VICTORIA UNIVERSITY PRESENTS THE.... 2011 VALUATE SERIES

HEALTH, ENGINEERING AND SCIENCE

VCE CHEMISTRY UNIT 4: CHEMISTRY AT WORK

REVISION NOTES

DATE: THURSDAY 29 SEPTEMBER 2011 Prepared by: Neale Peters





BACHELOR OF INFORMATION TECHNOLOGY (NETWORK AND SYSTEMS COMPUTING) VTAC code 40811

The Bachelor of Information Technology (Network and Systems Computing) prepares students for a graduate level position within the IT industry. Currently there is a growing market need for graduates skilled in systems administration with networking expertise and this degree equips students with the knowledge and skills required. The program prepares students for IT Industry Certifications (CISCO/Microsoft) and for a career in the fields of networking, databases, and systems administration. The course is offered over three years on a full-time basis (part-time equivalent) at the Footscray Park Campus. With the skills you develop, you could be looking at a range of career options in: Business Analysis & Consulting

Business Analysis & Consulting Computing & Network Support Database Administration Network & Systems Administration Project Management Secondary Teaching Systems Security Consultancy Web-based Programming Prerequisites: Units 3 and 4 – a study score of at least 20 in English (any) and ANY Mathematics.

BACHELOR OF ENGINEERING SCIENCE (SPORTS ENGINEERING) VTAC code 40881

Bachelor of Engineering Science (Sports Engineering) prepares students for a career in the fields of sports, sports science, and exercise and rehabilitation. The primary objective of this program is to produce graduates who are universally recognised as leading practitioners in their field and who, as Sports Engineers, are capable of making a contribution to society and the community.

This program develops students into highly skilled engineering technologists who will be able to provide knowledge-based practical engineering services/solutions to the sports, sports science, and exercise and rehabilitation industries. The course is offered over three years on a full-time basis and will take full advantage of the new \$53 million specialist Sports and Exercise Sciences complex at the Footscray Park campus. With the skills you develop, you could be looking at a range of career options such as:

Scientists Coaches Elite Athletes Sporting Goods Manufacturers

Venue Managers

Prerequisites: Units 3 and 4-a study score of at least 24 in English (any) and in one of further mathematics, mathematical methods or specialist mathematics.

BACHELOR OF SCIENCE (Specialisations in Biotechnology, Chemistry or Environmental Management) VTAC code 40691

We produce graduates with a thorough knowledge of contemporary science for careers in industry, government and education. If you want to be a: biotechnologist; chemist; ecologist or environmental scientist; the Bachelor of Science (Specialisation) is the course for you. The course offers major studies in the abovementioned professions, where students can choose to specialise in one or two science disciplines. This is a three year course with elective choices in the latter two years that allows students the flexibility to add other studies of interest to their specialisation. Specialisations are offered subject to student numbers.

Science at Victoria University is industry focussed, offers an intensive hands-on laboratory experience, has modern laboratories with state-ofthe-art equipment, provides opportunities for industry projects and placements and overall better prepares students for careers in the science profession. Those students with scientific research in mind can progress into Honours and postgraduate studies. Prerequisites: Units 3 and 4 - a study score of at least 20 in English (any) and ANY Mathematics.

SCHOLARSHIPS ENTER AT 70

Available for all Engineering, IT (networking and systems computing), Science Specialisation and Nutrition, Health and Food Sciences courses for students with an ATAR (Enter) of 70 and above who meet the requirements. See www.vu.edu.au/hes for more information and application form.

ALTERNATIVE ENTRY FOR

ENGINEERING (VTAC code 41441)

SCIENCE (VTAC code 41451)

Alternative entry program to engineering and science courses for students who have:

• Successfully completed year 12 with the required prerequisites, but may not have achieved the required study score in all prerequisites; or

• Have not studied the required mathematics prerequisite.

All admissions are on an individual basis. All applicants offered a place would be required to enroll in one or more subjects from the Foundation Year.

Prerequisites: Units 3 and 4 - English (any) and mathematics (any). ATAR (ENTER) 50+

VCE CHEMISTRY

UNIT 4: CHEMISTRY AT WORK

REVISION LECTURE

Neale Peters 29 September 2011

> vu.edu.au CRICOS Provider No: 00124K



UNIT 4 CHEMISTRY EXAM DETAILS

- EXAM FORMAT SAME AS UNIT 3
 - Monday 14 November, 9.00 am
 - 15 min Reading Time
 - 90 min Writing Time
 - ~20 multi-choice questions (~20-25 min)
 - short answer questions
 - equal weighting on Areas of Study 1 and 2
 - 1. Industrial Chemistry
 - 2. Supplying & Using Energy
- NEW COURSE IN 2008
 - Industrial Chemistry shifted from Unit 3 into Unit 4
 - BEWARE WHEN USING EXAMS FROM 2007 OR EARLIER FOR REVISION

UNIT 4 CHEMISTRY AoS 1: INDUSTRIAL CHEMISTRY

Significant changes to Unit 4 in the Study Design in 2008

• Much of the content was previously Unit 3 material

Important when using pre 2008 resources - use UNIT 3 EXAMS

- collision theory and factors that affect the rate of a reaction including activation energy;
- energy profile diagrams and the use of ΔH notation;
- reversible reactions: homogeneous equilibria and the equilibrium law, Le Chatelier's Principle and factors which affect the position of equilibrium;
- pH as a measure of strength of acids and bases; K_w, K_a for weak acids;
- principles of waste management used in the chemical industry;
- the industrial production of the selected chemical
 - factors affecting the production including rate and equilibrium position, catalysts, temperature, pressure
 - waste management including generation, treatment and reduction
 - health and safety
 - uses of the selected chemical

UNIT 4 CHEMISTRY AoS 2: SUPPLYING & USING ENERGY

- Relatively few changes in new Study Design
- Pre 2008 use Unit 4 Exams but note some shifts in emphasis
- comparison of energy sources: types, uses and sustainability of sources including brown coal, natural gas, nuclear fission and biochemical fuels;
- application of calorimetry to measure energy changes in chemical reactions in solution calorimetry and bomb calorimetry;
- use of the electrochemical series in predicting the products of redox reactions and writing half equations;
- limitations of predictions made using the electrochemical series;
- the construction and operation of simple galvanic primary and secondary cells;
- the construction and operation of fuel cells: advantages and disadvantages of fuel cells compared to conventional energy sources;
- the construction and operation of simple electrolytic cells: comparison of electrolytic cells;
- application of Faraday's laws in electrochemistry.

UNIT 4 CHEMISTRY RELEVANT UNIT 3 CONTENT

- Mole & stoichiometry
 - Equilibrium Law
 - ΔH calculations
 - Faraday's Laws
- Acid-base reactions and pH calculations
 - relates especially to $K_{\rm w}$ and $K_{\rm a}$
- Redox reactions, oxidation numbers and half-equations
 - Electrochemical Series
 - Cells
- Biofuels
 - Comparison of energy sources

UNIT 4 CHEMISTRY DATA BOOKLET

- RELEVANT TO UNIT 4
 - 1. Periodic table
 - 2. Electrochemical series
 - ☑ VERY IMPORTANT
 - 3. Physical Constants, especially
 - ☑ charge on electron
 - ☑ Faraday constant
 - \boxtimes K_w at 298K
 - $\boxtimes \$ Specific heat capacity of water
 - 4. SI prefixes
 - 11. Acid-base indicators (K_a)
 - 12. K_a values for some weak acids
 - 13. Molar enthalpies of combustion

- NOT RELEVANT TO UNIT 4
 - 5. ¹H NMR data
 - 6.13H NMR data
 - 7. IR data
 - 8. Amino acids
 - 9. Fatty acids
 - 10. Biomolecules

FAMILIARISE YOURSELF THOROUGHLY WITH THE RELEVANT SECTIONS

UNIT 4 CHEMISTRY Important Formulae

MOLE/STOICHIOMETRY

OTHER

n=m/M n=N/N_A n=cV n=V/V_m pV=nRT n(e⁻)=Q/F Q=It, so $n(e^{-})=It/F$ pH= -log[H⁺] [H⁺]= 10^{-pH} E=VIt (hence E=VQ) Δ E= m c Δ T Δ E= calibration factor x Δ T K_w= [H⁺][OH⁻]

 $\mathsf{K}_{\mathsf{a}} = \frac{[\mathsf{H}^+][\mathsf{A}^-]}{[\mathsf{H}\mathsf{A}]}$

d (density) = m/V

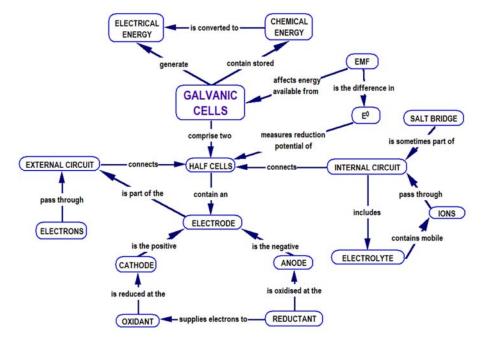
UNIT 4 CHEMISTRY REVISING EFFECTIVELY - NOTES

- Prepare detailed notes for descriptive topics that require memorisation, principally
 - 1. Energy Sources Uses and sustainability
 - · brown coal, natural gas, nuclear fission, biochemical fuels, etc
 - 2. One Industrial Process
 - Ammonia, ethene, sulfuric acid, or nitric acid
- For topics with a more conceptual focus, distil the key concepts
 - Conceptual grasp is more important than memorising details of cells studied
 - Perhaps develop a GLOSSARY of terms and definitions,
 - eg for GALVANIC CELLS:

CELL, HALF CELL, INTERNAL CIRCUIT, EXTERNAL CIRCUIT, ANODE, CATHODE, OXIDANT, REDUCTANT, ELECTROLYTE, etc

UNIT 4 CHEMISTRY REVISING EFFECTIVELY - NOTES

... and/or develop concept maps to summarise the important ideas



UNIT 4 CHEMISTRY REVISING FOR UNDERSTANDING

- Don't just memorise formulae and plug in numbers
 - rehearse the *meaning* of each quantity
 - know the appropriate units
- The meaning of a quantity can make the formula unnecessary; eg:
 - 'molar' quantities

•

- molar mass, M=m/n : mass of one mole of a substance
- molar volume, V_m =V/n : volume of one mole of a substance (gas)
- molar charge (Faraday Constant), F=Q/n : charge of one mole of electrons
- specific heat capacity: c(H₂O) = 4.18 J K⁻¹ g⁻¹
 - it takes 4.18 Joules of heat to make 1g of water hotter by 1 °C
 - \Rightarrow hence , 4.18 J for every gram of water for every 1 °C of temp.
 - $\Rightarrow \Delta E = c x m x \Delta T = m c \Delta T$

UNIT 4 CHEMISTRY REVISING FOR UNDERSTANDING

How many Faradays of charge are required to form 1.50 mol of Aluminium in the Hall Cell: Al³⁺(I) + 3e⁻→ Al(I) ?

The robotic student thinks:
"OK, I've got the moles of aluminium, so I could use n=m/M. No I don't need the mass. What do I need? Charge; OK that's Q isn't it – I need that formula with Q in it There's Q=It, but I don't have the current or time
... so it must be the other one: Q=nF
... or is it Q=n/F? Q=nF? Q=n/F? (dammit!!) No, I'm sure it's Q=nF
OK, there's 1.50 moles, so: n=1.50"
and so writes:

Q=nF=1.50 x 96500 = 144750

UNIT 4 CHEMISTRY REVISING FOR UNDERSTANDING

How many Faradays of charge are required to form 1.50 mol of Aluminium in the Hall Cell: $AI^{3+}(I) + 3e^{-} \rightarrow AI(I)$?

The logical student says:

"Let's see: usually charge is in Coulombs but I need the number of Faradays here. one Faraday of charge is the charge on one mole of electrons

... so what I really need here is the number of moles of electrons

oh - that's easy: the half-equation tells me I need 3 moles of electrons per mole of AI"

and so writes:

 $n(e^{-}) = 3 \times n(AI) = 4.50 \text{ mol}$ $\Rightarrow 4.50 \text{ Faradays of charge needed}$



UNIT 4 CHEMISTRY A TRICKY QUESTION

A mixture of brown NO_2 and colorless N_2O_4 gases in a rigid vessel reaches equilibrium according to the equation:

 $2NO_2(g) \Leftrightarrow N_2O_4(g)$

(brown)

The colorless, inert gas argon is added to the vessel to increase the total pressure. What effect does this have on the color of the mixture? •If you have memorised all the variations on Le Chatelier's principle, you might think as follows:

"OK, the pressure increases

... so this is one of those problems where what matters is the number of particles on either side of the equation.

Here there are fewer particles on the right

my notes said: "a pressure increase causes a shift to the side with fewer particles"

... so this one will shift to the right"

• and so write:

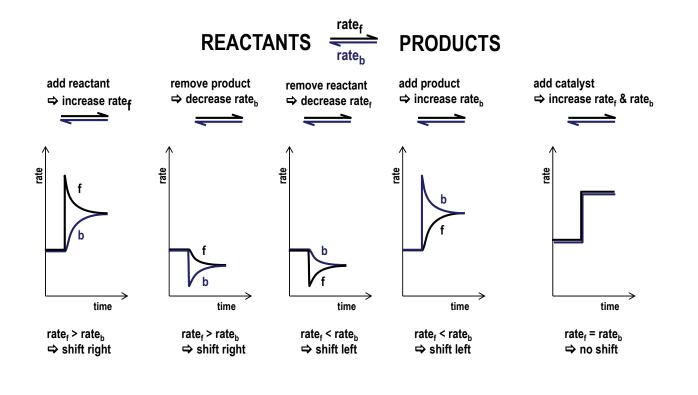
"pressure increases, so by LCP there is an equilibrium shift to the right, the side with fewer particles, to partially oppose the pressure increase ⇔mixture becomes less brown"

X

UNIT 4 CHEMISTRY A TRICKY QUESTION

- Let's analyse the fundamental principles here:
- What is chemical equilibrium?
 - a dynamic, steady state resulting from the *equal rates* of opposing changes, ie forward and reverse reactions
- What is an equilibrium 'shift'?
 - a change in the composition of a mixture resulting from the *unequal rates* of forward and reverse reactions
- When will an equilibrium shift occur?
 - when any change causes the rates of forward and reverse reactions to become unequal
 - · reaction rates are governed by COLLISION theory

UNIT 4 CHEMISTRY EQUILIBRIUM SHIFTS – A RATE ISSUE



UNIT 4 CHEMISTRY A TRICKY QUESTION

A mixture of brown NO_2 and colorless N_2O_4 gases in a rigid vessel reaches equilibrium according to the equation:

 $2NO_2(g) \Leftrightarrow N_2O_4(g)$

(brown)

The colorless, inert gas argon is added to the vessel to increase the total pressure. What effect does this have on the color of the mixture?

How does the Key Idea of rates apply?

- the addition of argon does not change the concentration of reactants or products
- ➡ the rate of collisions between reactant particles (and between product particles) is not changed
- ⇒ so that either
 - the rates of forward and reverse reactions are unaffected by the argon, or
 - the argon has a catalytic effect that increases the rates of forward and reverse reactions equally
- ⇒ either way the rates remain equal
- and hence:

The addition of argon affects the forward and reverse reactions equally (or not at all) so that no shift occurs

⇒no change in the colour of the mixture



UNIT 4 CHEMISTRY SUMMARISING

- What's the 'difficulty' here?
- TOP LEFT. BOTTOM RIGHT • Le Chatelier's principle is a useful way to predict an equilibrium shift.
 - Le Chatelier's principle is not the 'reason' that an equilibrium shift occurs.
 - The KEY IDEA in analysing equilibrium changes is the *relative rates* of forward and reverse reactions
 - **OIL RIG**

5)

- How to ready for tricky problems?
 - · Don't become over-reliant on mnemonics, formulae, mathematical tricks without understanding their basis
- BACKWARD.1 In your revision focus on the KEY IDEAS and do what you can to deepen your understanding n=mM

UNIT 4 CHEMISTRY GENERAL REVISION

- 1. Summarise the KEY IDEAS and the necessary descriptive, factual detail from each topic in your REVISION NOTES
- 2. Work a range of problems on each topic from
 - textbook
 - tests and SACs
 - "CheckPoints" (Roger Slade and Maureen Slade, Cambridge Uni Press)
 - commercially available exams and topic tests from, eg
 - STAV, Insight, IARTV, NEAP Lisa Chem
- 3. Constantly revise and add to your REVISION NOTES as you progress - review and read them regularly
- Make your teacher work!! 4.
 - ask her/him to check your notes
 - clarify any marking/solutions ambiguities on practice exams
- 5. Complete as many full papers as you can manage the time for
 - under examination conditions
 - reading time, no interruptions etc

UNIT 4 CHEMISTRY SOME SPECIFIC STRATEGIES

Analyse each mnemonic/trick/formula/quantity you use

Make sure you can explain what each one means or why it works

Example

Molar mass, M

• M is just the mass of one *mole* of any substance: memorising the formula M=m/n should be unnecessary

Example

"Top Left-Bottom Right" or "Backward-Z"

- this can only be applied to an Electrochemical Series sorted from highest to lowest E⁰ value
- it's a special case of the KEY IDEA that the most likely redox reaction is always between the strongest available reductant and the strongest available oxidant

UNIT 4 CHEMISTRY SOME SPECIFIC STRATEGIES

USE THE EXAMINERS' REPORTS

- These are available from the VCAA website for all VCAA exams that have been sat and marked.
 - take careful note of questions that were done poorly and the examiners' thoughts on why this was the case
 - · look carefully at the mark allocation
 - look at 'popular' but incorrect multiple-choice answers and try to determine why they were selected (and why they are wrong!)
 - examine your own responses critically in the light of the examiners' expectations
 - add noteworthy remarks to your topic summaries as reminders
- NB: before 2008 use Unit 3 Exams for Area of Study 1

UNIT 4 CHEMISTRY SOME SPECIFIC STRATEGIES

PROBLEM SOLVING STRATEGIES

- · First, try to visualise the entire solution pathway
 - for stoichiometric calculations you will have a well-rehearsed sequence:
 - 1. find $n(X) \rightarrow 2$. use mole ratio to find $n(Y) \rightarrow 3$. find answer eg m(Y)
 - · for some calculation problems the pathway may require more thought
- If stuck, try to identify what the 'precursor' to the final answer will be
 - for example, where the problem is to calculate a pH, the precursor is usually [H⁺] reinterpret the question with this as your target
- Trial and error
 - when all else fails calculate *something* from the data given
 - calculating n(X) might be a dead-end; on the other hand it might be worth a mark
 - that calculated value might just suggest what the next step should be and get you started

UNIT 4 CHEMISTRY SOME SPECIFIC STRATEGIES

READ BEYOND THE COURSE

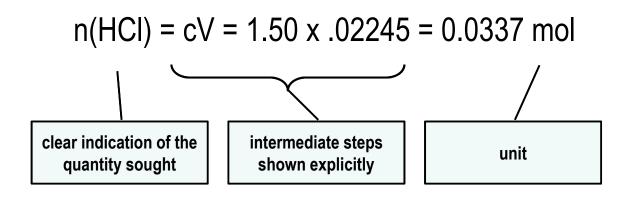
- The more extensive your knowledge of a topic the better equipped you will be to answer VCE-level questions
 - · as a minimum, your textbook should have been read cover to cover
 - · re-read sections that you feel less confident with
 - re-do questions that have caused you difficulty
 - · if you have access to other VCE texts read sections of them as well
 - a slightly different angle from an alternative source might allow a concept you have struggled with to 'click'
 - there are also a number of good online sources
 - eg <u>www.chemguide.co.uk</u>
 - · these sometimes go beyond what is required for VCE but that's not a bad thing

UNIT 4 CHEMISTRY MAXIMISING MARKS

- · How do you ensure you earn the maximum marks?
 - Get the answer right!!
 - Correct chemical language
 - equations balanced
 - states included in every equation
 - · correct use of subscripts/superscripts in chemical formulae
 - Significant figures
 - · Clear and logical setting out of calculations
 - consequential marks
 - Correct units

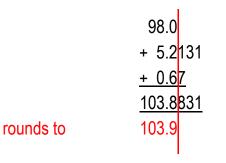
UNIT 4 CHEMISTRY MAXIMISING MARKS

CLEAR & LOGICAL SETTING OUT IS CRITICAL



UNIT 4 CHEMISTRY MAXIMISING MARKS

- SIGNIFICANT FIGURES ADDING/SUBTRACTING
 - for addition/subtraction the result is rounded to the smallest number of DECIMAL PLACES:
 - eg if adding



- NB: the periodic table in the DATA BOOK gives atomic masses to *one decimal place*.
 - · molar masses should be to one decimal place

UNIT 4 CHEMISTRY MAXIMISING MARKS

SIGNIFICANT FIGURES - MULTIPLYING/DIVIDING

• for multiplication/division the result is rounded to the smallest number of SIGNIFICANT FIGURES:

eg the amour of a 1.5 M so	nt (moles) of HCI lution is	in 22.45 mL	BUT the amou of a 1.5 <u>0</u> M so	unt (moles) of HC olution is	l in 22.45 mL
	1.5 x <u>0.02245</u> <u>0.033675</u>	(2 sig figs) (4 sig figs)		1.50 x <u>0.02245</u> <u>0.033675</u>	(3 sig figs) (4 sig figs)
rounds to	0.034 mol	(2 sig figs)	rounds to	0.0337 mol	(3 sig figs)

AREA OF STUDY 1

INDUSTRIAL CHEMISTRY

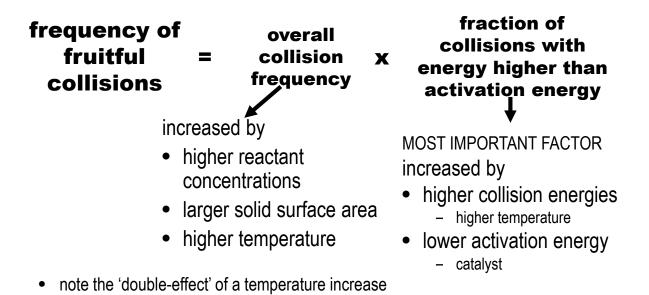
UNIT 4 CHEMISTRY- AOS1 STUDY DESIGN - KEY KNOWLEDGE

- collision theory and factors that affect the rate of a reaction including activation energy;
- energy profile diagrams and the use of ΔH notation;
- reversible reactions: homogeneous equilibria and the equilibrium law, Le Chatelier's Principle and factors which affect the position of equilibrium;
- pH as a measure of strength of acids and bases; K_w, K_a for weak acids;
- · principles of waste management used in the chemical industry;
- the industrial production of the selected chemical
 - factors affecting the production including rate and equilibrium position, catalysts, temperature, pressure
 - waste management including generation, treatment and reduction
 - health and safety
 - uses of the selected chemical

UNIT 4 CHEMISTRY– AOS1 Rates & Collision Theory

KEY POINTS

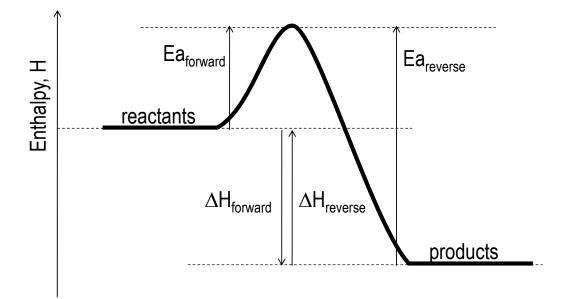
· the rate of a reaction is determined by the frequency of fruitful collisions



UNIT 4 CHEMISTRY– AOS1 Energy Profile Diagrams

KEY POINTS

- $\Delta H > 0$ for endothermic reactions; $\Delta H < 0$ for exothermic reactions
- E_a is always positive minimum energy required to break bonds to initiate reaction



UNIT 4 CHEMISTRY- AOS1 **AH Notation**

KEY IDEAS:

- ΔH values apply to specific *equations* •
- the magnitude of ΔH relates to the mole amounts in the equation ٠
- ΔH values are not affected by the conditions of the reaction •

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$$
 $\Delta H = -111 \text{ kJ mol}^{-1}$

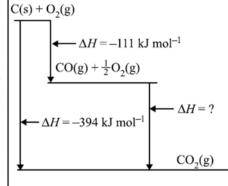
From Sample Exam 2007 Q18

 $C(s) + O_2(g) \rightarrow CO_2(g)$

$$\Delta H = -394 \text{ kJ mol}^{-1}$$

Give ΔH for these equations:

enthalpy



 $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ -394-(-111) = -283 kJ mol⁻¹ $CO_2(g) \rightarrow O_2(g) + C(s)$

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

2 x (-111) = -222 kJ mol⁻¹

-(-394) = +394 kJ mol⁻¹

 $2CO_2(g) \rightarrow O_2(g) + 2CO(g)$ 2 x -(-283) = +586 kJ mol⁻¹

UNIT 4 CHEMISTRY- AOS1 AH vs Heat of Combustion

KEY IDEA:

 Heat of Combustion is the energy released when a unit quantity (1 mol; 1 g; 1 kg; 1 L, etc) of a fuel is completely combusted

eg for combustion of butane

$2C_4H_{10}(g) + 9O_2 \rightarrow 8CO_2 + 10H_2O(g)$ $\Delta H = -5748 \text{ kJ mol}^{-1}$

The HEAT of COMBUSTION of butane is

- heat released by combustion of 1 mol = 5748/2 = 2874 kJ mol⁻¹ ٠
- heat released by combustion of 1 g = 2874/58 = 49.6 kJ g⁻¹ ٠
- heat released by combustion of 1 L at SLC = 2874/24.5 = 117 kJ L⁻¹
- heat released by combustion of 1 L at 200 kPa and 350 K

= 2874/(8.31*350/200) = 198 kJ L⁻¹

UNIT 4 CHEMISTRY- AOS1 AH vs Heat of Combustion

From Sample Exam 2007 Question 4

Octane, C_8H_{18} , is a major constituent of petrol used in cars. b. i. Write a balanced equation for the complete combustion of octane. $C_8H_{18}(I) + 12.5O_2(g) \rightarrow 8CO_2(g) + 9H_2O(I)$ or $2C_8H_{18}(I) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(I)$

ii. Give the value and sign of ΔH for this reaction.

From the DATA BOOKLET, $\Delta H_c(\text{octane}) = -5464 \text{ kJ mol}^{-1}$

ie combustion of 1 mol of octane releases 5464 kJ of heat

For $C_8H_{18}(I) + 12.5O_2(g) \rightarrow 8CO_2(g) + 9H_2O(I)$ $\Delta H = -5464 \text{ kJ mol}^{-1}$

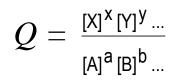
For $2C_8H_{18}(I) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(I)$

 ΔH = -10928 kJ mol⁻¹

UNIT 4 CHEMISTRY- AOS1 EQUILIBRIUM LAW

KEY POINTS

• $aA + bB + \dots \Leftrightarrow xX + yY + \dots$



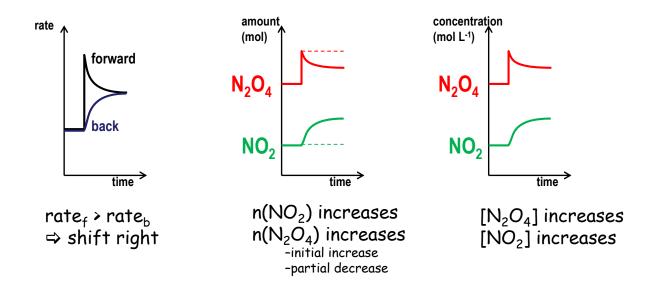
- for any equilibrium mixture, Q = K
 - K is a constant whose value depends only on the temperature
 - K is independent of
 - the initial composition of the mixture or any subsequent changes
 - pressure, volume, dilution, etc
 - the presence of other chemical species
- three possible cases for any mixture
 - 1. Q<K the system is not at equilibrium and a net forward reaction occurs
 - 2. Q>K the system is not at equilibrium and a net back reaction occurs
 - 3. Q=K the system is already at equilibrium and no net reaction occurs

UNIT 4 CHEMISTRY- AOS1 EQUILIBRIUM LAW

- If a system is at equilibrium
 - rates of forward and back reactions are equal
 - concentrations (or pressures of gases) are constant
 - Q = K
- If a system is at not at equilibrium
 - rates of forward and back reactions are unequal
 - one of the reactions is 'winning', so that ...
 - concentrations (or pressures of gases) are changing
 - · we see changes in the macroscopic properties of the mixture
 - colour
 - pH
 - total gas pressure
 - etc

UNIT 4 CHEMISTRY- AOS1 EQUILIBRIUM SHIFTS - GRAPHS

 $N_2O_4(g) \leftrightarrows 2NO_2(g);$ K = 5.5 x 10⁻³ M; $\Delta H>0$ (endothermic) If additional N_2O_4 is added to an equilibrium mixture:

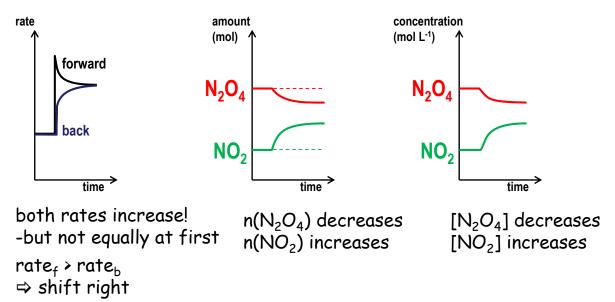


UNIT 4 CHEMISTRY- AOS1 EQUILIBRIUM SHIFTS - GRAPHS

 $N_2O_4(g) \leftrightarrows 2NO_2(g);$ K = 5.5 x 10⁻³ M;

 Δ H>0 (endothermic)

If the temperature is increased, we expect a net forward reaction since the reaction is endothermic:

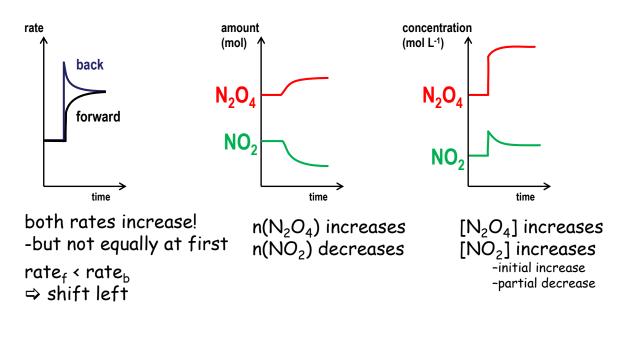


UNIT 4 CHEMISTRY- AOS1 EQUILIBRIUM SHIFTS - GRAPHS

 $N_2O_4(g) \leftrightarrows 2NO_2(g);$ K = 5.5 x 10⁻³ M;

 Δ H>0 (endothermic)

If the volume is reduced (ie gases compressed):



UNIT 4 CHEMISTRY- AOS1 Le CHATELIER'S PRINCIPLE

- Used to predict equilibrium shifts but not to account for them
 - shifts tend to partially oppose any imposed change, eg

IMPOSED CHANGE increase in concentration of a reactant	SHIFT OBSERVED ⇒ shift right to reduce concentrations of reactants
decrease in concentration of a product	⇒ shift right to increase concentrations of products
increase in temperature	\Rightarrow shift in the endothermic direction to reduce temperature
dilution of a solution	⇒ shift to the side with more dissolved particles to increase overall concentration
compression of a gas mixture	⇒ shift to the side with fewer particles to reduce the overall pressure
addition of catalyst	⇔ no shift

UNIT 4 CHEMISTRY- AOS1 pH & K_w

KEY IDEAS:

- pH is merely a function of [H⁺]: pH = -log[H⁺]
 - hence [H⁺] = 10^{-pH}
- Acid-base character depends on relative concentrations of [H⁺] & [OH⁻]
 - If [H⁺]>[OH⁻] the solution is acidic
 - If $[H^+] < [OH^-]$ the solution is basic
 - If $[H^+]=[OH^-]$ the solution is neutral
- pH measures only [H⁺] so pH alone is no indication of acid-base character
 - for neutral solutions pH=7 only at 25 °C

UNIT 4 CHEMISTRY- AOS1 pH & K_w

pH problems cause more difficulty than they should. A "pH problem" is actually a "[H⁺] problem"

Which of the following will have a pH of 2?

- A. 100 mL of HCl with a pH=3 added to 10 mL of HCl with a pH=1
- B. 100 mL of HCl with a pH=3 added to 100 mL of HCl with a pH=1
- C. 100 mL of NaOH with a pH=13 added to 100 mL of HCl with a pH=1
- D. 100 mL of HCl with a pH=1 added to 100 mL of water

try thinking:

Which of the following will have a $[H^+] = 0.01 \text{ M}$?

- A. 100 mL of HCl with $[H^+]=0.001M$ added to 10 mL of HCl with $[H^+]=0.1M$
- B. 100 mL of HCI [H⁺]=0.001M added to 100 mL of HCI with [H⁺]=0.1M
- C. 100 mL of NaOH with [OH⁻]=0.1M added to 100 mL of HCl with [H⁺]=0.1M
- D. 100 mL of HCl with [H⁺]=0.1M added to 100 mL of water

	n(H ⁺) ₁ (mol)	n(H ⁺) ₂ (mol)	n(H ⁺) _{total}	V _{total}	[H+]
А	0.001x0.1=0.0001	0.1x0.01=0.001	0.0011	0.110 L	0.010 M
В	0.001x0.1=0.0001	0.1x0.1=0.01	0.0101	0.200 L	0.051 M
С	equal amounts of H ⁺ and OH⁻ being mixed ⇔neutral				
D	0.1x0.1=0.01	0.0	0.01	0.200 L	0.050 M

UNIT 4 CHEMISTRY- AOS1 pH & K_w

• $K_w = [H^+][OH^-]$ is the equilibrium constant for the *endothermic reaction*:

 $H_2O(I) \Leftrightarrow H^+(aq) + OH^-(aq)$

- as temperature increases
 - K_w increases
 - the ionisation reaction shifts to the right, *increasing [H⁺] and [OH]*

Which of the following describes a solution with a pH=7.0 at 70 °C?	$[H^+] = 10^{-pH} = 10^{-7} M$ At higher temperatures K _w increases, so K _w > 10 ⁻¹⁴ ⇒ $[H^+]x[OH^-] > 10^{-14}$
A. acidic	⇒ [OH ⁻] > 10 ⁻¹⁴ /[H ⁺]
B. basic	⇔ [OH ⁻] > 10 ⁻¹⁴ / 10 ⁻⁷
C. neutral	⇔ [OH⁻] > 10-7
D. none of the above	⇔ [OH⁻] > [H⁺]
	⇒ the solution is basic!

UNIT 4 CHEMISTRY– AOS1 Acidity Constants, K_a

- KEY IDEAS:
 - K_a expresses the extent of ionisation of an acid
 - · calculations only for weak acids that remain largely un-ionised
 - very low K_a values

Name	Formula	Ka
Ammonium ion	NH4 ⁺	5.6 × 10 ⁻¹⁰
Benzoic	C ₆ H ₅ COOH	6.4 × 10 ⁻⁵
Boric	H ₃ BO ₃	5.8 × 10 ⁻¹⁰
Ethanoic	CH3COOH	1.7×10^{-5}
Hydrocyanic	HCN	6.3 × 10 ⁻¹⁰
Hydrofluoric	HF	7.6×10^{-4}
Hypobromous	HOBr	2.4 × 10 ⁻⁹
Hypochlorous	HOCI	2.9 × 10 ⁻⁸
Lactic	HC ₃ H ₅ O ₃	1.4×10^{-4}
Methanoic	HCOOH	1.8×10^{-4}
Nitrous	HNO ₂	7.2×10^{-4}
Propanoic	C ₂ H ₅ COOH	1.3×10^{-5}

12.	Acidity	constants.	K., of	some	weak acids
		,	a,		

UNIT 4 CHEMISTRY- AOS1 Industrial Process

AMMONIA, ETHENE, SULFURIC ACID, or NITRIC ACID

- Learn ONE process in detail
- Raw Materials (and their sources)
- · Equations including reaction details and conditions

eg for H₂SO₄ (Contact Process)

- Burner:
 - $S(I) + O_2(g) \rightarrow SO_2(g)$
 - exothermic, redox (S oxidised $0 \rightarrow +4$)
 - molten sulfur sprayed into furnace
- Converter:
 - $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
 - exothermic, redox (S oxidised $+4 \rightarrow +6$)
 - ~400-500 °C; ~1 atm
 - multiple passes over V2O5 catalyst

• Absorption:

 $\mathrm{SO}_3(\mathsf{g}) + \mathrm{H}_2\mathrm{SO}_4(\mathsf{I}) \to \mathrm{H}_2\mathrm{S}_2\mathrm{O}_7(\mathsf{I})$

- product is *oleum*
- exothermic, not redox
- avoids problems caused by excessive heat from direct mixing with water
- Dilution:

$$H_2S_2O_7(I) + H_2O(I) \rightarrow 2H_2SO_4(I)$$

- exothermic, not redox

UNIT 4 CHEMISTRY- AOS1 Industrial Process

Rate and Equilibrium considerations, especially compromises

• eg in sulfuric acid production, in the converter:

 $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

- exothermic reaction ⇒ high yield at *lower temperatures*
- higher rate obtained at *higher temperature*
 - ~450 $^\circ$ C used is a compromise
- fewer product particles ⇒ high yield at *higher pressure*
- higher rate obtained at higher pressure
 - high pressure gives favourable yield and rate BUT ~1 atm used is a compromise with *cost*
- catalyst is important in obtaining adequate rate
- multiple passes over catalyst (with cooling between) to maximise conversion to product

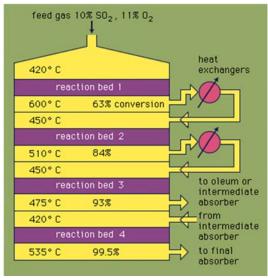


Image: BRITANNICA.COM

UNIT 4 CHEMISTRY- AOS1 Industrial Process

- For properties and uses, make sure you can provide specific *examples*, with *equations* where necessary
- Again, using sulfuric acid as an example:

PROPERTIES

- strong, diprotic acid $H_2SO_4(aq) \rightarrow HSO_4^-(aq) + H^+(aq)$ $HSO_4^-(aq) \leftrightarrows SO_4^{2-}(aq) + H^+(aq)$
- oxidant $2H_2SO_4(I) + Mg(s) \rightarrow$ $MgSO_4(aq) + SO_2(g) + 2H_2O(I)$
- dehydrating agent $C_6H_{12}O_6(s) \rightarrow 6C(s) + 6H_2O(g)$

USES, eg

fertiliser production

$$H_2SO_4(I) + 2NH_3(g) \rightarrow (NH_4)_2SO_4(s)$$

- source of sulfate ions in a range of fertilisers
- removal of metal oxides
 CuO(s) + H₂SO₄(aq) →
 CuSO₄(aq) + H₂O(l)

UNIT 4 CHEMISTRY– AOS1 Waste Management

- Methods of waste handling and disposal will depend on
 - the hazards associated with the material
 - explosive
 - toxic
 - carcinogenic
 - · corrosive, etc
 - the properties of the material
 - water solubility
 - volatility
 - reactivity
 - stability, etc
- Methods of waste management include
 - modifying procedures to reduce or eliminate wastes •
 - recycling of wastes
 - treatment of wastes to reduce hazards
 - disposal of wastes

A.

B.

D.

UNIT 4 CHEMISTRY– AOS1 Waste Management

..., a chemist was left with several materials to be disposed of in a • safe manner. These included

i. 120 mL of ethyl ethanoate	organic ester; not water soluble
ii. 150 mL unused 0.10 M NaCl	soluble ionic compound; common & safe
iii. a solid compound of lead dried and weighed on filter paper.	heavy metal – toxic; solid

Which one of the following alternatives describes an appropriate method of c. disposal of each of the above wastes ...?

2008 Unit 4, Question 13

120 mL ethyl ethanoate	150 mL unused 0.10 M NaCl	Solid lead compound
waste container labelled 'ORGANIC LIQUIDS ONLY'	down the sink	waste container labeller 'DRY SOLIDS ONLY'
waste container labelled 'ORGANIC LIQUIDS ONLY'	a stock bottle of 0.10 M NaCl prepared for the experiment	in the rubbish bin
waste container labelled 'AQUEOUS WASTE ONLY'	waste container labelled 'AQUEOUS WASTE OTLY'	in the rubbish bin
waste container labelled 'AQUEOUS WASTE ONLY'	a stock bottle of 0.10 M NaC1 prepared for the experiment	waste container fabeller 'DRY SOLIDS ONLY'

AREA OF STUDY 2 SUPPLYING & USING ENERGY

UNIT 4 CHEMISTRY- AOS2 STUDY DESIGN - KEY KNOWLEDGE

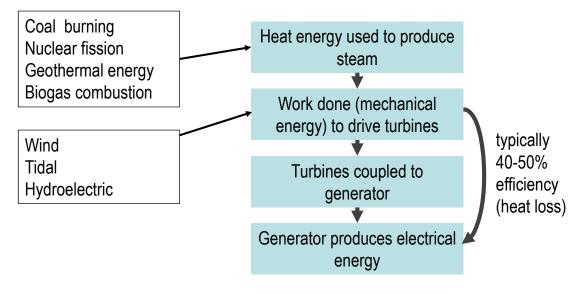
- comparison of energy sources: types, uses and sustainability of sources including brown coal, natural gas, nuclear fission and biochemical fuels;
- application of calorimetry to measure energy changes in chemical reactions in solution calorimetry and bomb calorimetry;
- use of the electrochemical series in predicting the products of redox reactions and writing half equations;
- limitations of predictions made using the electrochemical series;
- the construction and operation of simple galvanic primary and secondary cells;
- the construction and operation of fuel cells: advantages and disadvantages of fuel cells compared to conventional energy sources;
- the construction and operation of simple electrolytic cells: comparison of electrolytic cells;
- application of Faraday's laws in electrochemistry.

UNIT 4 CHEMISTRY– AOS2 Comparison of Energy Sources

Little on recent exams but definitely KEY KNOWLEDGE in Study Design:

"comparison of energy sources: types, uses and sustainability of sources including brown coal, natural gas, nuclear fission and biochemical fuels"

The following energy transformation associated with Power Plants is generally important:



UNIT 4 CHEMISTRY– AOS2 Comparison of Energy Sources

• From 2007 Unit 4

Question 20

During the production of electricity in a coal-fired power station, energy is present in the following forms.

- I mechanical energy of turbine
- II chemical energy of coal and oxygen
- III thermal energy of steam

The amount of energy in each of these forms that take part in the generation of a fixed quantity of electricity is, **from lowest to highest**

- A. III, I, II
- B. I, II, III
- C. I, III, II
- **D.** II, III, I

energy is lost at each stage:

 $\begin{array}{cccc} & & & & & \\ ll & & & & \\ chemical energy \longrightarrow & thermal energy \longrightarrow & mechanical energy \longrightarrow & electrical energy \\ (coal/oxygen) & (steam) & (turbine/generator) \end{array}$

UNIT 4 CHEMISTRY– AOS2 Calorimetry

CALIBRATION

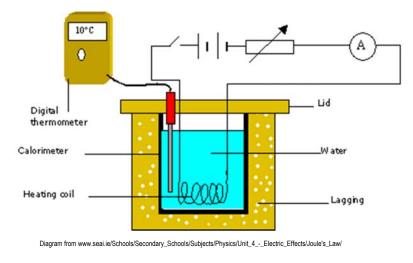
- · A calorimeter is a calibrated 'black box'
- A calorimeter's calibration factor relates
 - a temperature change (measurable)
 - a corresponding energy change (not directly measurable)
- · calibration involves
 - 1. Adding a known quantity of energy
 - using an electric heater: E=VIt
 - using a known reaction: E=n x (molar heat of reaction)
 - 2. Measuring the corresponding temperature change
 - 3. Calculating the ratio

calibration factor =

energy added

temperature change

UNIT 4 CHEMISTRY- AOS2 Solution Calorimetry



KEY COMPONENTS:

- insulated container
- thermometer
- *fixed* volume of water or aqueous solution

OFTEN INCLUDE:

- stirrer
- heating coil for calibration

used for any reactions in the aqueous phase, eg

- acid + base
- heat of solution (ie dissolving)



UNIT 4 CHEMISTRY– AOS2 Bomb Calorimetry

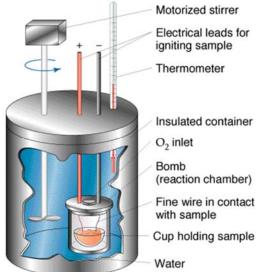


Diagram: www.chem.ufl.edu/~itl/2045/lectures/lec_9.html

used for non-aqueous reactions

- combustion of fuels (very important)
- decomposition (eg explosives)

KEY COMPONENTS:

- insulated container
- thermometer
- fixed volume of water
- enclosed reaction chamber (the 'bomb')
- ignition wire to start reaction
- stirrer

CAN INCLUDE:

heating coil for calibration

UNIT 4 CHEMISTRY- AOS2 Electrochemical Series

Key reactions involving water oxygen and hydrogen

F⁰ in volt

			E* in volt
	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$		+2.87
	$H_2O_2(aq) + 2H^*(aq) + 2e^- \rightleftharpoons 2H_2O(1)$		+1.77
	$\operatorname{An}^{+}(\operatorname{aq}) + e^{-} \rightleftharpoons \operatorname{Au}(s)$	굞	+1.68
S	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	Ü	+1.36
S	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(1)$	N S	+1.23
Ā	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	H	+1.09
INCREASE	$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$	Ê	+0.30
ž	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	E	+0.77
н	$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	S S	+0.68
யீ	$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	REDUCTANTS ON	+0.54
STRONGER AS	$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$		+0.40
4	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	Ĩ	+0.34
μ	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	Ï	+0.15
9	$S(s) + 2H^{+}(aq) + 2e^{-} \ e^{-} H_2S(g)$	7	+0.14
ō	$2H^{+}(aq) + 2e^{-} \rightleftharpoons H_{2}(g)$	RIGHT- STRONGER	0.00
Ĕ	$Pb^{2+}(aq) + 2e^- Pb(s)$	뒩	-0.13
	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	Q	-0.14
LEFT -	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	6	-0.23
F	$Co^{2+}(aq) + 2e^- \ co(s)$	Ť	-0.28
Щ	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$		-0.44
7	$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	AS	-0.76
ō	$2H_2O(1) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	'n	-0.83
S	$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$		-1.03
5	$Al^{3+}(aq) + 3e^- \ carrow Al(s)$	ň	-1.67
Ā	$Mg^{2+}(aq) + 2e^- \ columna Mg(s)$	코	-2.34
OXIDANTS ON	$Na^{+}(aq) + e^{-} \rightleftharpoons Na(s)$	DECREAS	-2.71
X	$Ca^{2+}(aq) + 2e^- \ ca(s)$	ЗS	-2.87
0	$K^{+}(aq) + e^{-} \longleftarrow K(s)$	ŝ	-2.93
	$Li^{+}(aq) + e^{-} \leftarrow Li(s)$		-3.02

KEY IDEAS

•Each line represents a redox equilibrium

•E⁰ values relates to the equilibrium constant, K, for a redox reaction

- with very large (+) E⁰ values (top)
 - the equilibrium lies heavily to the right
 - strong tendency for oxidant to gain e⁻
- with very small (-) E⁰ values (bottom)
 - · the equilibrium lies heavily to the left
 - strong tendency for reductant to lose e⁻

 $^{\bullet}\text{E}^{0}$ values are measured against the standard $\text{H}^{\text{+}}/\text{H}_{2}$ half cell

· this is an arbitrary standard

UNIT 4 CHEMISTRY– AOS2 Predicting Spontaneous Reactions

A USEFUL GENERAL IDEA

- in any situation where two half-equations are combined
 - the one with the higher E⁰ value will go forward
 - the one with the lower E⁰ value will go backward
- for spontaneous reaction we need E⁰(oxidant)>E⁰(reductant)
- hence
 - "top left bottom right"
 - "backward-Z"

$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ -(0.13
-------------------------------------------	------

- $\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Sn}(s)$ -0.14
 - $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ -0.23
 - $\operatorname{Co}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Co}(s)$ -0.28
- $Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$ -0.44
 - $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ -0.76

UNIT 4 CHEMISTRY- AOS2 Predicting Spontaneous Reactions

Question 17

The following reactions occur spontaneously as written.

Using this information, predict which one of the following pairs of reactants will react spontaneously.

A. $Co(s) + Fe^{2+}(aq)$ **B.** $Cr^{2+}(aq) + Fe^{2+}(aq)$ C. $Cr^{2+}(aq) + Pb^{2+}(aq)$

- **D**. $Pb(s) + Co^{2+}(aq)$
- 1. $Cr^{3+} + e^{-} Cr^{2+} E^{0_{1}}$ 2. $Co^{2+} + 2e^{-} \Rightarrow Co = E^{0}_{2}$ 3. Pb²+ + 2e⁻ ≒ Pb E°3 4. $Fe^{2+} + 2e^{-} \Rightarrow Fe E^{0}$
- E⁰₃>E⁰₂>E⁰₁>E⁰₄

UNIT 4 CHEMISTRY– AOS2 Electrochemical Series - Limitations

- In some circumstances predictions based on the electrochemical series are not borne out in practice
 - · reactions may occur that are not predicted
 - · reactions that are predicted may apparently not occur

REASON 1: NON-STANDARD CONDITIONS

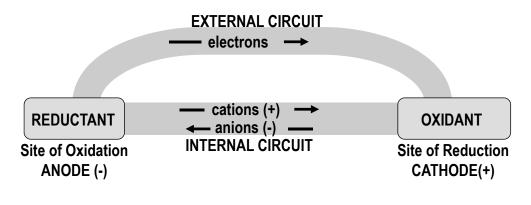
- E⁰ values and hence the order of the electrochemical series hold only for STANDARD CONDITIONS:
 - T = 25 °C
 - c = 1 M for solutions
 - p = 1 atm = 101.3 kPa for gases

REASON 2: EQUILIBRIUM v RATE

- when a *spontaneous reaction* is predicted, this means that the predicted reaction has a *large equilibrium constant* (K is a function of the E⁰ difference)
- no conclusion can be drawn about the rate at which a predicted reaction will occur
 - a predicted reaction may have a very large activation energy and thus be too slow to detect

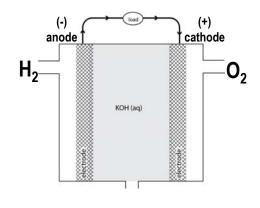
UNIT 4 CHEMISTRY- AOS2 Galvanic Cells

- All functioning galvanic cells comprise an *oxidant* and a *reductant* isolated from each other but connected by
 - 1. An *external circuit* through which *electrons* are conducted from reductant to oxidant.
 - 2. An *internal circuit* through which *ions* are conducted. The flow of charge in the internal circuit exactly balances the flow of electrons in the external circuit.
- These features are present in *all* galvanic cells.



UNIT 4 CHEMISTRY– AOS2 Fuel Cells

- · Primary and Secondary cells:
 - reactants are completely enclosed and stored within the cell.
- Fuel cells:
 - · reactants continuously supplied from outside the cell.
 - Mainly for gaseous reactants, especially oxygen gas as oxidant.
 - · Thus fuel cells are used to obtain electrical energy from
 - combustion reactions, where O₂ is reacted with a *fuel* (hence the term 'fuel cell')
 - corrosion reactions, where O2 is reacted with a metal
 - In a typical fuel cell
 - O₂ is reduced at the cathode (+)
 - the 'fuel' eg H₂ is oxidised at the anode (-)



UNIT 4 CHEMISTRY– AOS2 Electrolysis

- Non-spontaneous redox reactions can be forced to progress by the application of an external EMF.
 - · A DC power source is used to force electrons
 - onto the (-) electrode, coercing reduction (hence cathode)
 - out of the (+) electrode, coercing oxidation (hence anode)
 - · Applications include
 - recharging secondary cells
 - · 'electrowinning' of metals from ores
 - production of useful chemicals (eg Cl₂)
 - · electroplating
 - · electrorefining to purify metals like copper
- · Electrode reactions can be predicted from the electrochemical series
 - list all possible oxidants the strongest (highest E⁰) will react
 - list all possible reductants the strongest (lowest E⁰) will react
 - remember that the solvent (H₂O) and the electrode materials must be considered as candidates

UNIT 4 CHEMISTRY– AOS2 Faraday's Laws

- Essentially just STOICHIOMETRY calculations
 - using half-equations to establish mole-ratios for electrons
 - using n = Q/F to calculate amount (moles) of electrons

2004 Question 9

96.5 C of electricity is used to completely deposit silver metal (Ag) from an aqueous solution [of] Ag⁺(aq). Another 96.5 C is used to completely deposit copper (Cu) from an aqueous solution [of] $Cu^{2+}(aq)$.

The silver metal deposited would

- A. have half the mass of the copper deposited.
- B. have twice the mass of the copper deposited.
- C. be half the mole of the copper deposited.
- D. be twice the mole of the copper deposited.
- n(e⁻) = Q/F = 96.5/96500 = 0.001 mol
- n(Ag) = n(e⁻) = 0.001 mol ⇒ m(Ag) = nM = 0.001 x 107.9 = 0.108 g
- n(Cu) = ½ x n(e⁻) = 0.0005 mol ⇒ m(Cu) = nM = 0.0005 x 63.5 = 0.0318 g

CONTACT DETAILS

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Monday 19 4:00PM - 7:00PM Tuesday 20 4:00PM - 7:00PM Footscray Park Campus Ballarat Road, Footscray Melways Ref. Map 42 C2

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