Equilibria

Review

ICE table

$H_2 + I_2 \rightleftharpoons 2HI$

10 10 0

↓

15 mol

	H_2	+	I_2		2 HI
I	10		10		0
C	-7.5		-7.5		+15
E	2.5		2.5		15

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

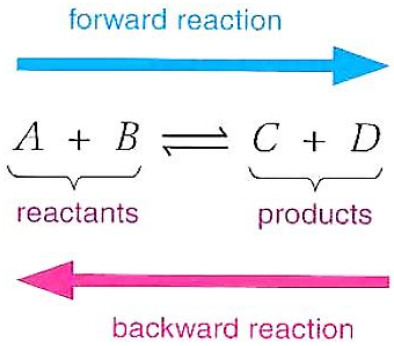
Industrial preparation of ammonia

$N_{2(g)}+3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Esterification

$CH_3COOH_{(l)} + CH_3CH_2OH_{(l)} \rightleftharpoons CH_3COOCH_2CH_{3(l)} + H_2O_{(l)}$

1. reversible reaction



The products react together to re-form reactants at the same time as the reactants are forming products. This type of reversible reaction is called an **equilibrium reaction**. We use the sign ⇌ in

equilibrium reactions to show that they are **reversible**.

dynamic equilibrium means that the molecules or ions of reactants and products are continuously reacting. Reactants are continuously being changed to products and products are continuously being changed back to reactants.

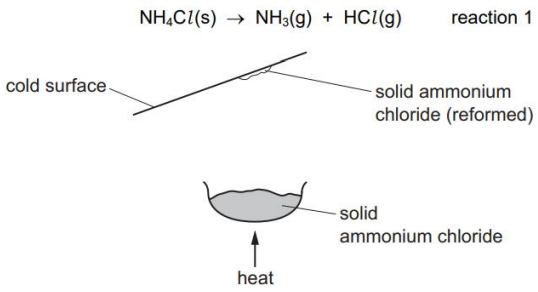
An equilibrium reaction has four particular features under constant conditions:

forward and backward reaction rate is equal

Q. When a sample of ammonium chloride is warmed it decomposes into ammonia and hydrogen chloride gas.

NH_4Cl NH_3 HCl

When the mixture of hot ammonia and hydrogen chloride gases hit a cold surface, a white solid of ammonium chloride reforms.



Which statements are correct?

1. Reaction 1 is in dynamic equilibrium. ✓

2. Reaction 1 is reversible. ✓

3. Reaction 1 is an endothermic reaction. ✓

A. 1, 2 and 3 are correct

B. 1 and 2 only are correct

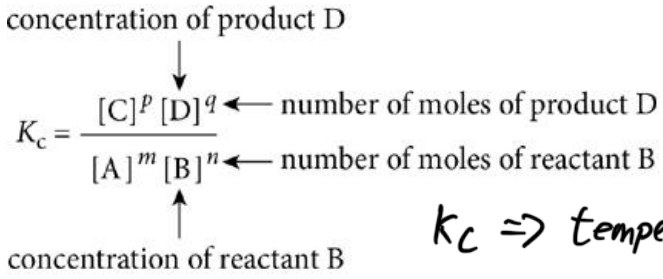
C. 2 and 3 only are correct

D. 1 only is correct

Characteristics of equilibrium

2.Equilibrium constant, Kc

$mA + nB \rightleftharpoons pC + qD$



K_c => temperature only !

Q. Nitrogen and hydrogen react together to form ammonia.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

0.1 0.1 0

$\frac{1}{2}n$ $\frac{3}{2}n$ n

0.1 $-\frac{1}{2}n$ 0.1 $-\frac{3}{2}n$

0.1 mol of nitrogen and 0.1 mol of hydrogen were mixed in a closed container of volume 1 dm^3.At equilibrium *n* mol ammonia is formed. What is the concentration of hydrogen at equilibrium?

A. 0.1 – n

C. 0.1 − 1.5n

B. 0.1 − 0.667n

D. 0.1 − 0.5n

Units of Kc

$H2 + I2 \rightleftharpoons 2HI$

$2SO2\,(g) + O2\,(g) \rightleftharpoons 2SO3\,(g)$

Hydrogen and iodine can react reversibly to produce hydrogen iodide. The equation is shown.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

4 x 0

4.00 mol of hydrogen gas and X mol of iodine vapour are mixed in a sealed container of volume 1.00 dm^3 at a temperature of 460 K. The system is allowed to reach equilibrium.

−1 −1 +2

The equilibrium mixture contains 2.00 mol of hydrogen iodide. The equilibrium constant, K_c, for the reaction at 460 K is 4.0.

3 X−1 2

What is the value of X?

A 0.50 mol **B** 1.17 mol **C** 1.33 mol **D** 2.50 mol

$$\frac{c[HI]^2}{c[H_2] \times c[I_2]}$$

$$\frac{4}{3 \times (x-1)} = 4$$

$$x - 1 = \frac{1}{3}$$

NO. 1

Nitrogen reacts with hydrogen to produce ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

A mixture of 2.00 mol of nitrogen, 6.00 mol of hydrogen and 2.40 mol of ammonia is allowed to reach equilibrium in a sealed vessel of volume 4 dm^3. It is found that 2.32 mol of nitrogen were present in the equilibrium mixture.

Which expression will give the value of K_c?

A. $\frac{(1.76)^2}{(2.32)(6.96)^3}$

B. $\frac{(1.76)^2}{(2.32)(6.32)^3}$

C. $\frac{(2.08)^2}{(2.32)(6.32)^3}$

D. $\frac{(2.40)^2}{(2.32)(6.00)^3}$

NO. 2

An aqueous solution was prepared containing a mixture of 1.0mol of $AgNO_3$ and 1.0mol of $FeSO_4$ in 1.00dm^3 of water. When equilibrium was established, there was 0.44mol of Ag^+ (aq) in the mixture.

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

What is the numerical value of K_c?

A. 0.62
B. 1.40
C. 1.62
D. 2.89

NO. 3

In aqueous solution, sulfuric acid dissociates as shown.

$H_2SO_4 \rightarrow HSO_4^- + H^+$ This reaction goes to completion.

$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$ This reaction reaches equilibrium with constant K_c.

Analysis of a 2.00 mol dm^{-3} solution of H_2SO_4 found the HSO_4^- concentration to be 1.988 mol dm^{-3}.

What is K_c?

A. 1.381×10^5 dm^3 mol^{-1}
B. 82.34 dm^3 mol^{-1}
C. 1.214×10^{-2} mol dm^{-3}
D. 7.244×10^{-5} mol dm^{-3}

C

HSO_4 H^+ SO_4
I 2 0 0
C −0.012 +0.012 +0.012
E 1.988 0.012 0.012

$\frac{2.012 \times 0.012}{1.988} = C$

NO. 4

PCl_5 decomposes as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

1.0 mol of $PCl_5(g)$, 1.0 mol of $PCl_3(g)$ and 1.0 mol of $Cl_2(g)$ are placed in a container of volume 1 dm^3 at 250 °C and allowed to reach equilibrium.

At this temperature, the equilibrium mixture contains 1.8 moles of PCl_3.

What is the value of K_c at 250 °C?

A. 1
B. 1.8
C. 9
D. 16.2

+2
2.012
−0.8 +0.8 +0.8
1.8 1.8
0.2

The units of K_c for an equilibrium reaction are mol^{-1} dm^3.

What could be the equation for the equilibrium?

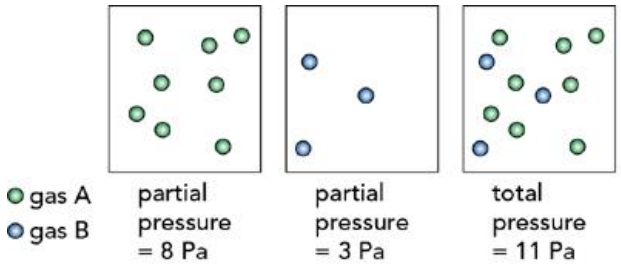
1. A(aq) + B(aq) ⇌ C(s) + D(aq)
2. P(aq) + Q(aq) ⇌ R(aq)
3. W(aq) + 2X(aq) ⇌ Y(aq) + Z(aq)

A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

$\frac{1}{mol\ dm^{-3}}$

3.Equilibrium constant, Kp(Equilibria in gas reactions)

Partial pressure



$P_{total} = P_A + P_B + P_C$

The total pressure of a gas equals the sum of the partial pressures of the individual gases.

ptotal = pA + pB + pC …

where pA, pB, pC are the partial pressures of the individual gases in the mixture.

For the general reaction $aA+bB \rightleftharpoons cC+dD$ in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Kp indicates the equilibrium constant formula in terms of partial pressures.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

In the reaction: $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

the equilibrium partial pressures at constant temperature are $SO_2 = 1.0 \times 10^6$ Pa, $O_2 = 7.0 \times 10^6$

Pa, SO_3 = 8.0 × 10^6 Pa. Calculate the value of K_p for this reaction.

Write the equilibrium constant expression for each reaction.

a. $N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$

b. $2\,C_8H_{18}(g) + 25\,O_2(g) \rightleftharpoons 16\,CO_2(g) + 18\,H_2O(g)$

c. $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

In this question you should assume that all gases behave ideally.

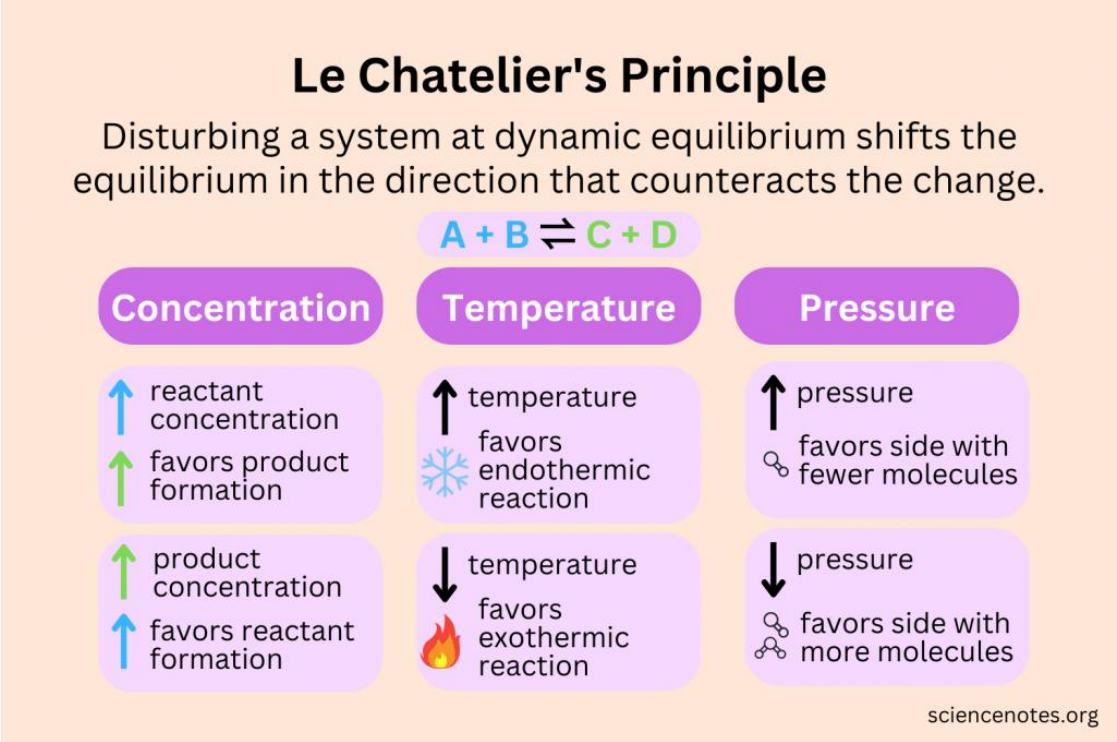
Hydrogen and iodine react reversibly in the following reaction. The system reaches dynamic equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -9.5 \text{ kJ mol}^{-1}$$

Which statement **must** be true for the K_p of this equilibrium to be constant?

A. The partial pressures of H_2, I_2 and HI are equal.
B. The external pressure is constant.
C. The forward and reverse reactions have stopped.
D. The temperature is constant.

4.Le Chatelier’ s principle



If one or more factors that affect a dynamic equilibrium is changed, the position of equilibrium moves to minimise this change.

Le Chatelier's principle states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium. If a chemical reaction is at equilibrium and experiences a change in pressure, temperature, or concentration of products or reactants, the equilibrium shifts in the opposite direction to offset the change.

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

What happens when we increase the pressure?

What happens when we decrease the pressure?

Predict the effect of increasing the temperature on the reaction:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

$\Delta H_r = +41.2 \text{ kJ mol}^{-1}$

In the reaction

$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$

increasing the temperature increases the amount of carbon dioxide formed at constant pressure.
Is this reaction exothermic or endothermic? Explain your answer.

A **catalyst** is a substance that increases the rate of a chemical reaction. Catalysts reduce the time taken to reach equilibrium, but they have no effect on the position of equilibrium once this is reached. This is because they increase the rate of the forward and reverse reactions equally.

→ exo

SO_3 is manufactured from SO_2 and O_2 in the Contact process.

The reaction is exothermic. $2SO_2 + O_2 \rightleftharpoons 2SO_3$

Which row shows the effect on the equilibrium yield obtained in the Contact process of increasing the temperature and of adding a vanadium(V) oxide catalyst?

	increasing the temperature	adding vanadium(V) oxide as catalyst
A	equilibrium yield decreases	equilibrium yield increases
B	equilibrium yield decreases	equilibrium yield unchanged
C	equilibrium yield increases	equilibrium yield unchanged
D	equilibrium yield increases	equilibrium yield increases

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

a. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + \mathbf{O}_{2(g)}$: the amount of HgO is doubled.
b. $NH_4HS_{(s)} \rightleftharpoons \mathbf{NH}_{3(g)} + H_2S_{(g)}$: the concentration of H_2S is tripled.
c. $\mathbf{n\text{-}butane}_{(g)} \rightleftharpoons isobutane_{(g)}$: the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Ethanol combines with ethanoic acid to form ethyl ethanoate according to the following reaction.

$C_2H_5OH(l) + CH_3CO_2H(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$ $\Delta H^{\ominus} = -6$ kJ mol^{-1}

9.2 g ethanol, 12 g ethanoic acid and 8.8 g ethyl ethanoate are mixed and allowed to stand at 298K, until equilibrium is reached.

The resulting equilibrium mixture is found to contain 4.8 g ethanoic acid.

The experiment is repeated at 323K.

Which statements are correct ? (M_r: C_2H_5OH- 46; CH_3CO_2H- 60; $CH_3CO_2C_2H_5$-88)

1. There are 0.22 moles of ethyl ethanoate in the mixture at equilibrium at 298K.
2. The equilibrium mixture at 323K will contain more than 4.8 g of ethanoic acid.
3. If a small amount of water is added at the start of either experiment the value of K_c would not be affected.

A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

Nitric acid is produced by oxidising ammonia. The first step is to react ammonia with oxygen in the presence of a catalyst to form nitrogen monoxide.

$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$ $\Delta H = -1636$ kJ mol^{-1}

Which set of conditions will produce the greatest yield of nitrogen monoxide at equilibrium?

	temperature	pressure
A	high	high
B	high	low
C	low	high
D	low	low

The reaction between sulfur dioxide and oxygen is reversible.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H^{\ominus} = -196\text{kJ mol}^{-1}$$

Which conditions of pressure and temperature favour the **reverse** reaction?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

Ethene can be oxidised to form epoxyethane, C_2H_4O.

$$C_2H_4(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons C_2H_4O(g) \quad \Delta H^{\theta} = -107 \text{ kJ mol}^{-1}$$

Which set of conditions gives the greatest yield of epoxyethane at equilibrium?

	pressure	temperature / °C
A	high	100
B	high	200
C	Low	100
D	Low	200

Hydrogen iodide gas decomposes reversibly producing iodine vapour and hydrogen.

$$2HI(g) \rightleftharpoons I_2(g) + H_2(g) \quad \Delta H = +12 \text{ kJ mol}^{-1}$$

The position of the equilibrium for this reaction may be altered by changing the external conditions.

Which row correctly describes the change in position of equilibrium?

	effect of increasing the pressure	effect of increasing the temperature
A	moves to the right	moves to the right
B	moves to the right	moves to the left
C	no change	moves to the right
D	no change	moves to the left

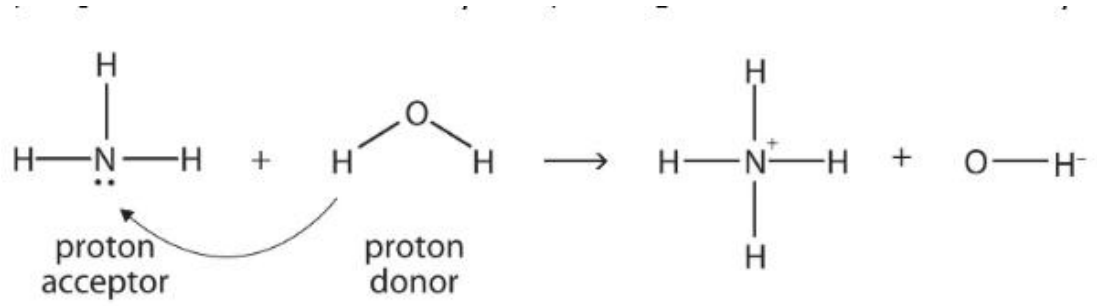
5.Brønsted-Lowry Acids and Bases

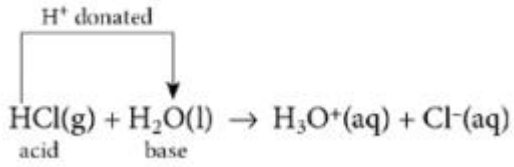
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. **A Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. **A Brønsted-Lowry base** is any species that can accept a proton from another molecule.

In short, a Brønsted-Lowry acid is a proton donor (PD), while a Brønsted-Lowry base is a proton acceptor (PA).

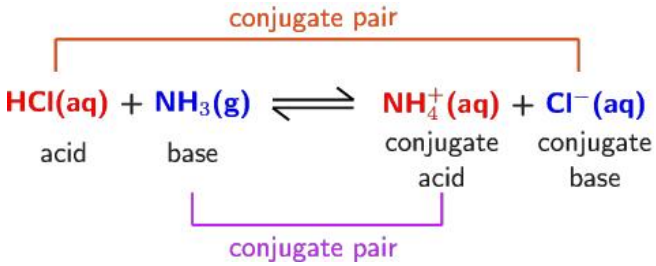
A *Brønsted–Lowry acid* *is a proton donor.*

A *Brønsted–Lowry base* *is a proton acceptor*





Conjugate Pairs



Q. In which reaction is water behaving as a Brønsted–Lowry base?

A. $H_2O + Na \rightarrow NaOH + ½H_2$

B. $H_2O + H_3PO_4 \rightarrow H_3O^+ + H_2PO_4^-$

C. $H_2O + CaO \rightarrow Ca(OH)_2$

D. $NH_3 + [Cu(H_2O)_6]^{2+} \rightarrow NH_4^+ + [Cu(H_2O)_5(OH)]^+$

Q. In which reaction does ammonia behave as a Brønsted-Lowry base?

A. $NH_3 + CH_3CH_2Br \rightarrow CH_3CH_2NH_2 + HBr$

B. $NH_3 + H_2O + CO_2 \rightarrow (NH_4)HCO_3$

C. $2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2$

D. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

Which statement about the ammonium ion is correct?

A. It can act as a Brønsted-Lowry base.

B. It can react with OH^- to give ammonia.

C. It is pyramidal with bond angles of 107°.

D. The nitrogen atom is sp^2 hybridised.

NH_4^+

Sulfur dioxide is used as a preservative in wine making.

The following equations describe the reactions that occur when sulfur dioxide dissolves in water.

$$H_2O + SO_2 \rightleftharpoons HSO_3^- + H^+$$
$$HSO_3^- + H^+ \rightleftharpoons SO_3^{2-} + 2H^+$$

Which statement about **these two reactions** is correct?

A. HSO_3^- acts as a base.

B. SO_2 acts as an oxidising agent.

C. SO_3^{2-} acts as an acid.

D. SO_3^{2-} acts as a reducing agent.

Which statement explains the observation that magnesium hydroxide dissolves in aqueous ammonium chloride, but not in aqueous sodium chloride?

A. The ionic radius of the NH_4^+ ion is similar to that of Mg^{2+} but not that of Na^+.
B. NH_4Cl dissociates less fully than $NaCl$.
C. The Na^+ and Mg^{2+} ions have the same number of electrons.
D. The NH_4^+ ion can donate a proton.

6. Strong and weak acids and bases

Hydrated aluminium ions undergo the following reaction.

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$

Which statement about this reaction is correct?

A. $H_2O(l)$ and $[Al(H_2O)_5OH]^{2+}(aq)$ are a conjugate acid-base pair.

B. $H_2O(l)$ is acting as an acid as it is donating H^+ ions.

C. If $OH^-(aq)$ is added, the equilibrium will move to the right.

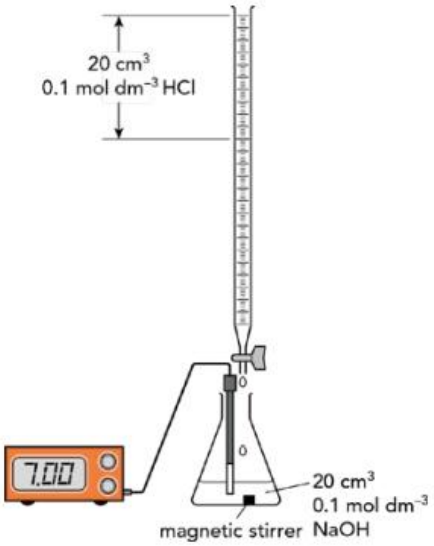
D. K_c varies as the pH is varied.

7. Titration

titration, process of chemical analysis in which the quantity of some constituent of a sample is determined by adding to the measured sample an exactly known quantity of another substance with which the desired constituent reacts in a definite, known proportion.

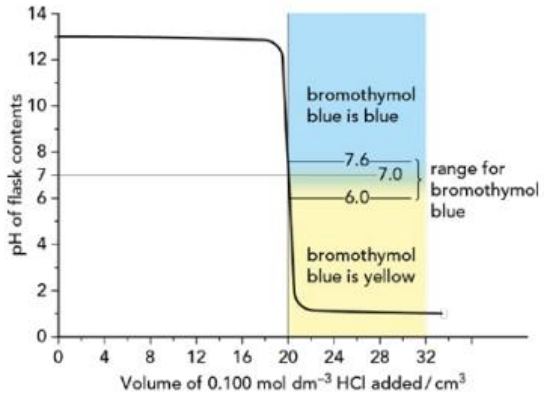
The process is usually carried out by gradually adding a standard solution (i.e., a solution of known concentration) of titrating reagent, or titrant, from a burette, essentially a long,

graduated measuring tube with a stopcock and a delivery tube at its lower end. The addition is stopped when the **equivalence point** is reached.

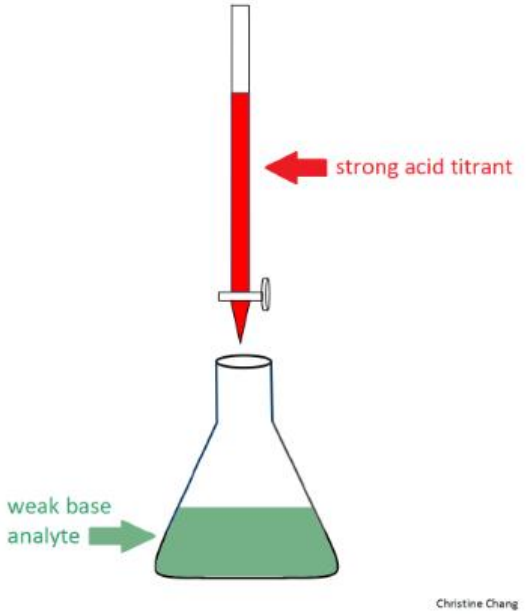


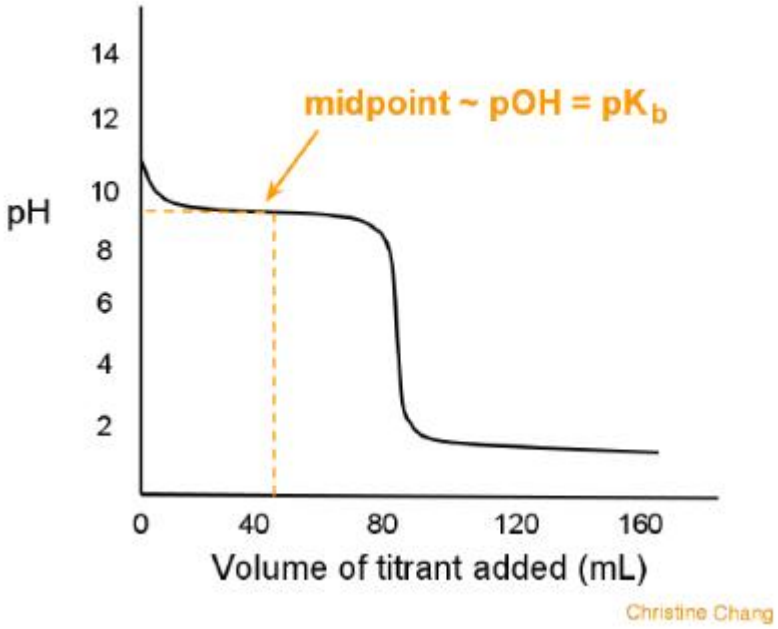
Strong acids with strong bases

Figure 8.18 shows how the pH changes when 0.100 mol dm^{-3} sodium hydroxide (a strong base) is titrated with 0.100 mol dm^{-3} hydrochloric acid (a strong acid) in the presence of bromothymol blue indicator.



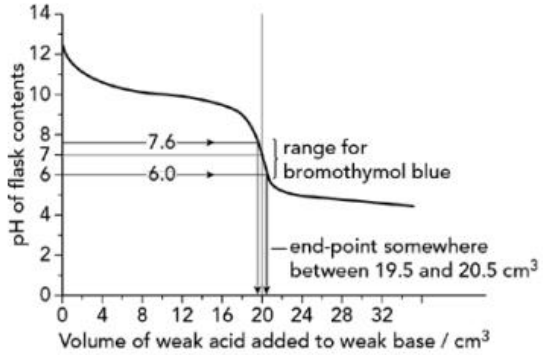
Titration of a Weak Base with a Strong Acid





Weak acids with weak bases

Figure 8.22 shows how the pH changes when 0.100 mol dm^{-3} aqueous ammonia (a weak base) is titrated with 0.100 mol dm^{-3} aqueous benzoic acid (a weak acid).



The sketch graph shows the change in pH when an acid and an alkali react with one being added slowly to the other. Both acid and alkali have a concentration 0.1 mol dm−3.

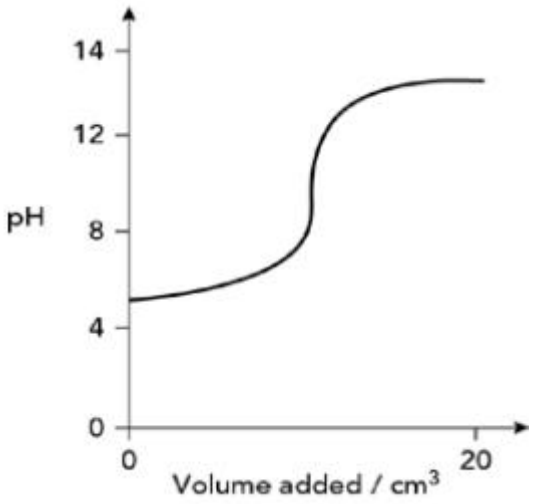
Which one of these statements is correct?

A. Weak alkalis being added to a weak acid

B. Strong alkali is being added to a strong acid

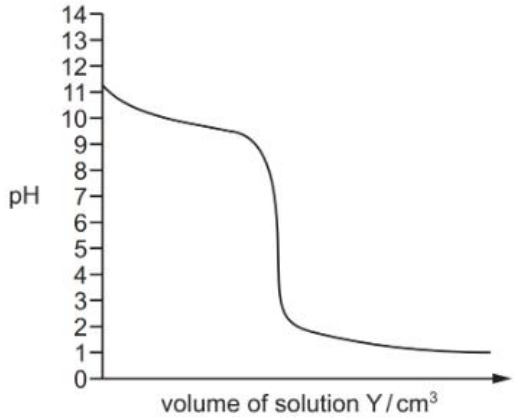
C. Strong acid is being added to a weak alkali.

D. Strong alkali is being added to a weak acid.



Solutions X and Y both have a concentration of 0.10 mol dm^{-3}. A fixed volume of solution X is added to a conical flask, and solution Y is added from a burette to the conical flask. A titration is performed.

The diagram shows the pH titration curve for the acid–base reaction between the solutions.



What are solutions X and Y?

	solution X	solution Y
A	ammonia	nitric acid
B	ammonia	ethanoic acid
C	potassium hydroxide	nitric acid
D	potassium hydroxide	ethanoic acid

Element X has the second largest atomic radius in its period. An atom of X has three occupied electron shells only.

The oxide of X is shaken with water.

What could be the pH of the resulting solution?

A. 5
B. 7
C. 9
D. 14

8.Summary