Chemical Equilibrium

Chapter

1

1.5 (2009:10)

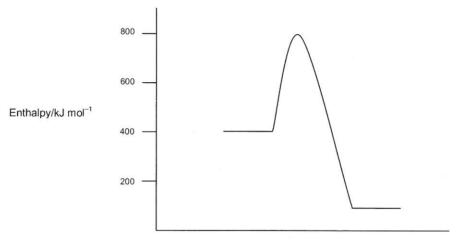
The reaction used in the production of ammonia gas is shown below.

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$
 $\Delta H = -92 \text{ kJ mol}^{-1}$

Addition of a catalyst will increase the rate of this reaction. Which one of the following will occur on the addition of a catalyst?

- (a) The equilibrium yield of ammonia remains constant.
- (b) The rate of the forward reaction increases relative to the rate of the reverse reaction.
- (c) The proportion of successful collisions remain constant.
- (d) The endothermic reaction is favoured.

Use the potential energy diagram shown below to answer the next two questions.



Reaction coordinate

2. 1.7 (2009:11)

Which one of the following gives the correct values for the enthalpy change (ΔH) and the activation energy (E_a) for the forward reaction?

| | $\Delta H/kJ \text{ mol}^{-1}$ | $E_a/kJ \text{ mol}^{-1}$ | |
|-----|--------------------------------|---------------------------|--|
| (a) | -300 | +700 | |
| (b) | +300 | +400 | |
| (c) | -300 | +800 | |
| (d) | -300 | +400 | |

3. 1.7 (2009:12)

A catalyst was added to the reaction mixture. Comparing the catalysed reaction with the uncatalysed reaction, which one of the following will remain the same?

- (a) the enthalpy change of the reaction
- (b) the activation energy for the forward reaction
- (c) the energy of the transition state
- (d) the activation energy for the reverse reaction

4. 1.7 (2010:15)

Which one of the following statements about the addition of a catalyst to a chemical reaction is **false**?

- (a) It increases the rate of the reaction relative to the uncatalysed reaction.
- (b) It provides a reaction pathway that has a smaller activation energy than that for the uncatalysed reaction.
- (c) It causes a greater fraction of collisions between reaction particles to result in a reaction relative to the uncatalysed reaction.
- (d) It causes particles involved in a reaction to move faster than those in the uncatalysed reaction.

5. 1.9 (2010:16)

Consider the following reaction at equilibrium:

$$2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g) \Delta H = -197 \text{ kJ mol}^{-1}$$

Which one of the following changes will increase the concentration of $SO_3(g)$ in the mixture when equilibrium is re-established?

- (a) decreasing the concentration of SO₂ at constant temperature and pressure
- (b) decreasing the concentration of O₂ at constant temperature and pressure
- (c) decreasing the temperature of the system
- (d) decreasing the pressure of the system

6. 1.1 (2010:17)

A small rise in temperature of gaseous reactants in a system results in an increase in the rate of reaction. Which one of the following is the **main** reason for this change?

- (a) an increase in the speed of reactant particles, leading to a higher rate of collision
- (b) an increase in the pressure inside the reaction vessel, leading to a higher rate of collision
- (c) an increase in the proportion of collisions with more than the activation energy
- (d) an increase in the activation energy of the reaction

Time

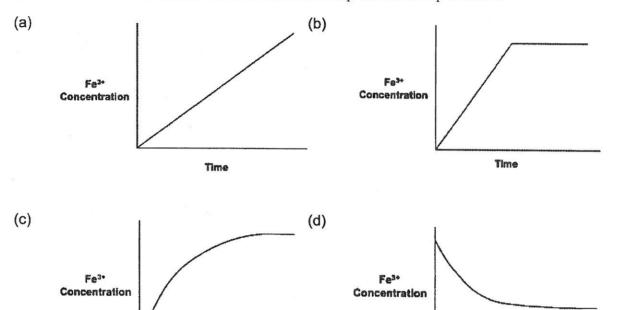
7.

1.4 (2010:18)

When aqueous solutions of Ag^+ and Fe^{2+} are mixed, Ag and Fe^{3+} form according to the following equilibrium.

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$$

Which one of the following concentration versus time graphs best represents the way in which the ${\rm Fe^{3+}}$ concentration varies as the reaction proceeds to equilibrium?



8. 1.1 (2011:10)

An enzyme is a biological catalyst. Esters can be hydrolysed, as represented below by an esterase enzyme.

In the presence of esterase which one of the following statements is true for this process?

(a) The position of the equilibrium for this reaction is shifted to the right.

Time

- (b) The rate of forward reaction and rate of reverse reaction both increase equally.
- (c) The rate of forward reaction increases more than the rate of reverse reaction.
- (d) The rate of forward reaction increases and rate of reverse reaction decreases.

1.9 (2011:11) 9.

Hydrogen can be produced by the reaction

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3 H_2(g)$$
 $\Delta H > 0$

Which one of the following will increase the equilibrium yield of hydrogen?

- (a) increasing the total pressure of the reaction system
- decreasing the partial pressure of the water vapour
- (c) removing carbon monoxide from the system as it is produced
- (d) decreasing the temperature of the system

1.4 (2011:12) 10.

Which of the properties listed below are characteristic of a gaseous system in dynamic equilibrium?

- The concentrations of reactants are equal to the concentrations of products. (i)
- (ii) The concentrations of reactants and products are constant.
- (iii) The rate of the forward reaction is equal to the rate of the reverse reaction.
- (iv) The pressure of the system is constant.
- (a) (i), (ii) and (iii)
- (b) (i), (ii) and (iv)
- (c) (ii), (iii) and (iv)
- (d) (iii) only

1.9 (2012:17) 11.

The reaction of iron(III) oxide with carbon monoxide gas is shown below:

$$Fe_2O_3(s) + 3 CO(g) = 2 Fe(\ell) + 3 CO_2(g)$$

Which one of the following changes to the system will decrease the rate of the forward reaction?

- (a) decreasing the volume of the reaction vessel
- decreasing the pressure of CO(g) in the vessel
- decreasing the Fe₂O₃(s) particle size
- (d) decreasing the concentration of CO₂(g) in the system

12. 1.6 (2012:18)

Ammonium chloride (NH₄C ℓ) dissolves readily in water at room temperature. If a sample of ammonium chloride is dissolved in a beaker of water, the beaker becomes cold to the touch. Which one of the following is the **best** explanation for this observation?

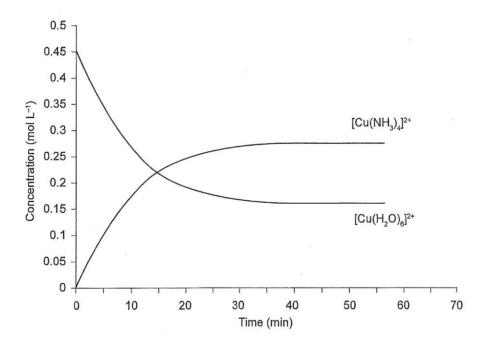
- (a) The reaction is exothermic with a small activation energy.
- (b) The reaction is exothermic with a large activation energy.
- (c) The reaction is endothermic with a small activation energy.
- (d) The reaction is endothermic with a large activation energy.

Questions (2013:12) and (2013:13) refer to the information and graph below.

Aqueous solutions of copper(II) ions and ammonia form the equilibrium represented below.

$$[Cu(H_2O)_6]^{2+}(aq) + 4 NH_3(aq) \Rightarrow [Cu(NH_3)_4]^{2+}(aq) + 6 H_2O(\ell)$$
 pale blue deep royal blue

The following graph shows the changes in concentration with time for $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ ions when solutions of copper(II) nitrate and ammonia are mixed.



1.4 (2013:12)

Which one of the following statements is true for this equilibrium system?

- (a) The system reaches equilibrium at approximately 35 minutes.
- (b) At equilibrium, the concentration of NH_3 will always be four times greater than the concentration of $[Cu(NH_3)_4]^{2+}$.
- (c) Adding ammonia to the system will decrease the equilibrium constant.
- (d) At equilibrium, the rate of the forward reaction is less than the rate of the reverse reaction.

1.9 (2013:13)

14. Which one of the following would be observed if a small quantity of concentrated nitric acid was added to the system after it had reached equilibrium?

- (a) The solution would be a deeper royal blue colour.
- (b) The solution would be a paler blue colour.
- (c) There would be no change in the colour of the system.
- (d) Copper(II) nitrate crystals would precipitate from solution.

1.1 (2013:14) 15.

Consider the following reaction.

$$2 SO_2(g) + O_2(g) \Rightarrow 2 SO_3(g) + 198 kJ$$

After equilibrium has been established, which one of the following would immediately increase the rate of the reverse reaction?

- (a) adding a catalyst
- (b) increasing the concentration of SO_2
- (c) cooling the reaction vessel and its contents
- (d) adding a small amount of neon gas

1.10 (2014:10) 16.

Consider the following endothermic reaction

$$N_2O(g) + NO_2(g) \Rightarrow 3 NO(g)$$
 $\Delta H = +156 \text{ kJ mol}^{-1}$

Which one of the following changes to the system at equilibrium will increase the value of its equilibrium constant, K?

- (a) increased pressure
- (b) addition of a catalyst
- (c) increased temperature
- (d) decreased temperature

17.

1.11 (2014:11)

Which one of the following is the equilibrium law expression for the equilibrium represented below?

$$2 \operatorname{CrO_4^{2-}}(aq) + 2 \operatorname{H}^+(aq) \rightleftharpoons \operatorname{Cr_2O_7^{2-}}(aq) + \operatorname{H_2O}(\ell)$$

(a)
$$\frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$$

(b)
$$\frac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$$

$$\text{(c)} \quad \frac{[\text{CrO}_4^{\ 2-}]^2[\text{H}^+]^2}{[\text{Cr}_2\text{O}_7^{\ 2-}][\text{H}_2\text{O}]}$$

$$(d) \ \ \frac{[Cr_2O_7^{2-}][H_2O]}{[CrO_4^{2-}]^2[H^+]^2}$$

18.

1.9 (2014:12)

Aqueous solutions of iron(III) ions and thiocyanate ions form the equilibrium represented below.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$
 pale brown colourless deep red

The reaction is exothermic.

Which one of the following statements about changes to the system and the effect on the colour of the solution is true?

- (a) Adding water will make it turn darker red.
- (b) Cooling the solution will make it turn darker red.
- (c) Adding a small volume of aqueous Na₂CO₃ solution will turn it darker red.
- (d) Adding solid iron(III) chloride to the solution will make it lighter red.

19.

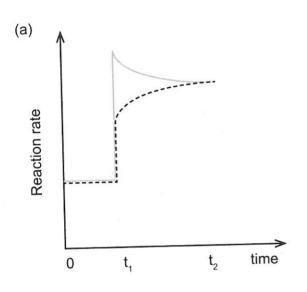
Consider the following equilibrium.

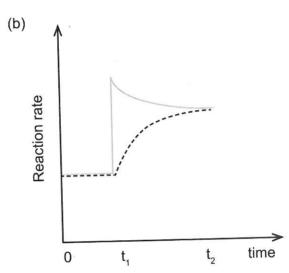
$$2 C\ell F_3(g) \rightleftharpoons 3F_2(g) + C\ell_2(g)$$
 $\Delta H = negative$

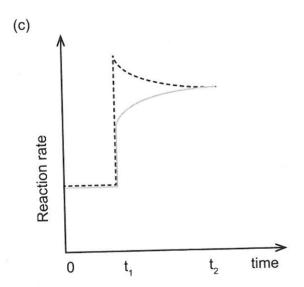
The system is initially at equilibrium. At time t_1 , the temperature of the system was increased. Which of the following **best** represents the changes in the forward and reverse reaction rates until equilibrium is re-established at time, t_2 ?

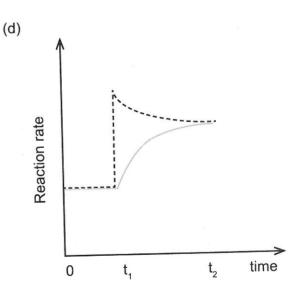
The forward reaction rate is represented by

The reverse reaction rate is represented by









Questions (2015:06) and (2015:07) refer to the reaction represented by the equation shown below.

$$Pb(s) + PbO_2(s) + 4 H^+(aq) + 2 SO_4^{2-}(aq) \Rightarrow 2 PbSO_4(s) + 2 H_2O(\ell)$$

20. 1.10 (2015:06)

Which one of the following is the equilibrium law expression for this reaction?

(a)
$$K = \frac{1}{[H^+]^4[SO_4^{2-}]^2}$$

(b)
$$K = \frac{[H_2O]^2}{[H^+]^4[SO_4^{2-}]^2}$$

(c)
$$K = \frac{[PbSO_4]^2}{[H^+]^4[SO_4^{2-}]^2}$$

(d)
$$K = \frac{1}{[H^+]^2[SO_4^{2-}]}$$

21. 1.10 (2015:07)

Assuming equilibrium has been established, which one of the following will cause a decrease in pH?

- (a) adding more solid lead
- (b) adding solid sodium sulfate
- (c) removing solid lead sulfate
- (d) adding barium nitrate solution

22. 1.9 (2016:01)

The decomposition of hydrogen peroxide in a closed system is represented by the equation below.

$$2 H_2 O_2(aq) \rightleftharpoons 2 H_2 O(\ell) + O_2(g)$$
 $\Delta H < 0$

Which one of the following will increase the equilibrium yield of oxygen?

- (a) decreasing the concentration of hydrogen peroxide
- (b) increasing the total pressure of the system
- (c) decreasing the temperature of the system
- (d) adding an inert gas to the system

1.8 (2016:02)

Sulfur can be obtained from hydrogen sulfide found in natural gas according to the equation below.

$$2 H_2S(g) + SO_2(g) \rightarrow 2 H_2O(g) + 3 S(g)$$
 $\Delta H > 0$

Which one of the following changes will initially decrease the rate at which sulfur is produced?

- (a) reduce the partial pressure of the hydrogen sulfide $(H_2S(g))$
- (b) increase the partial pressure of sulfur dioxide $(SO_2(g))$
- (c) add a metal catalyst to the reaction vessel
- (d) heating the reaction vessel

24. 1.11 (2016:03)

Consider the equilibrium system below.

$$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$$

If the equilibrium constant (K) for this reaction is 4.1×10^{-31} , which one of the following statements is **true** for the system where the initial partial pressures of nitrogen and oxygen were equal to each other?

- (a) Once equilibrium is reached, the reverse reaction rate is much faster than the forward reaction rate.
- (b) The partial pressure of NO(g) is less than the partial pressure of $N_2(g)$.
- (c) The actual ratio of gaseous N₂ particles to NO gaseous particles is 1:2.
- (d) When nitrogen gas is injected into a vessel containing mostly oxygen gas, the partial pressure of oxygen decreases dramatically.

1.9 (2016:04)

1.7 (2016:08)

A 500 mL solution of dichromate ions and chromate ions at equilibrium is described by the equation below.

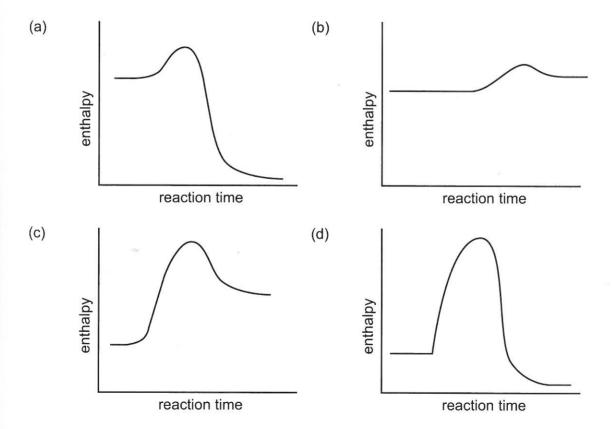
$$\operatorname{Cr_2O_7^{2-}}(aq) + \operatorname{H_2O}(\ell) \rightleftharpoons 2 \operatorname{CrO_4^{2-}}(aq) + 2 \operatorname{H}^+(aq)$$
 orange yellow

Which of the following **best** describes the effect of adding 10 mL of concentrated potassium hydroxide solution to the system once equilibrium has been re-established.

| | Relative change in concentration of Cr ₂ O ₇ ²⁻ (aq) | Relative change in concentration of CrO ₄ ²⁻ (aq) | Relative change in concentration of H ⁺ (aq) | Colour change of solution |
|-----|---|---|---|------------------------------|
| (a) | increase | decrease | decrease | more orange |
| (b) | decrease | increase | decrease | more yellow |
| (c) | no change | no change | no change | no change |
| (d) | decrease | increase | increase | more yellow |

26.

Which of the following energy profile diagrams **best** represents a spontaneous, exothermic reaction?



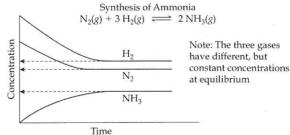
Chapter 1: Chemical Equilibrium

along with H2. The answer is 'c'.

- 1.(2009:10-a) A catalyst speeds up both the forward and backward reactions. It thus speeds up the rate at which equilibrium is attained. However, it does not alter the position of equilibrium. This means that it does not alter the equilibrium concentrations. Therefore, a catalyst does not affect the overall stoichiometry of a reaction and thus does not affect the yield of a reaction. The answer is 'a'.
- 2.(2009:11-d) The answer could be worked out from the energy profile diagram: Activation energy (E_a) = (800 kJ mol⁻¹ 400 kJ mol⁻¹) = 400 kJ mol⁻¹. Heat of reaction (ΔH) = (100 kJ mol⁻¹ 400 kJ mol⁻¹) = -300 kJ mol⁻¹. The answer is 'd'.
- 3.(2009:12-a) A catalyst creates an alternate pathway with a lower activation energy for both the forward and reverse reaction and hence reduces the energy of the transition complex. The heat of reaction, ΔH , however, is not affected. Thus the change in enthalpy remains the same for the both the forward and reverse reactions. The answer is 'a'.
- 4.(2010:15-d) A catalyst increases the rate of a reaction by providing an alternative, low activation energy pathway for the reaction. This enables a greater fraction of effective collisions for a large number of molecules slightly below the activation energy barrier. A catalyst does not provide any extra energy for the particles with energy to move faster. The answer is 'd'.
- 5.(2010:16-c) This reaction is exothermic where 3 moles of gases react to form 2 moles of gases. According to Le Châtelier's principle, a decrease in SO_2 concentration will favour the reactants, and so will a decrease in concentration of O_2 , in order to make up the decrease. Also, a decrease in pressure will favour the side with more gaseous moles. Therefore, the only possibility is to increase the concentration of SO_3 in this exothermic reaction (from among the given alternatives) is to decrease the temperature. The answer is 'c'.
- 6.(2010:17-c) A small rise in temperature does not significantly increase the speed of particles or the pressure. Activation energy requirement without a catalyst is a constant value for a reaction and is not affected by temperature. A large number of molecules just below the activation energy barrier, may gain just the energy they need to go above the barrier and react. The answer is 'c'.
- 7.(2010:18-c) The rate of formation of Fe³⁺ increases rapidly at first. The rate at which the concentration increases gradually slows down as reactants are used up until the concentration becomes constant. The graph should show the initial forward reaction relatively fast but then slowing down and eventually becoming constant. The answer is 'c'.
- 8.(2011:10-b) Enzymes are biological catalysts which increase the rate of both the forward and the reverse reactions. Apart from enabling the reaction to reach equilibrium sooner, they do not affect equilibrium. See the diagram below. Answer is 'b'.



- 9.(2011:11-c) The reaction is: $CH_4(g) + H_2O(g) = CO(g) + 3 H_2(g)$. $\Delta H > 0$ In this reaction, the products occupy a larger volume. In accordance with LCP, an increase in pressure will shift the equilibrium towards the reactants as they occupy a smaller volume. This will effectively decrease the yield of hydrogen. Decreasing the partial pressure of water vapour will have a similar effect. Furthermore, this is an endothermic reaction and so a decrease in temperature will decrease the yield of H_2 . Therefore, one way to increase the yield of hydrogen is to remove carbon monoxide. This will drive the reaction forward to produce more CO and
- 10.(2011:12-c) When a reaction has reached equilibrium, all the observable and measurable properties of the reactants and the products remain constant. However, it is better to remember that they are not equal. The answer is 'c'. See the diagram below.



- 11.(2012:17-b) In this reaction (Fe₂O₃(s) + 3 CO(g) \rightleftharpoons 2 Fe(ℓ) + 3 CO₂(g)), by decreasing the volume, the pressure on the gases increase, increasing the rate of reaction on both directions. Decreasing the particle size would increase the rate of reaction due to an increase in the surface area of the reacting particles. By decreasing the concentration of CO₂, the forward reaction rate is increased. By decreasing the pressure of carbon monoxide, the gas particles have less effective collisions per unit time and hence the rate decreases. The answer is 'b'.
- 12.(2012:18-c) Since the reaction readily takes place at room temperature, the activation energy requirement is very small. Since heat energy is absorbed from the environment and the beaker becomes cold, the reaction is endothermic. The answer is 'c'.

- 13.(2013:12-a) A reading of the graph indicates that the system reaches equilibrium at about 35 minutes. It is important to realise that the equilibrium ratio of molar concentrations is not the same as the stoichiometric ratio of the reactants. Also, the equilibrium constant is not affected by factors other than a change in temperature of the system. Furthermore, the rates of the forward and the reverse reactions are equal at equilibrium. This leaves only alternative 'a' which is the correct response.
- 14.(2013:13-b)

The reaction is: $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \Rightarrow [Cu(NH_3)_4^{2+}(aq) + 6H_2O(\ell)]$

The addition of a small amount of HNO₃, will reduce the concentration of NH₃. The NH₃ reacts with H⁺ to form NH₄⁺ and so decreases the concentration of NH₃. The reverse reaction that follows decomposes

 $[Cu(NH_3)_4^{2+}](aq)$. This results in the solution becoming pale blue. The answer is 'b'.

15.(2013:14-a) The reaction is: $2 SO_2(g) + O_2(g) = 2 SO_3(g) + 198 \text{ kJ}$ Catalysts tend to reduce the activation energy requirements and create a new reaction pathway with a lower activation energy. This will increase both the forward and the reverse reaction rates. On the other hand,

increasing the concentration of SO₂ and, cooling the system, will increase the rate of the forward reaction. Introducing an inert gas into the system does not change any concentrations and so has no effect. The answer is 'a'.

16.(2014:10-c) The value of the equilibrium constant for a chemical reaction depends only on the temperature. An increase in temperature increases the numerical value of the equilibrium constant for that reaction and a decrease in temperature decreases its numerical value. Equilibrium shifts to the product side as [NO] increases and the $[N_2O]$ and $[NO_2]$ decreases. The answer is 'c'.

17.(2014:11-a) Removing $H_2O(\ell)$ from the equation, the equilibrium law expression for the reaction is, $K_{eq} = \{[Cr_2O_7^{2-}] \div [CrO_4^{2-}] \times [H^+]^2\}$. The answer is 'a'. 18.(2014:12-b) The reaction equation is: $Fe^{3+}(aq) + SCN^-(aq) = [Fe(SCN)]^{2+}(aq)$ pale brown colourless deep red

Adding water dilutes the mixture and both the colours becomes paler and no other effect can be noticed. Adding aqueous Na_2CO_3 will precipitate some Fe^{3+} ions as $Fe_2CO_3(s)$. In accordance with LCP the equilibrium shifts to the reactant side to produce more Fe^{3+} ion to make up the loss and the colour becomes more brownish. Adding solid $FeC\ell_3$ will dissolve and increase the Fe^{3+} concentration. This will shift the equilibrium to the product side making the solution deep red. Since this is an exothermic reaction, cooling the solution will shift the equilibrium to the product side making the solution deep red. The answer is 'b'.

19.(2015:04) Answer 'c'. Remember the graph is showing Rate - both increase with temperature and then a new equilibrium is established.

20.(2015:06) Answer 'a'. K = [products]/[reactants]. We do not include species with (s) or (ℓ).

21.(2015:07) Solid lead does not appear in the K expression. Adding Na₂SO₄will increase pH. Lead sulfate is a solid. Answer 'd'. Barium sulfate is insoluble and removes sulfate ions moving the equation to the LHS.

- 22.(2016:01-c) The reaction is exothermic cooling the system would give more oxygen as the reaction moves to the RHS. Adding inert gas would have no effect, as $[O_2]$ does not change. Decreasing the conc of H_2O_2 would lead to a lower forward rate and less O₂. Increasing the pressure would increase [O₂] which would result in less O₂ forming. The answer is c.
- 23.(2016:02-a) Note the question asks for decrease in rate. Answers b, c and d always increase reaction rate. Decreasing the partial pressure of H₂S will decrease the rate of collisions and thus the rate of formation of sulfur. The answer is a.
- 24.(2016:03-b) Answer a is wrong. At equilibrium the forward and reverse reaction rates are equal. Answer c would suggest a much larger K value. Answer d would be correct for a large Kc reaction. The value of Kc is very small. Thus [products]/[reactants] is small i.e. there are few products. The answer is b.
- 25.(2016:04-b) This is a classic question. If you are told something not in the equation is added, be sure it will probably react with something in the equation either as acid/base or a precipitate. The added solution is concentrated so there is no need to worry about diluting the reactants and products. Here the H⁺ is destroyed so the equation moves to the right - the answer is b.
- 26.(2016:08-a) The words spontaneous, exothermic means a reaction with a small E_a and a negative $\triangle H$. The answer is a.

Chapter 2: Acids and Bases

- 1.(2009:14-d) A weak electrolyte is a solution that contains few ions. The answer is clearly 'd'.
- 2.(2009:15-c) Water acts as a base when it accepts protons. Alternative 'c' indicates this reaction.
- 3.(2009:17-c) Since, $c_1 \times V_1 = c_2 \times V_2$, 2.00 M × 0.02 L = $c_2 \times$ 0.220 L; the new concentration of the solution is 1.82 × 10⁻² M. $pH = -log [H^+]$; and the $pH = -log 1.82 \times 10^{-2} M = 0.74$. The answer is 'c'.
- 4.(2009:18-b) Both Ca(OH)2 and NaOH are strong bases. However, Ca(OH)2 solution is at a lower concentration of 1.00×10^{-3} mol L⁻¹. The answer is 'b'.
- 5.(2009:19-a) The reaction is: $Na_2CO_3 + 2 HC\ell \rightarrow 2 NaC\ell + H_2O + CO_2$. The number of moles of $HC\ell$ needed is twice the number of moles of Na₂CO₃. Since the concentrations of both the acid and the base are the same, the volume of $HC\ell$ should be twice the volume of Na_2CO_{3} , which is $20 \times 2 = 40$ mL. When this molar equivalent amount is added, the colour changes from yellow to orange. (An additional amount of HCl would be required to change the colour to red to make it more acidic.) The answer is 'a'.
- 6.(2010:05-b) The Equilibrium constant for HC ℓ is very large because it is a strong acid. Since HC ℓ is a strong acid, its conjugate base, $C\ell^-$, is very weak. On the other hand, NH_4^+ is a weak acid and its conjugate base, NH_3 must be relatively stronger. Therefore, $C\ell^-(aq)$ is a weaker base than $NH_3(aq)$. Also, it is important to note that the pH of a