can be calculated using the amounts, in moles, of the components in the equilibrium mixture, using **expression 5.1**.

$$K_c = \frac{\text{Products}}{\text{Reactants}} K_c = \frac{n(\text{Ester}) \times n(\text{H}_2\text{O})^2}{n((\text{CH}_2\text{COOH})_2) \times n(\text{C}_2\text{H}_5\text{OH})^2}$$

*Products*  
*Reactants*  
*Ester*  
*Powers tells you the stoichiometry of the equilibrium*  
**Expression 5.1**

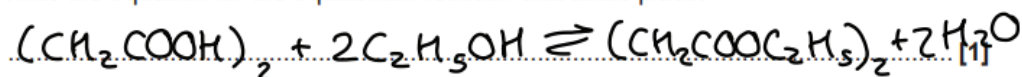
A student carries out an experiment to determine the value of  $K_c$  for this equilibrium.

- The student mixes together **0.0500 mol of succinic acid** and **0.150 mol of ethanol**, with a small amount of an acid catalyst.
- The mixture is allowed to reach equilibrium.
- The student determines that **0.0200 mol** of succinic acid are present in the equilibrium mixture.

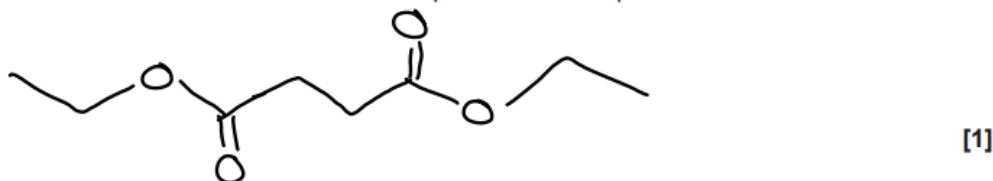
- (i) Which technique could be used to determine the equilibrium amount of succinic acid?

titration ..... [1]

- (ii) Write the equation for the equilibrium reaction that takes place.



- (iii) Draw the skeletal formula of the ester present in the equilibrium mixture.



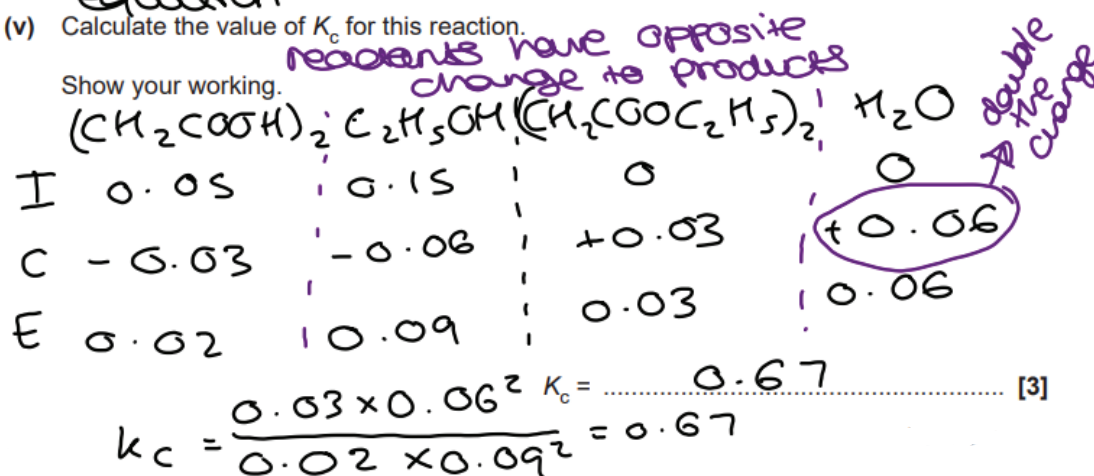
- (iv)  $K_c$  is the equilibrium constant in terms of equilibrium concentrations.

Why can **expression 5.1** be used to calculate  $K_c$  for this equilibrium?

volumes cancel out / same number of moles on each side of the equation ..... [1]

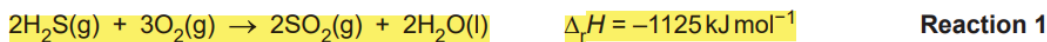
- (v) Calculate the value of  $K_c$  for this reaction.

Show your working.



11. Sulfuric acid is an important chemical used to make detergents, fertilisers and dyes. It is manufactured in a multi-step process.

- (a) In the first step of the manufacture of sulfuric acid, sulfur dioxide,  $\text{SO}_2$ , can be made from the combustion of hydrogen sulfide,  $\text{H}_2\text{S}$ , shown in **Reaction 1**.



- (i) Explain why the enthalpy change for **Reaction 1** has a negative value.

Use ideas about enthalpy changes associated with bond breaking and bond making.

More energy released by forming bonds than required when breaking bonds

[1]

- (ii) Some standard entropy values are given below.

Substance	$\text{H}_2\text{S}(\text{g})$	$\text{O}_2(\text{g})$	$\text{SO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
$S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$	206	205	248	70

Using calculations, explain whether **Reaction 1** is feasible at  $20^\circ\text{C}$ .

**Calculations**

$$\Delta S = ((2 \times 248) + (2 \times 70)) - ((2 \times 206) + (3 \times 205))$$

$$\Delta S = -391 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -0.391 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = -1125 - ((273 + 20) \times -0.391)$$

$$\Delta G = -1010 \text{ kJ mol}^{-1}$$

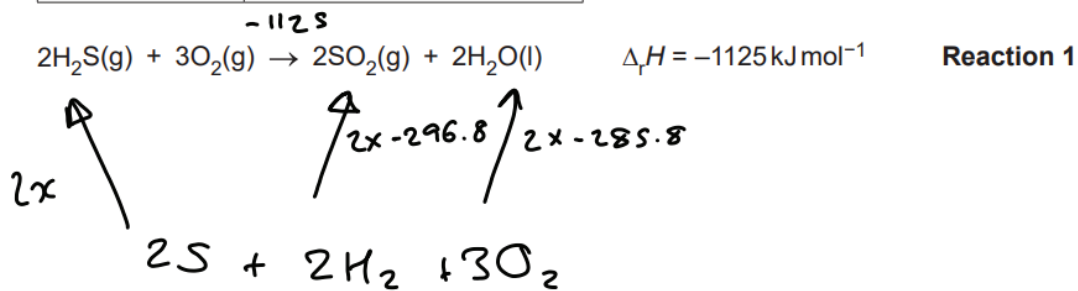
Explanation for feasible or non feasible ..... feasible because

$$\Delta G < 0$$

[4]

- (iii) Calculate the standard enthalpy change of formation,  $\Delta_f H^\ominus$ , of hydrogen sulfide using the enthalpy change for **Reaction 1**, and the standard enthalpy changes of combustion below.

Substance	$\Delta_c H^\ominus / \text{kJ mol}^{-1}$
S(s)	-296.8
H <sub>2</sub> (g)	-285.8



$$(-296.8 \times 2) + (-285.8 \times 2) + 1125 = -40.2 = 2x$$

$$x = -\frac{40.2}{2} = -20.1$$

$\Delta_f H^\ominus$  of hydrogen sulfide = .....  $\frac{-40.2}{2}$  .....  $\text{kJ mol}^{-1}$  [3]

- (b) The second step in the manufacture of sulfuric acid is the conversion of  $\text{SO}_2$  into sulfur trioxide,  $\text{SO}_3$ , using **Equilibrium 1**.



An industrial chemist carries out some research into **Equilibrium 1**.

- The chemist fills a  $10.2 \text{ dm}^3$  container with  $\text{SO}_2(\text{g})$  at RTP, and then adds  $12.0 \text{ g}$  of  $\text{O}_2(\text{g})$ .
- The chemist adds the vanadium(V) oxide catalyst, and heats the mixture. The mixture is allowed to reach equilibrium at a pressure of  $2.50 \text{ atm}$  and a temperature of  $1000 \text{ K}$ .
- A sample of the equilibrium mixture is analysed, and found to contain  $0.350 \text{ mol}$  of  $\text{SO}_3$ .

- (i) Write an expression for  $K_p$  for **Equilibrium 1**.

Include the units.

$$K_p = \frac{P(\text{SO}_3)^2}{P(\text{SO}_2)^2 \times P(\text{O}_2)}$$

units =  $\text{atm}^{-1}$  [2]

- (ii) Determine the value of  $K_p$  for **Equilibrium 1** at  $1000 \text{ K}$ .

Show all your working.

Give your answer to **3 significant figures**.

$$\frac{10.2}{24} = 0.425 \text{ mol of SO}_2$$

$$\frac{12}{32} = 0.375 \text{ mol of O}_2$$

	$\text{SO}_2$	$\text{O}_2$	$\text{SO}_3$
I	0.425	0.375	0
C	-0.350	$-\frac{0.35}{2}$	+0.350
E	0.075	0.200	0.350

$$P(\text{SO}_2) = \frac{0.075}{0.625} \times 2.5 = 0.3 \text{ atm}$$

$$P(\text{O}_2) = \frac{0.2}{0.625} \times 2.5 = 0.8 \text{ atm}$$

$$P(\text{SO}_3) = \frac{0.35}{0.625} \times 2.5 = 1.4 \text{ atm}$$

$K_p = 27.2$  [5]

$$\frac{\text{atm}^2}{\text{atm}^3} = \frac{1}{\text{atm}}$$

$$\frac{\text{volume (dm}^3)}{24} = \text{mol} \quad \text{RTP}$$



$$\text{partial pressure} = \text{mol fraction} \times \text{total pressure}$$

$$\text{total moles} = 0.625 \text{ mol}$$

$$K_p = \frac{(1.4)^2}{(0.3)^2 \times (0.8)}$$

$$K_p = 27.2 \text{ atm}^{-1}$$

- (iii) The chemist repeats the experiment in (b) at a different temperature.

The chemist finds that the value of  $K_p$  is greater than the answer to (b)(ii).

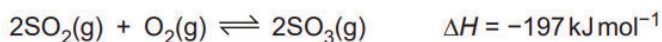
Explain whether the temperature in the second experiment is higher or lower than 1000 K.

Greater  $K_p$  value means equilibrium position shifted to the right so lower temperature because forward reaction is exothermic [2]

- (iv) Explain the significance of the expression:  $K_p \gg 1$ .

equilibrium position far to the right [1]

(c) Vanadium(V) oxide,  $V_2O_5(s)$ , is used as a catalyst in **equilibrium 1**.

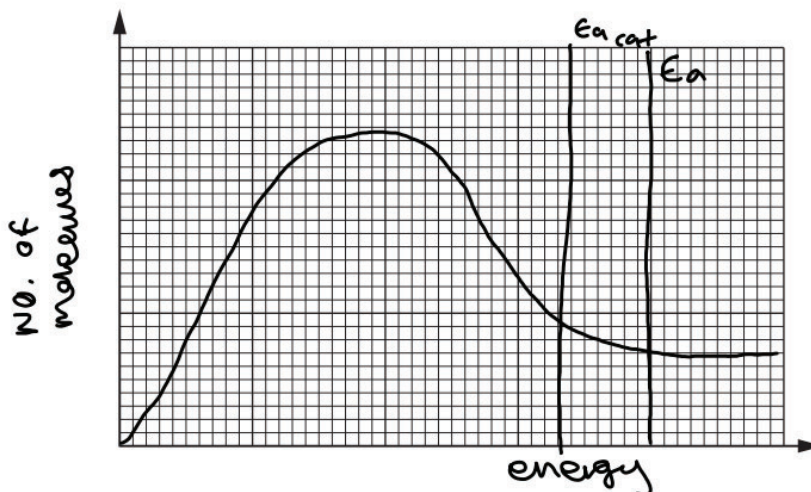


**Equilibrium 1**

(i) Explain how the presence of  $V_2O_5(s)$  increases the rate of reaction.

Include a labelled sketch of the Boltzmann distribution, on the grid below.

Label the axes.



more molecules collide with energy  
above activation energy (with  
catalyst).

[4]

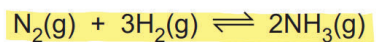
(ii) Explain whether vanadium(V) oxide is acting as a homogeneous or heterogeneous catalyst.

Heterogeneous because catalyst is in  
a different phase/state.

[1]



12. The reversible reaction of nitrogen and hydrogen to form ammonia is shown below.



In the equilibrium mixture, the partial pressure of  $\text{N}_2$  is 18.75 MPa and the partial pressure of  $\text{H}_2$  is 2.50 MPa.

The total pressure is 25 MPa.

What is the value of  $K_p$ , in  $\text{MPa}^{-2}$ ?

- A  $1.2 \times 10^{-4}$   
B 0.048  
C 0.075  
D 21

$$K_p = \frac{P(\text{NH}_3)^2}{P(\text{N}_2)P(\text{H}_2)^3}$$

$$18.75 + 2.5 = 21.25$$

$$25 - 21.25 = 3.75 \text{ MPa}$$

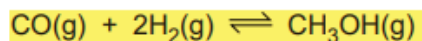
$$K_p = \frac{3.75^2}{18.75 \times (2.5)^3} = 0.048 \text{ MPa}^{-2}$$

Your answer

B

[1]

13. Methanol,  $\text{CH}_3\text{OH}$ , can be made industrially by the reaction of carbon monoxide with hydrogen, as shown in **equilibrium 1**.



$$\Delta H = -91 \text{ kJ mol}^{-1}$$

**Equilibrium 1**

- (a) Predict the conditions of pressure and temperature that would give the **maximum equilibrium yield of  $\text{CH}_3\text{OH}$**  in **equilibrium 1**.

Explain your answer.

Right hand side has fewer gaseous moles  
So high pressure  
Forward reaction was exothermic so low temperature

↑  
want to favour forward reaction

[3]

- (b) A catalyst is used in the production of methanol in **equilibrium 1**.

State **two** ways that the use of catalysts helps chemical companies to make their processes more sustainable and less harmful to the environment.

1. lower energy demand

2. less  $\text{CO}_2$  emissions

[2]

(c) Standard entropy values are given below.

Substance	CO(g)	H <sub>2</sub> (g)	CH <sub>3</sub> OH(g)
S°/JK <sup>-1</sup> mol <sup>-1</sup>	198	131	238

A chemist proposed producing methanol at 525K using **equilibrium 1**.

Explain, with a calculation, whether the production of methanol is feasible at 525K.

$$\Delta S = 238 - (198 + (2 \times 131)) = -222 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -0.222 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

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

$$\Delta G = -91 - (525 \times -0.222) = 25.55$$

$$\text{kJ mol}^{-1}$$

not feasible as  $\Delta G > 0$

[5]

(d) At 298K, the free energy change,  $\Delta G$ , for the production of methanol in **equilibrium 1** is  $-2.48 \times 10^4 \text{ J mol}^{-1}$ .

$\Delta G$  is linked to  $K_p$  by the relationship:  $\Delta G = -RT \ln K_p$

$R$  = gas constant

$T$  = temperature in K.

Calculate  $K_p$  for **equilibrium 1** at 298K.

Give your answer to **3 significant figures**.

$$\ln K_p = \frac{\Delta G}{-RT}$$

$$\ln K_p = \frac{-2.48 \times 10^4}{-8.314 \times 298}$$

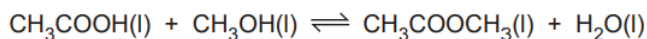
$$= 10.01$$

$$K_p = e^{-10.01} = 2.22 \times 10^4$$

$$K_p = \frac{p(\text{CH}_3\text{OH})}{p(\text{CO}) \times p(\text{H}_2)^2}$$

$$K_p = 2.22 \times 10^4 \text{ units atm}^{-2} \quad [3]$$

14. A student investigates the reaction between ethanoic acid,  $\text{CH}_3\text{COOH}(\text{l})$  and methanol,  $\text{CH}_3\text{OH}(\text{l})$ , in the presence of an acid catalyst. The equation is shown below.

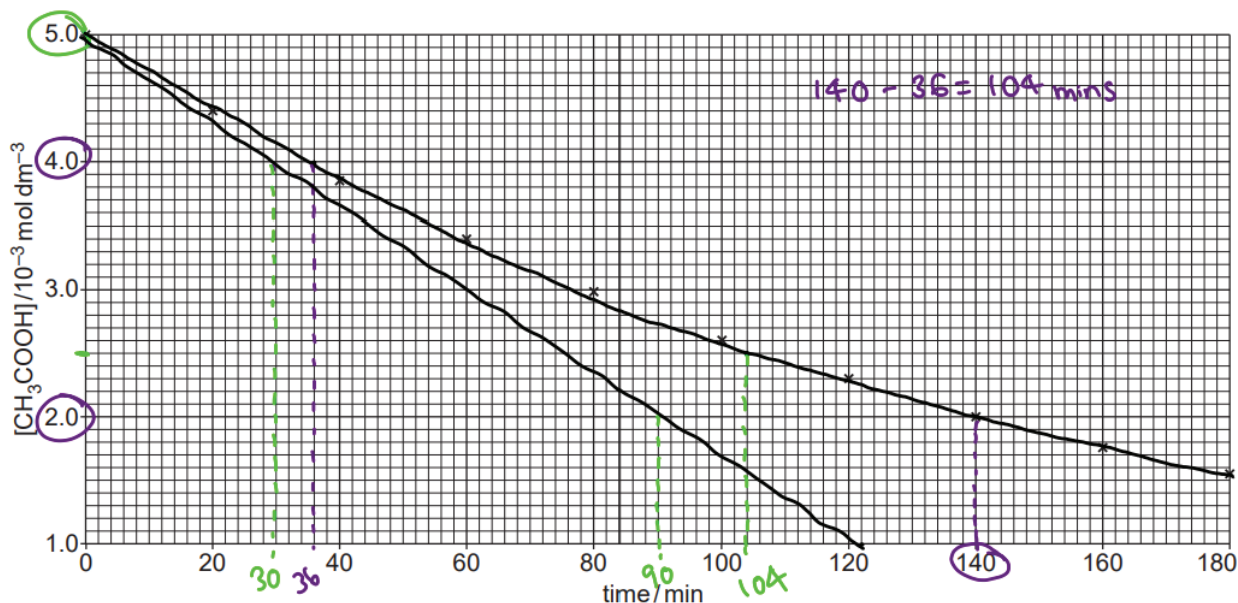


- (a) The student carries out an experiment to determine the order of reaction with respect to  $\text{CH}_3\text{COOH}$ .

The student uses a large excess of  $\text{CH}_3\text{OH}$ . The temperature is kept constant throughout the experiment.

The student takes a sample from the mixture every 20 minutes, and then determines the concentration of the ethanoic acid in each sample.

From the experimental results, the student plots the graph below.



- (i) Explain why the student uses a large excess of methanol in this experiment.

- To keep  $[\text{CH}_3\text{OH}]$  constant.....
- Zero order with respect to  $\text{CH}_3\text{OH}$ ..... [1]
- To ensure equilibrium is far to the right.

- (ii) Use the half-life of this reaction to show that the reaction is first order with respect to  $\text{CH}_3\text{COOH}$ .

Show your working on the graph and below.

constant  $\frac{1}{2}$  lives of 104 mins so first order [2]

- (iii) Determine the initial rate of reaction.

$$(I) k = \frac{\ln 2}{104} = 6.66 \times 10^{-3} \text{ min}^{-1} \quad k = \frac{\ln 2}{t_{1/2}}$$

$$6.66 \times 10^{-3} \times 5 \times 10^{-3} = 3.33 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$(II) \frac{(4-2) \times 10^{-3}}{90-30} = 3.33 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$\text{initial rate} = 3.33 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1} [2]$$

- (b) The student carries out a second experiment to determine the value of  $K_c$  for this reaction.

The student mixes 9.6g of  $\text{CH}_3\text{OH}$  with 12.0g of  $\text{CH}_3\text{COOH}$  and adds the acid catalyst.

When the mixture reaches equilibrium, 0.030 mol of  $\text{CH}_3\text{COOH}$  remains.

Calculate  $K_c$  for this equilibrium.

$$K_c = \frac{[\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{OH}][\text{CH}_3\text{COOH}]}$$



$$\frac{9.6}{12 + 3 + 16 + 1} = 0.3 \text{ mol } \text{CH}_3\text{OH}$$

$$\frac{12}{12 + 3 + 12 + (16 \times 2) + 1} = 0.2 \text{ mol } \text{CH}_3\text{COOH}$$

	$\text{CH}_3\text{OH}$	$\text{CH}_3\text{COOH}$	$\text{CH}_3\text{COOCH}_3$	$\text{H}_2\text{O}$
I	0.3	0.2	0	0
C	-0.17	-0.17	+0.17	+0.17
E	0.13	0.03	0.17	0.17

$$K_c = \frac{[0.17/V][0.17/V]}{[0.13/V][0.03/V]} = 7.4 \quad K_c = 7.4 [4]$$