Topics in the November 2010 Exam Paper for CHEM1101

Click on the links for resources on each topic.

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- Periodic Table and the Periodic Trends

2010-N-3:

- Filling Energy Levels in Atoms Larger than Hydrogen
- Atomic Electronic Spectroscopy

2010-N-4:

- Nuclear and Radiation Chemistry

2010-N-5:

- Lewis Structures
- VSEPR

2010-N-6:

- Lewis Structures

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- Chemical Equilibrium
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- First and Second Law of Thermodynamics

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- Electrochemistry
- Batteries and Corrosion

Marks 6

- The electron affinity is negative if energy is released upon addition of an electron. If it is positive, the resultant anion is unstable. Explain why beryllium has a positive electron affinity, while that of fluorine is highly negative.

An additional electron in Be will have to go into a 2*p* orbital, which has a planar node through the nucleus and thus does not feel nuclear charge. Consequently this leads to a higher energy system.

In F, the high nuclear charge and small atom offset the above effect and the extra electron is tightly bound.

Why is the ionisation potential of oxygen slightly smaller than nitrogen, despite being further across the period?

The electron removed from O ($1s^2\ 2s^2\ 2p^4$) is the one in the 2*p* orbital with 2 electrons in it. This electronic repulsion offsets the greater nuclear charge of O compared to N.

How is this related to the slightly positive electron affinity of nitrogen?

The electron affinity of N is ΔH for the process $2p^3 \rightarrow 2p^4$.

The ionisation potential for O is ΔH for the process $2p^4 \rightarrow 2p^3$.

The only difference (apart from the direction of the reaction) is the nuclear charge on the atom.

Marks 10

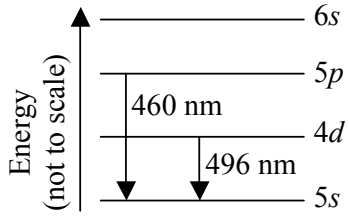
- Both strontium and strontianite are named after Strontian, a village in Scotland near which the mineral was first discovered. Strontium displays crimson (red) colouration in a flame. Give the ground state configuration for Sr.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$

Indicating only valence electrons, the electronic transition $5s5p \rightarrow 5s^2$ in strontium brings about 460 nm photons. Can this transition be responsible for the crimson colour of Sr flames? Explain.

No. 460 nm radiation is blue.

Another transition, $5s4d \rightarrow 5s^2$, occurs at 496 nm. Show the transitions responsible for 460 nm and 496 nm photons on the energy level diagram to the right.



Calculate, in eV, the energy gap between the 4*d* and 5*p* orbitals of strontium.

The gap between 5*p* and 5*s* is 460 nm. This corresponds to an energy difference of:

$$E_1 = hc / \lambda = (6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1}) / (460 \times 10^{-9}\ \text{m})$$
$$= 4.32 \times 10^{-19}\ \text{J}$$

The gap between 4*d* and 5*s* is 496 nm. This corresponds to an energy difference of:

$$E_2 = hc / \lambda = (6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1}) / (496 \times 10^{-9}\ \text{m})$$
$$= 4.00 \times 10^{-19}\ \text{J}$$

The 4*d* – 5*p* gap is, from the figure above, the difference between these:

$$E = (4.32 \times 10^{-19} - 4.00 \times 10^{-19})\ \text{J} = 3.31 \times 10^{-20}\ \text{J}$$

As 1 eV = 1.602×10^{-19}, this corresponds to:

$$E = (3.31 \times 10^{-20} / 1.602 \times 10^{-19})\ \text{eV} = 0.20\ \text{eV}$$

Answer: **0.20 eV**

ANSWER CONTINUES ON THE NEXT PAGE

Explain why the 4*d* orbitals of strontium are of a higher energy than the 5*s* orbitals.

The 5*s* orbital experiences a higher nuclear charge more than the 4*d* as it is more penetrating – it has more spherical nodes and spends a higher amount of time near the nucleus.

This stabilises the 5*s* orbital, pulling it down in energy.

Electron spins cannot flip easily during a transition. Explain why the excited state of Sr, 5*s*5*p* with parallel spins, is long-lived.

A spin up 5*p* electron cannot drop into a 5*s* orbital if a spin up electron is already there as this would violate the Pauli Exclusion principle.

As there is no lower energy orbital available that it can drop into, the species is long-lived.

Marks 8

- Sixteen unstable isotopes of strontium are known to exist. Of greatest importance are ^{90}Sr with a half-life of 28.78 years and ^{89}Sr with a half-life of 50.5 days. ^{90}Sr is found in nuclear fallout as it is a by-product of nuclear fission.

  Calculate the activity (in Bq) of 20.0 g of ^{90}Sr.

As 1 mol of ^{90}Sr has a mass of 90.0 g, the number of nuclei, N, in 20.0g is:

number of nuclei = number of moles × Avogadro's constant

$$N = \left(\frac{20.000}{90.0}\ \text{mol}\right) \times (6.022 \times 10^{23}\ \text{nuclei mol}^{-1}) = 1.34 \times 10^{23}\ \text{nuclei}$$

The activity (A) is related to N by $A = \lambda N$ where λ is the decay constant. The half life, $t_{½}$, is related to the decay constant, λ, by $t_{½} = \ln 2/\lambda$. Hence,

$$\lambda = \ln 2/(28.78 \times 365 \times 24 \times 60 \times 60\ \text{s}) = 7.64 \times 10^{-10}\ \text{s}^{-1}$$

The activity is thus,

$$A = \lambda N = (7.64 \times 10^{-10}\ \text{s}^{-1}) \times (1.34 \times 10^{23}\ \text{nuclei})$$

$$= 1.02 \times 10^{14}\ \text{nuclei s}^{-1} = 1.02 \times 10^{14}\ \text{Bq}$$

Answer: **1.02×10^{14} Bq**

Calculate the age (to the nearest year) of a sample of ^{90}Sr that has an activity one-eighth of a freshly prepared sample.

The number of radioactive nuclei changes with time according to the equation:

$$\ln(N_0/N_t) = \lambda t$$

As the activity is proportional to the number of nuclei, this can also be written in terms of activities:

$$\ln(A_0/A_t) = \lambda t$$

If the activity has decreased to one eighth of its original value, $A_0/A_t = 8$. Hence:

$$\ln(8) = (7.64 \times 10^{-10}\ \text{s}^{-1}) \times t$$

$$t = 2.72 \times 10^{9}\ \text{s} = (2.72 \times 10^{9} / (365 \times 24 \times 60 \times 60)\ \text{years} = 86.3\ \text{years}$$

Answer: **86 years**

ANSWER CONTINUES ON THE NEXT PAGE

Determine the specific activity of ^{90}Sr in Ci g^{-1}.

From above, the activity of 20.0 g of ^{90}Sr is 1.02×10^{14} Bq so the activity of one gram is $(1.02 \times 10^{14}$ Bq$)/ (20$ g$) = 5.11 \times 10^{12}$ Bq g^{-1}.

As 1 Ci = 3.70×10^{10} Bq, this corresponds to:

specific activity = $(5.11 \times 10^{12}) / (3.70 \times 10^{10})$ Ci g^{-1} = 138 Ci g^{-1}

Answer: **138 Ci g^{-1}**

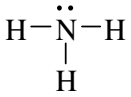
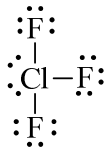
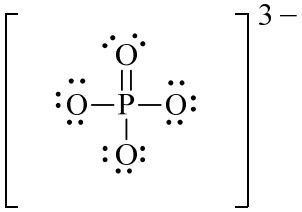
^{90}Sr presents a long-term health problem as it substitutes for calcium in bones. Comment on why Sr can substitute for Ca so readily.

Sr has similar electronic structure to Ca - both have s^2 valence shell configuration.

The Sr^{2+} and Ca^{2+} cations have the same charge and are of similar size.

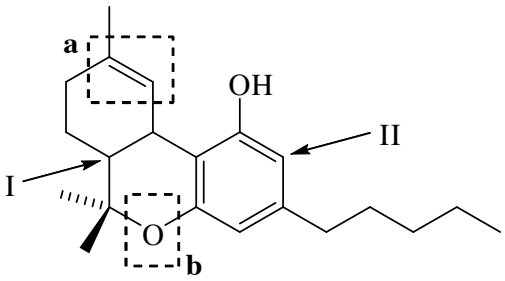
Marks 6

- Complete the table below showing the number of **valence** electrons, the Lewis structures and the predicted shapes of the following species. Ammonia, NH_3, is given as an example.

Formula	Number of electron pairs on central atom (discounting multiple bonds)	Lewis Structure	Name of molecular shape
NH_3	4		trigonal pyramidal
ClF_3	**5**		**T-shaped**
PO_4^{3-}	**4**		**tetrahedral**

Marks 5

- The structure of tetrahydrocannabinol, the active ingredient in marijuana, is shown below.



What is the molecular formula of tetrahydrocannabinol?	**$C_{21}H_{30}O_2$**

Name the functional groups indicated in the boxes **a** and **b**.

a	**alkene**
b	**ether**

What are the approximate bond angles at the carbon atoms labelled I and II?

Atom	Bond angle
I	**109.5°**
II	**120°**

Marks 5

- Water solutions of NaOH (100.0 mL, 2.0 M) and HCl (100.0 mL, 2.0 M), both at 24.6 °C, were mixed together in a coffee cup calorimeter. The temperature of the solution rose to 38.0 °C during the reaction process. Write a balanced ionic equation to describe the reaction in the calorimeter.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Is the process an endothermic or exothermic reaction? **exothermic**

Assuming a perfect calorimeter, determine the standard enthalpy change for the neutralisation reaction. Assume the density of water is 1.00 g mL^{-1}. The heat capacity of water is 4.18 J g^{-1} K^{-1}.

The temperature rise is (38.0 – 24.6) °C = 13.4 °C. The temperature *difference* corresponds to 13.4 K.

After mixing, the total volume of solution is (100.0 + 100.0) mL = 200.0 mL. With a density of 1.00 g mL^{-1}, this corresponds to 200. g.

The heat change is given by $q = m\,C\,\Delta T$ where C is the specific heat capacity. Hence:

$$q = (200.\text{ g}) \times (4.18\text{ J g}^{-1}\text{ K}^{-1}) \times (13.4\text{ K}) = 11200\text{ J}$$

100.0 mL of 2.0 M NaOH (or HCl) contains:

number of moles = concentration × volume

$$= (2.0\text{ mol L}^{-1}) \times (0.1000\text{ L}) = 0.20\text{ mol}$$

As 11200 J are *released* by 0.20 mol, the is the molar enthalpy change is therefore:

$$\Delta H = -(11200\text{ J}) / (0.20\text{ mol}) = 56000\text{ J mol}^{-1} = 56\text{ kJ mol}^{-1}$$

Answer: **-56 kJ mol^{-1}**

Marks

- The reaction below is endothermic. **3**

$$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$$

Indicate whether the equilibrium will shift right, shift left, or remain unchanged when disturbed in the following ways.

adding more NO(g)	**left**
increasing the pressure at constant temperature	**left**
removing $NO_2(g)$	**right**
increasing the volume at constant temperature	**right**
adding some Ar(g)	**no change**
increasing the temperature at constant pressure	**right**

- Automobile airbags are inflated by the decomposition of sodium azide according to the following equation. **3**

$$6NaN_3(s) + Fe_2O_3(s) \rightarrow 3Na_2O(s) + 2Fe(s) + 9N_2(g)$$

What mass of NaN_3 is required to produce 63 L of nitrogen gas at 25 °C and 1.76 atm?

Using the ideal gas law, $PV = nRT$, 63 L of N_2 at 25 °C at a pressure of 1.76 atm corresponds to:

$$n = PV / RT$$
$$= (1.76 \text{ atm}) \times (63 \text{ L}) / ((0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (25 + 273) \text{ K}))$$
$$= 4.5 \text{ mol}$$

From the chemical equation, 6 mol of NaN_3 leads to 9 mol of N_2. The amount of NaN_3 required is therefore:

$$\text{moles of } NaN_3 = (6 / 9) \times 4.5 \text{ mol} = 3.0 \text{ mol}$$

The molar mass of NaN_3 is (22.99 (Na) + 3 × 14.01 (N)) g mol^{-1} = 65.02 g mol^{-1}. This amount therefore corresponds to:

$$\text{mass of } NaN_3 = \text{molar mass} \times \text{number of moles}$$
$$= (65.02 \text{ g mol}^{-1}) \times (3.0 \text{ mol}) = 2.0 \times 10^2 \text{ g}$$

Answer: **2.0×10^2 g**

Marks 3

- pAt 1000 K, a reaction mixture containing $SO_2(g)$, $O_2(g)$ and $SO_3(g)$ was allowed to come to equilibrium in a reaction vessel. The reaction is:

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

At equilibrium, the system was found to contain the following concentrations: $[SO_2] = 0.00377$ M, $[O_2] = 0.00430$ M and $[SO_3] = 0.00185$ M.
Calculate K_c for this reaction.

The equilibrium constant in terms of concentrations is given by:

$$K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]} = \frac{(0.00185)^2}{(0.00377)^2(0.00430)} = 56$$

K_c = **56**

If a mixture containing $[SO_2] = 0.0471$ M, $[O_2] = 0.0280$ M, and $[SO_3] = 0.00125$ M is placed in the vessel, is the reaction at equilibrium? If not, which way will it shift in order to achieve equilibrium, right or left?

With these initial concentrations,

$$Q = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]} = \frac{(0.00125)^2}{(0.0471)^2(0.0280)} = 0.025$$

As $Q < K_c$, the reaction will proceed to the right to increase the concentration of the product and reduce the concentrations of the reactants.

- What does it mean to say that a reaction has reached equilibrium? **Marks 1**

A reaction is at equilibrium when the rate of the forward reaction equals the rate of the backward reaction.

- Consider the following equilibrium. **4**

$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g)$ $\quad K_c = 7.0$ at 400 K

If 0.44 mol of Br_2 and 0.44 mol of Cl_2 are introduced into a 2.0 L container at 400 K, what are the equilibrium concentrations of $Br_2(g)$, $Cl_2(g)$ and $BrCl(g)$?

The initial concentrations are:

$[Br_2(g)]$ = number of moles / volume = (0.44 mol) / (2.0 L) = 0.22 M
$[Cl_2(g)]$ = (0.44 mol) / (2.0 L) = 0.22 M
[BrCl(g)] = 0 M

A reaction table can then be used:

	$Br_2(g)$	$Cl_2(g)$	$\rightleftharpoons$	$2BrCl(g)$
initial	**0.22**	**0.22**		**0**
change	**$-x$**	**$-x$**		**$+2x$**
equilibrium	**$0.22 - x$**	**$0.22 - x$**		**$2x$**

The equilibrium constant in terms of concentrations is then:

$$K_c = \frac{[BrCl(g)]^2}{[Br_2(g)][Cl_2(g)]} = \frac{(2x)^2}{(0.22-x)(0.22-x)} = \frac{4x^2}{(0.22-x)^2} = 7.0$$

or

$$\frac{2x}{0.22-x} = (7.0)^{1/2}$$

$$x = 0.125$$

Hence,

$[Br_2(g)]$ = (0.22 – 0.125) M = 0.095 M
$[Cl_2(g)]$ = (0.22 – 0.125) M = 0.095 M
[BrCl(g)] = 0.25 M

$[Br_2(g)]$ = **0.095 M**	$[Cl_2(g)]$ = **0.095 M**	$[BrCl(g)]$ = **0.25 M**

	Marks
• The heat of combustion of acetylene, $C_2H_2(g)$, is –1301 kJ mol^{-1}. What is the heat of formation of acetylene gas? Data: $\Delta_f H°$ of $CO_2(g)$ = –393.5 kJ mol^{-1} $\Delta_f H°$ of $H_2O(l)$ = –285.8 kJ mol^{-1}	**4**

The heat of combustion corresponds to the reaction below in which one mol of $C_2H_2(g)$ is burnt:

$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

Using $\Delta_{rxn}H° = \Sigma m\Delta_f H°$(products) - $\Sigma n\Delta_f H°$(reactants), this becomes:

$\Delta_{combustion}H° = [2 \times \Delta_f H°\ (CO_2(g) + \Delta_f H°\ (H_2O(l)] - [\Delta_f H°\ (C_2H_2(g)]$

or

$$[\Delta_f H°\ (C_2H_2(g)] = [2 \times \Delta_f H°\ (CO_2(g) + \Delta_f H°\ (H_2O(l)]\ - \Delta_{combustion}H°$$
$$= [(2 \times -395.5) + (--285.8) - (-1301)]\ \text{kJ mol}^{-1}$$
$$= +228\ \text{kJ mol}^{-1}$$

$\Delta_f H°$ = **+228 kJ mol^{-1}**

Marks 6

- The following redox reaction occurs in a voltaic cell:

$$2Sc(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Sc^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Calculate the cell potential, E_{cell}, at 25 °C when $[Cr_2O_7^{2-}(aq)] = 6.2 \times 10^{-5}$ M, $[Sc^{3+}(aq)] = 0.35$ M, $[Cr^{3+}(aq)] = 0.75$ M and the pH is 1.85. The standard cell potential, $E°_{cell}$, for this cell is 3.70 V.

Using pH = $-\log_{10}[H^+(aq)]$, $[H^+(aq)] = 10^{-1.85}$ M.

The reaction involves transfer of 6 e^-, as $2Sc \rightarrow 2Sc^{3+}$, so $n = 6$.

For the reaction,

$$Q = \frac{[Sc^{3+}(aq)]^2[Cr^{3+}(aq)]^2}{[Cr_2O_7(aq)^{2-}][H^+(aq)]^{14}} = \frac{(0.35)^2(0.75)^2}{(6.2 \times 10^{-5})(10^{-1.85})^{14}} = 8.83 \times 10^{28}$$

The cell potential is given by the Nernst equation:

$$E_{cell} = E° - \frac{RT}{nF}\ln Q = (3.70\ V) - \frac{(8.314\ J\ K^{-1}\ mol^{-1})(298\ K)}{(6 \times 96485\ C\ mol^{-1})}\ln(8.83 \times 10^{28})$$

$$= +3.41\ V$$

Answer: **+3.41 V**

What is the effect on the E_{cell} of decreasing the concentration of $Cr_2O_7^{2-}$ in the cathode compartment?

This change will increase the value of Q and so E_{cell} decreases.

What is the effect on the E_{cell} of adding a 0.35 M solution of $Sc(NO_3)_3$ to the anode compartment?

This will not change $[Sc^{3+}(aq)]$ so there is no effect on the value of E_{cell}.

Marks

- For each electrochemical cell described, write the half-reaction that occurs at each electrode and the overall balanced redox reaction. **4**

  A voltaic cell constructed using a scandium rod in a solution of scandium(III) ions (Sc^{3+}/Sc) as one half-cell and a nickel rod in a solution of nickel(II) ions (Ni^{2+}/Ni) as the other half-cell.

Cathode	**$Ni^{2+} + 2e^- \rightarrow Ni(s)$**
Anode	**$Sc(s) \rightarrow Sc^{3+} + 3e^-$**
Overall cell reaction	**$3Ni^{2+} + 2Sc(s) \rightarrow 3Ni(s) + 2Sc^{3+}$**

  A voltaic cell in which oxidation of Cr to Cr^{3+} by O_2 in the presence of acid occurs.

Cathode	**$O_2(g) + 4H^+ + 4e^- \rightarrow H_2O(l)$**
Anode	**$Cr(s) \rightarrow Cr^{3+} + 3e^-$**
Overall cell reaction	**$3O_2(g) + 12H^+ + 4Cr(s) \rightarrow 6H_2O(l) + 4Cr^{3+}$**

- An alkaline battery consists of a powdered Zn/gel anode and a C/MnO_2 cathode. At the anode, Zn is oxidised to Zn^{2+} which reacts with the OH^- ion present in the paste to form $Zn(OH)_2(s)$. Suppose that an alkaline battery was manufactured using Fe metal instead of Zn metal, and that the Fe was oxidised to Fe^{2+} at the anode. What effect would this have on the cell potential or emf of the battery? Explain your answer briefly. **2**

The reduction potentials of the $Zn^{2+}(aq)$ / Zn and $Fe^{2+}(aq)$ / Fe electrodes are:

$Zn^{2+} + 2e^- \rightarrow Zn(s)$ $\quad E° = -0.76$ V

$Fe^{2+} + 2e^- \rightarrow Fe(s)$ $\quad E° = -0.44$ V

This electrode is acting as the anode where *oxidation* occurs, and cell potential of the battery is:

$E_{cell} = E_{ox} + E_{red}$.

Replacing the Zn^{2+}/Zn electrode with a Fe^{2+}/Fe electrode would *reduce* the emf of the battery by about 0.32 V (assuming standard concentrations).