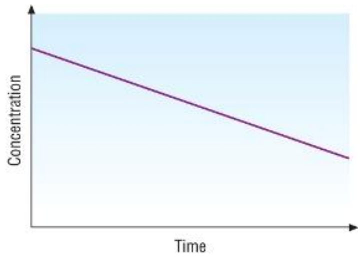
Standard answers and definitions:

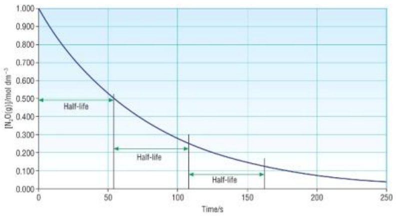
1A Rates of reaction:

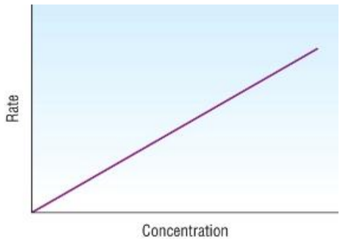
1. Rate = $\dfrac{\text{Change in [ ]}}{\text{Time}}$
   - Is the gradient on a [ ] / t graph
   - Units = mole dm^{-3} s^{-1}
2. Initial rate
   - Rate at t = 0
3. Rate equation = k [A]^{n} [B]^{n}
4. Rate constant
   - The constant of proportionality between rate and concentration of reactants
   - Units to be worked out by re arranging the rate equation and cancelling units
5. Order
   - The power to which the concentration of a reactant is raised
6. Zero order
   - Has no effect on the rate



- [ ] decreases as it is used up
- The change in [ ] has no effect on rate

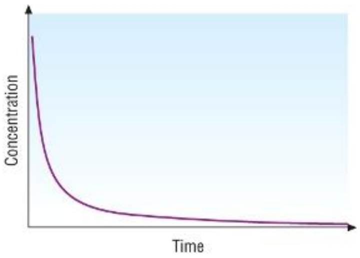
7. First order
   - Is directly proportional to the rate
   - If [ ] x2 the rate x2

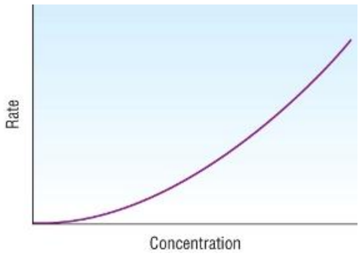




- [ ] has constant half lives
- [ ] increases, rate increases by equal amounts

8. Second order
   - Rate is affected by squares
   - If [ ] x2 the rate x4
   - If [ ] x3 the rate x9





- [ ] half lives increase
- [ ] increases, rate increases by increasing amounts

9. **Overall order**
    - **Sum of all the orders in the rate equation**
10. **Affect of increasing temperature on the rate equation**
    - **Increasing temperature increases the rate constant, k**
    - **As the concentrations haven't changed**
11. **Rate determining step**
    - **Slowest step in a multistep reaction mechanism**
12. **Orders and mechanisms**
    - **Use the rate equation and the mechanism**
    - **2nd order - 2 of the same collide in the rds - 2A (+ B) →**
    - **1st order - 1 collides (with something else? - A (+ B) →**
13. **Common mechanism from rate equations – (1):**
    - **Rate = k $[NO_2]^2$**

$$NO_{2(g)} \quad + \quad CO_{(g)} \quad \rightarrow \quad NO_{(g)} \quad + \quad CO_{2(g)}$$

First step	NO_2	+	NO_2	$\rightarrow$	NO_3	+	NO	**Slow - Rate Determining Step**
Second step	NO_3	+	CO	$\rightarrow$	NO_2	+	CO_2	**Fast**
Overall	NO_2	+	CO	$\rightarrow$	NO	+	CO_2	

14. **Common mechanism from rate equations – (2):**
    - **Rate = k $[CH_3COCH_3][H^+]$**

$$CH_3COCH_3 \quad + \quad I_2 \quad \rightarrow \quad CH_3COCH_2I \quad + \quad HI$$

First step	CH_3COCH_3	+	H^+	$\rightarrow (CH_3)_3COH^+$				**Slow - Rate Determining Step**
Second step	$(CH_3)_3COH^+$	+	I_2	$\rightarrow CH_3COCH_2I$	+	H^+ +	HI	**Fast**
Overall	CH_3COCH_3	+	I_2	$\rightarrow CH_3COCH_2I$	+		HI	

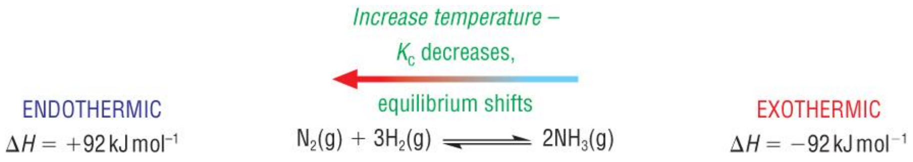
- **H^+ is a catalyst as it is used up in step (1) and regenerated in step (2)**

1B - Equilibria

15. **Features of an equilibrium**
    - **Closed system**
    - **Dynamic**
    - **Can be approached from either direction**
16. **What can be said about the forward and reverse reactions at equilibrium**
    - **The rate of the forward and reverse reactions are the same**
17. **Equilibrium expression**

$$K_c = \frac{[\text{PRODUCTS}]^p}{[\text{REACTANTS}]^r}$$

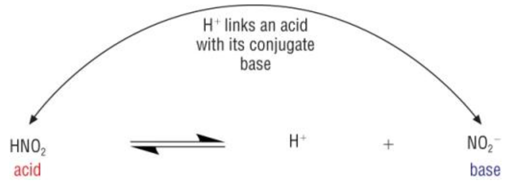
18. **Effect of temperature on equilibrium**



    - **Increasing temperature moves the eqm to the endothermic side (and vice versa)**
    - **This shifts it to the reactants side.**
    - **This reduces the value for products and increases the value for reactants.**
    - **Kc Decreases (and vice versa)**
19. **Effect of pressure on equilibrium**
    - **Increasing P moves the eqm to the side with fewer moles of gas (and vice versa)**
    - **Kc remains unchanged**
20. **Effect of concentration on equilibria**
    - **Increasing the concentration moves the eqm to the opposite side in order to remove (and vice versa)**
    - **Kc remains unchanged**
21. **What affects the value of Kc**
    - **Only temperature affects the value of Kc**
    - **Eqm shift in order to satisfy Kc for Pressure and concentration**
22. **What affect does a catalyst have on KC**
    - **None – it increases the rate of the forward and reverse reactions**
    - **Equilibrium is established quicker**

1C Acids and buffers

23. Acid – Bronsted Lowrey definition
    - Proton donor
24. Base – Bronsted Lowrey definition
    - Proton acceptor
25. Alkali
    - A base that dissolves in water forming OH^- ions
26. Strong acid
    - Dissociates fully
27. Weak acid
    - Partially dissociates
28. Di / Tri basic acids
    - The number of acidic hydrogen's an acid can release
29. Acid reactions:
    a. Carbonate + Acid → Salt + CO_2 + H_2O
    b. Base (metal oxide) + Acid → Salt + H_2O
    c. Alkali (metal hydroxide) + Acid → Salt + H_2O
30. Conjugate acid base pairs
    - The relationship between 2 species in equilibrium by a H^+ ion



31. Ionic product of water = $[H^+] \times [OH^-] = 1 \times 10^{-14}$
32. pH = -log $[H^+]$ (definition)
33. pH of a strong acid
    a. [Acid] = $[H^+]$ (assuming monobasic)
    b. pH = -log $[H^+]$
34. pH of a strong base
    a. [Base] = $[OH^-]$ (assuming monoacidic – x2 for di etc)
    b. $[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$
    c. pH = -log $[H^+]$
35. pH of a weak acid
    a. $[H^+]$ = √Ka x [Acid] (square root)
    b. pH = -log $[H^+]$
    c. Assumptions: i) $[H^+] = [A^-]$ ii) [Acid] is virtually unchanged as Ka is so small
36. pH of a Buffer solution
    a. $[H^+] = Ka \times \frac{[Acid]}{[Salt]}$
    b. pH = -log $[H^+]$
37. Definition of a buffer solution
    - Minimises the change in pH with the small addition of strong acid / base

38. How does a buffer solution work?

$HA_{(aq)} \leftrightarrows H^{+}_{(aq)} + A^{-}_{(aq)}$ **Reaction 1**

$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)}$ **Reaction 2**

a. **Addition of H^{+}**

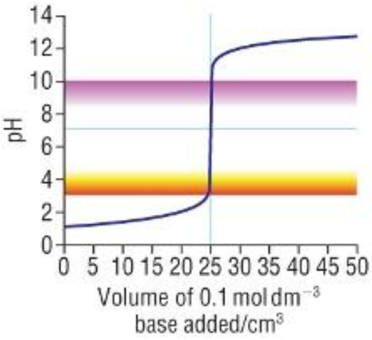
- **Shift equilibrium in (1) to the LHS in order to remove the added H^{+}**
- **H^{+}'s removed, pH maintained**

b. **Addition of OH^{-}**

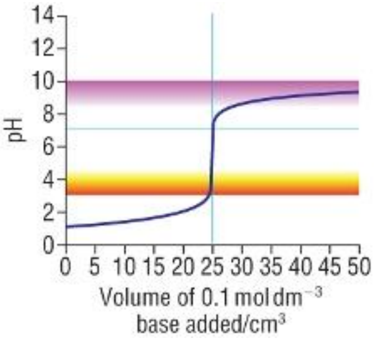
- **Added OH^{-}'s react with H^{+}'s in (1) according to reaction (2) removing added OH^{-}'s**
- **Equilibrium in (1) shifts to the RHS in to replace the lost H^{+}**
- **OH^{-}'s removed / H^{+}'s replaced, pH maintained**
- **How does a buffer solution work?**

39. Titration curves

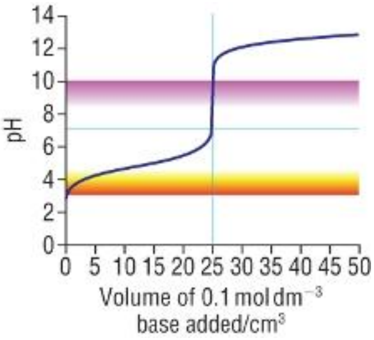
- **Equivalence point is at pH 7**
- **End point is when the indicator changes colour**
- **Pick an indicator that changes colour in the steep vertical part of the curve**



Strong acid / Strong base
pH 3 – 11



Strong acid / Weak base
pH 3 – 8



Weak acid / Strong base
pH 6 – 11

40. Indicators

$HIn \leftrightarrows H^{+} + In^{-}$

Colour 1 **Colour 2**

- **Equilibria controlled by addition of H^{+} / Removal of H^{+} with the addition of OH^{-}**

41. Enthalpy change of Neutralisation

- **Is the enthalpy change when aq acid is neutralised by aq base forming 1 mole of water**

42. Ionic equations

- **Separate into ions – aq only**
- **Cancel the spectator ions to give the ionic equation**

Full: $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

Ions: $H^{+}_{(aq)} + Cl^{-}_{(aq)} + Na^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)} + H_2O_{(l)}$

Ionic: $H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)}$

43. Calculating enthalpy change of neutralisation

a. $Q = \frac{mc\Delta T}{1000}$ (Kj)

REMEMBER m IS VOLUME OF LIQUID WITH THERMOMETER IN

b. $\text{Moles} = \frac{\text{mass}}{\text{Mr}} = C \times V(dm^3)$

REMEMBER TO USE LIMITING REAGENT

c. $\Delta H = \frac{Q\ (\text{Kj})}{\text{moles}}$

d. SIGN: ↑T (-)ve ↓T (+)ve

- Per mole of water formed the enthalpy changes of neutralisations should all be about the same
- Weak acids will be slightly less exothermic due the reaction occurring at a slower rate meaning heat has a longer time to be lost

2A Enthalpy:

44. Lattice enthalpy, ΔH_{le}
    - One mole of a compound is formed from its gaseous ions under standard conditions
45. Enthalpy change of formation, ΔH_f
    - One mole of a compound is made from its elements in their standard states under standard conditions
46. Enthalpy change of atomisation, ΔH_{at}
    - One mole of gaseous atoms are formed from its element in their standard state

47. 1st Ionisation energy, ΔH_{i1}
    - Each atom in a mole of gaseous atoms loses one electron forming 1 mole of gaseous 1+ ions
48. 1st Electron affinity, ΔH_{ea1}
    - Each atom in a mole of gaseous atoms gains one electron forming 1 mole of gaseous 1- ions
49. Calculating lattice enthalpy from Born – Haber cycles

    $\Delta H_{le} = \Delta H_f - \Sigma$ (all other enthalpy changes)
50. Enthalpy change of solution, ΔH_{sol}
    - One mole of a compound is completely dissolved under standard conditions
51. Enthalpy change of hydration, ΔH_{hyd}
    - One mole of aqueous ions are formed from their gaseous ions under standard conditions
52. Factors affecting lattice enthalpy:
    a. Size of ions
        - Smaller ions can pack closer together, therefore stronger electrostatic forces of attraction

    b. Ionic charge
        - Larger charge = stronger electrostatic forces of attraction
53. Factors affecting hydration enthalpy:
    a. Size of ions
        - Smaller ions water can get closer, therefore stronger forces of attraction

    b. Ionic charge
        - Larger charge = stronger forces of attraction between ion and water
54. Entropy
    - Quantitative measure of the degree of disorder in a system, $J\ mol^{-1}\ k^{-1}$
55. Change in entropy

$$\Delta S^{\theta}_{system} = \Sigma S^{\theta}_{products} - \Sigma S^{\theta}_{reactants}$$

- $\Delta S^{\theta}_{system}$ = Positive for a reaction to be likely

56. Gibbs free energy

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

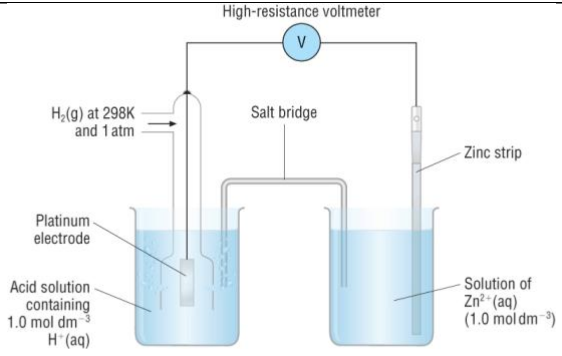
- Takes into account the surrounding, ΔH
- ΔG = Negative for a reaction to be likely
- Remember, ΔH is in KJ, ΔS is in J, so convert to KJ

2B Electrochemistry

58. Oxidation
    - Loss of electrons
59. Reduction
    - Gain of electrons
60. Writing balancing chemical equations using oxidation numbers
    a. Write the unbalanced equation
    b. Identify the elements undergoing REDOX
    c. Write in the oxidation numbers – YOU NEED ONE ATOM OF EACH
    d. Multiply up the lowest change in oxidation numbers
    e. Balance O by adding H_2O on the opposite side
    f. Balance H by adding H^+ on the opposite side
61. Writing balanced chemical equations using E_{cell}
    a. Write the 2 half equations with the most negative at the top and the electrons on the left
    b. Apply anticlockwise rule. Bottom left and top right are your reactants.
    c. Write the 2 half equations in the direction they react
    d. Balance using electrons
    e. Write the overall equation
62. Calculating E_{cell}

    $Emf \ = \ E^{\theta}_{pos} \ - \ E^{\theta}_{neg}$

    - The Emf must be greater than +/- 0.4v
63. What does E_{cell} value tell you
    - The most negative tends to the LHS
    - This means that electrons are being lost
    - This means they are being oxidised
    - This means that they are good reducing agents
    - The more negative, the better reducing agent
    - And vice versa for positive values
64. The standard 'Hydrogen' electrode

	• Remember, all labels required • That this is the reference electrode • Assigned the value E_{cell} = 0v

65. 3 types of batteries:
    a. Non rechargeable
    b. Rechargeable
    c. Fuel cells
66. Fuel cells
    - Carry the fuels that react in a REDOX reaction providing electricity
    - H_2 / O_2 No CO_2 produced so long as H_2 produced in a renewable way
    - More efficient

67. Storage of H_2
    - Pressure is problematic due to expense / safety
    - Adsorption – on a solid surface
    - Absorption – within a solid
    - Solids often contain toxic chemicals / have limited life span

3 Transition metals

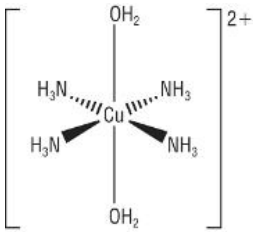
68. Definition
    - Contains at least on ion with an incomplete d sub – shell
69. Characteristics of transition metals
    - As metals plus
    - Variable oxidation states
    - Coloured compounds
    - Catalysts
70. Homogeneous catalyst
    - Catalyst and reactants in the same phase
71. Heterogeneous catalyst
    - Catalyst and reactants in different phases
72. Catalysts work by
    a. Transferring electrons:
        - Providing electrons forming an intermediate with a lower activation energy
        - Comes out unchanged

    b. Providing a site to react:
        - Adsorption
        - Weakens bonds
        - Reaction at a lower activation energy
        - Desorption
73. Electron configurations
    - A half filled or filled d sub – shell is more stable than a full s sub - shell
    - Cr $3d^5 4s^1$
    - Cu $3d^{10} 4s^1$
    - 4s fills before 3d / 4s empties before 3d
74. Precipitation reactions
    - $Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Cu(OH)_{2(s)}$ Pale blue →Blue ppt
    - $Co^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Co(OH)_{2(s)}$ Pink →Blue ppt →Beige ppt in air
    - $Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$ Green →Green ppt → Brown ppt in air
    - $Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Fe(OH)_{3(s)}$ Yellow →Brown ppt
75. Complex ion
    - Central metal ion surrounded by ligands
76. Ligand / multidentate ligands
    - Molecule / ion with a lone pair able to donate forming a dative covalent bond / coordinate bond
    - Bi, Tri etc dentate ligands – the number of dative bonds a ligand can make with the central metal ion
77. Dative covalent bond / coordinate bond
    - One atom has provided both electrons in the covalent bond
78. Coordination number
    - The number of coordinate bonds between ligands and central metal ion

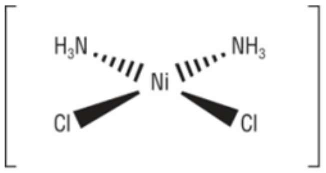
79. **Stereoisomer**

- **Same structural formula but different arrangement of atoms in space**

80. **Shapes of complex ions**

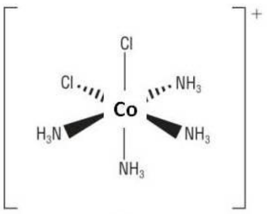


Octahedral = 90^{o}



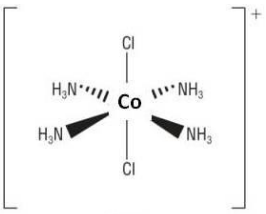
Square planar = 90^{o} / 180^{o}

81. **Cis / trans isomerism**



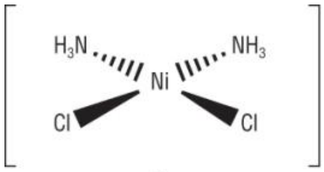
Cis

CIS = 2 ligands at 90^{o}



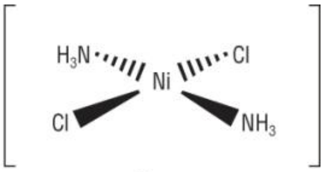
Trans

TRANS = 2 ligands at 180^{o}



Cis

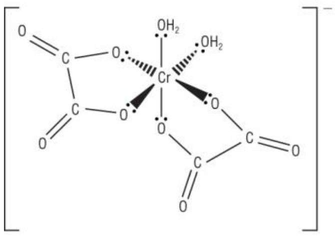
CIS = 2 ligands at 90^{o}



Trans

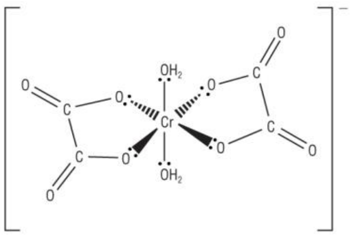
TRANS = 2 ligands at 180^{o}

82. **Cis / trans with bidentate ligands**



Cis

CIS = 2 ligands at 90^{o}

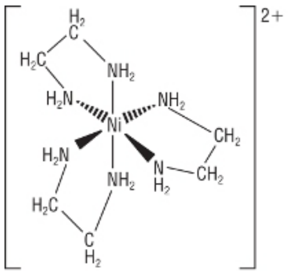


Trans

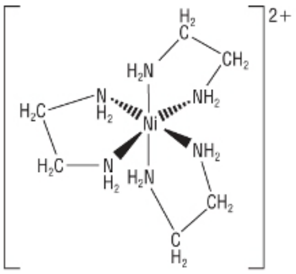
TRANS = 2 ligands at 180^{o}

- **The Cis isomer is also an optical isomer, see below**

83. **Optical isomerism**



Image



Mirror image

- **2 non superimposable images**
- **Can rotate plane polarised light**

84. **Ligand substitution**

- **One ligand in a complex ion is replaced with another ligand**

85. **Ligand substitution Cu^{2+} with ammonia:**

- **Ammonia, NH_3, in water also contains – OH^-**

a. **$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Cu(OH)_{2(s)}$ Pale blue → Blue ppt**

b. **$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$**

- **Pale blue → Dark blue (via a blue ppt (a)**

86. Ligand substitution Cu^{2+} with HCl (Cl^-)

- **$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$**
- **Pale blue → Yellow (via green at 1:1 ratio of the 2 complexes)**

87. Ligand substitution Co^{2+} with conc. HCl (Cl^-)

- **$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$**
- **Pink → Dark blue**

88. Stability constants

- **No different from Equilibria expressions, just ignore water**

$$K_{stab} = \frac{[PRODUCTS]^p}{[REACTANTS]^r}$$

89. What does K_{stab} mean?

- **High value >1 – product ligand predominates due to stronger bonds with the central metal ion**
- **Low value <1 - Reactant ligand predominates due to stronger bonds with the central metal ion**

90. REDOX titrations

a. **$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$**
   Purple Colourless

- **Used to calculate:**
- **% Fe in brass / iron tablets / anything**
- **Mr of an iron containing salt**
- **Purity of Iron sample**

b. **$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$**
   Brown Colourless

- **The iodine will be liberated from 1 or 2 other reactions, common examples but there could be others as an application of knowledge:**
- **$Cu \rightarrow Cu^{2+} \rightarrow I_2$**
- **$ClO^- / ClO^{3-} \rightarrow I_2$**
- **$Cr_2O_7^{2-} \rightarrow I_2$**
- **Take care with your ratios**