Topics in the June 2012 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2012-J-2:

- Bonding in H_2 - MO theory
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2012-J-3:

- Atomic Electronic Spectroscopy
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2012-J-4:

- Nuclear and Radiation Chemistry

2012-J-5:

- Nuclear and Radiation Chemistry

2012-J-6:

- Lewis Structures
- VSEPR

2012-J-7:

- Thermochemistry

2012-J-8:

- First and Second Law of Thermodynamics

2012-J-9:

- Polar Bonds
- Ionic Bonding

2012-J-10:

- Chemical Equilibrium

2012-J-11:

- Electrochemistry
- Batteries and Corrosion

Marks
5

- C_2 is a reaction intermediate observed in flames, comets, circumstellar shells and the interstellar medium. In 2011, a new state of C_2 was observed with 4 parallel spins.

How many *valence* electrons are there in C_2?

| 8 |

Complete the calculated MO diagram for the lowest energy state of C_2 *with 4 parallel spins* by inserting the appropriate number of electrons into the appropriate orbitals.
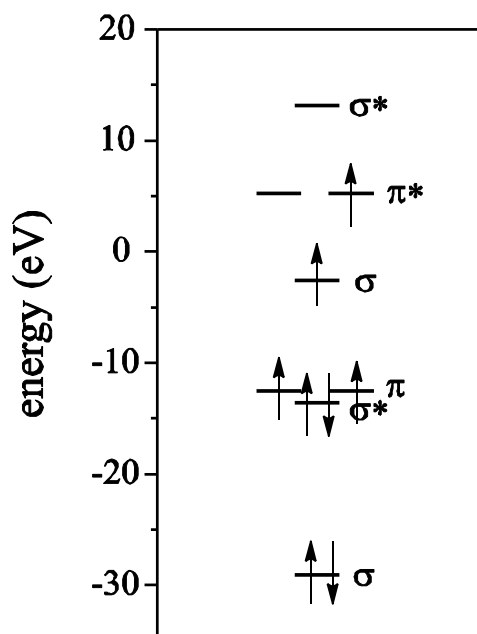
What is the bond order of this state of C_2?

| 1 |

Is this state paramagnetic? Give reasoning.

Yes. It has 4 unpaired electrons.

What is the bond order of the ground state of C_2?

| 2 |

	Marks
• An "excimer laser" is a type of ultraviolet laser used for lithography, micromachining and eye surgery. In one type of laser, an electrical discharge through HCl and Xe in a helium buffer gas yields metastable XeCl molecules, described like an ion pair. These then emit 308 nm light and dissociate into Xe and Cl atoms.	**6**

element	Ionisation energy / kJ mol^{-1}	Electron affinity / kJ mol^{-1}
Xe	1170.4	–
Cl	1251.1	–349

What energy, in eV, is required to convert a pair of Xe and Cl atoms into Xe^+ and Cl^- ions?

To form Xe^+ requires 1170.4 kJ mol^{-1} and in forming Cl^-, 349 kJ mol^{-1} is released. The total energy change is therefore:

total energy change = [(+1170.4) + (-349)] kJ mol^{-1} = +821.4 kJ mol^{-1}

or

total energy per pair of atoms = (+821.4 kJ mol^{-1}) / (6.022 × 10^{23} mol^{-1})
= 1.364 × 10^{-18} J

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

total energy per pair of atoms = (1.364 × 10^{-18}) / (1.602 × 10^{-19}) eV
= 8.51 eV

Answer: **8.51 eV**

What energy (in eV) is released when the XeCl molecules emit ultraviolet light?
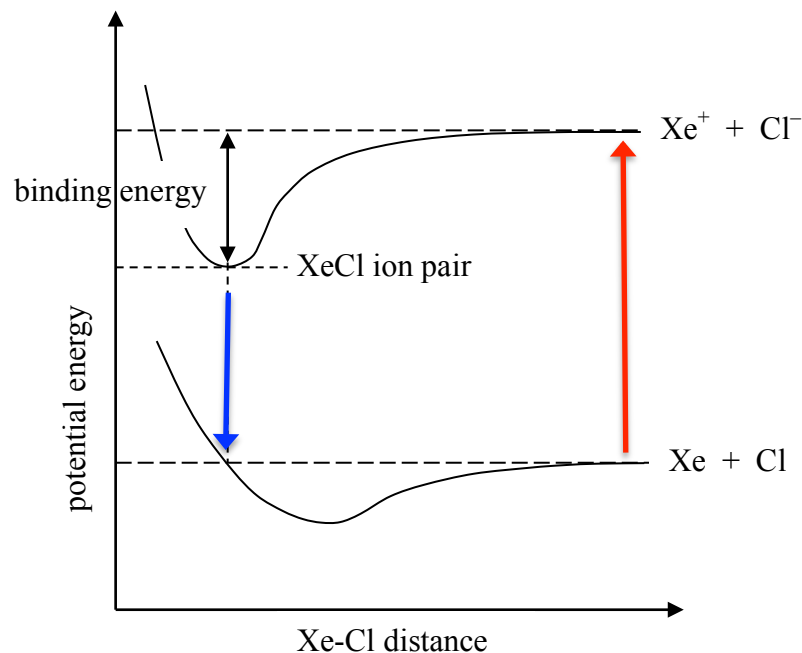
A wavelength of 308 nm corresponds to an energy of:

$E = hc / \lambda$
= (6.626 × 10^{-34} J s) × (2.998 × 10^8 m s^{-1}) / (308 × 10^{-9} m)
= 6.45 × 10^{-19} J

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

E = (6.45 × 10^{-19}) / (1.602 × 10^{-19}) eV
= 4.03 eV

Answer: **4.03 eV**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

What is the binding energy (in J) of the XeCl ion pair?

The binding energy of the ion pair is shown by the double headed arrow on the diagram above. This is the *difference* between the energy needed to form a pair of Xe^+ and Cl^- ions (8.51 eV; red arrow above) and the energy released when XeCl molecules emit light (4.03 eV; blue arrow above).

Binding energy = (8.51 – 4.03) eV = 4.48 eV

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

Binding energy = $(4.48 \times 1.602 \times 10^{-19})$ eV
= 7.18×10^{-19}

Answer: **7.18×10^{-19} J**

If the binding is electrostatic, what is the approximate equilibrium bond length of XeCl if the binding energy is given by the Coulomb formula: $E = \dfrac{q_1 q_2}{4\pi\varepsilon_0 r}$?

For Xe^+, $q = 1.602 \times 10^{-19}$ C. For Cl^-, $q = -1.602 \times 10^{-19}$ C.

Using $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1} and $E = 7.18 \times 10^{-19}$ J:

$r = q_1 q_2 / 4\pi\varepsilon_0 E$
$= (1.602 \times 10^{-19} \text{ C})^2 / (4\pi \times 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \times 7.18 \times 10^{-19} \text{ J})$
$= 3.21 \times 10^{-10}$ m = 321 pm or 3.21 Å

Answer: **321 pm or 3.21 Å**

**Marks
8**

- The generation of energy in a nuclear reactor is largely based on the fission of either ^{235}U or ^{239}Pu. The fission products include every element from zinc through to the *f*-block. Explain why most of the radioactive fission products are β-emitters.

> **The optimal neutron : proton ratio increases as *Z* increases.**
>
> **Splitting a large nucleus in two will almost certainly produce nuclides with similar neutron : proton ratios to the parent, which will now be too high. They will emit negative charge to convert neutrons to protons, bringing about a more satisfactory neutron : proton ratio. *i.e.* they will be β emitters.**

Much of the fission yield is concentrated in two peaks, one in the second transition row and the other later in the periodic table. Identify the missing "sister" products of the following daughter nuclides of ^{235}U by writing balanced nuclear equations. The fission reactions are triggered by the absorption of one neutron, and release three neutrons upon disintegration of the short-lived ^{236}U nucleus.

^{141}Ba	$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n$
^{95}Sr	$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{95}_{38}Sr + ^{138}_{54}Xe + 3\,^{1}_{0}n$

Many of the fission products are short lived, and spent fuel rods are eventually contaminated by longer-lived species. The radioactivity of spent fuel can be modelled simply by the exponential decay of the ^{137}Cs and ^{90}Sr. The % yields and half lives of these nuclides are given in the table.

nuclide	%Yield *per fission event*	Half-life (years)
^{90}Sr	4.505	28.9
^{137}Cs	6.337	30.23

After use, nuclear fuel rods are stored in ponds of cooling water, awaiting safe disposal. If 3 % of the mass of used fuel rods consists of fission products of ^{235}U and ^{239}Pu, what percentage of the mass is made up by each of these nuclides?

> **Using:**
>
> **percentage mass = percentage yield × (atomic mass / 235) × 3%**
>
> **% ^{90}Sr = 0.04505 × (90/235) × 0.03 × 100% = 0.05%**
>
> **% ^{137}Cs = 0.06337 × (137/235) × 0.03 × 100% = 0.11%**

^{90}Sr: **0.05%**	^{137}Cs: **0.11%**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

**Marks
8**

What are the specific activities of ^{90}Sr and ^{137}Cs in Bq g^{-1}?

For ^{90}Sr, the activity coefficient is given by

$\lambda = $ ln2 / $t_{1/2}$ = ln2 / (28.9 × 365 × 24 × 60 × 60) s^{-1} = 7.61 × 10^{-10} s^{-1}

The number of nuclei, N, in a gram is

N = (6.022 × 10^{23} / 90) = 6.69 × 10^{21}

Hence, the activity, A, is

$A = \lambda N$ = (7.61 × 10^{-10}) × (6.69 × 10^{21}) Bq g^{-1}= 5.09 × 10^{12} Bq g^{-1}

For ^{137}Sr, the activity coefficient is given by

λ = ln2 / $t_{1/2}$ = ln2 / (30.23 × 365 × 24 × 60 × 60) s^{-1} = 7.271 × 10^{-10} s^{-1}

The number of nuclei, N, in a gram is

N = (6.022 × 10^{23} / 137) = 4.40 × 10^{21}

Hence, the activity, A, is

$A = \lambda N$ = (7.271 × 10^{-10}) × (4.40 × 10^{21}) Bq g^{-1}= 3.19 × 10^{12} Bq g^{-1}

^{90}Sr: **5.09 × 10^{12} Bq g^{-1}**	^{137}Cs: **3.19 × 10^{12} Bq g^{-1}**

Assuming the majority of the activity of a spent fuel rod to be due to these nuclides, what will be the activity of a 1 tonne fuel rod 100 years after placing it in the pond?

As ^{90}Sr represents 0.05% of the mass (from 2012-J-4) and has an activity of 5.09 × 10^{12} Bq g^{-1} (from above), its initial activity, A_0, is

A_0 = (1 × 10^6) × (5.09 × 10^{12}) × (0.05 / 100) Bq

Activity decays with time according to

$A_t = A_0$ exp(-λt) = A_0 exp(-t × ln2 / $t_{1/2}$)

Hence

A_t = (1 × 10^6) × (5.09 × 10^{12}) × (0.05 / 100) exp(-100 × ln2 / 28.9) Bq
     = 2.3 × 10^{14} Bq

As ^{137}Cs represents 0.11% of the mass (from 2012-J-4) and has an activity of 3.19 × 10^{12} Bq g^{-1} (from above), its initial activity, A_0, is

A_0 = (1 × 10^6) × (3.19 × 10^{12}) × (0.11 / 100) Bq

Hence

A_t = (1 × 10^6) × (3.19 × 10^{12}) × (0.11 / 100) exp(-100 × ln2 / 30.23) Bq
     = 3.5 × 10^{14} Bq

The total activity is therefore (2.3 × 10^{14} + 3.5 × 10^{14}) Bq = 6 × 10^{14} Bq

Answer: **6 × 10^{14} Bq**

- Complete the table below showing the Lewis structures and the predicted shapes of the following species.

Marks
6

Formula	Lewis Structure	Approximate F-X-F bond angle(s)	Name of molecular shape
NF_3		**109°**	**trigonal pyramidal**
XeF_3^+		**90°, 180°**	**T-shaped**
XeF_4		**90°, 180°**	**square planar**
$XeOF_4$		**90°, 180°**	**square pyramid**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

**Marks
4**

• When 20.0 mL of 0.250 M Ba(OH)$_2$ at 47.5 °C is added to a constant pressure ("coffee cup") calorimeter containing 200.0 mL of 0.500 M H$_2$SO$_4$ also at 47.5 °C, a white precipitate is formed. The final temperature of the solution is 46.4 °C. Given that the enthalpy of neutralisation of H$^+$(aq) and OH$^-$(aq) is –56.5 kJ mol^{-1}, and assuming that the specific heat capacity and density of all solutions involved are the same as that of pure water (c = 4.184 J K^{-1} g^{-1} and ρ = 1.000 g mL^{-1}), calculate the enthalpy of solution of BaSO$_4$ in kJ mol^{-1}.

The number of moles of H$^+$ = 0.2000 L × 0.500 mol L^{-1} × 2) = 0.200 mol. The number of moles of OH$^-$ = 0.0200 L × 0.250 mol L^{-1} × 2) = 0.0100 mol. Hence, the limiting reagent is OH$^-$.

The enthalpy change due to neutralisation is therefor

$$\Delta_{\text{neutralisation}}H^o = (0.0100 \text{ mol}) \times (-56.5 \times 10^3 \text{ kJ mol}^{-1}) = -565 \text{ J}$$

The volume of the combined solutions is 220.0 mL. As the density is 1.000 g mL^{-1}, the mass of the solution is 220.0 g. Using $q = mc\Delta T$, the temperature *rise* from the neutralisation reaction is

$$\Delta T_{\text{neutralisation}} = q_{\text{neutralisation}} / mc$$
$$= (565 \text{ J}) / (220.0 \text{ g} \times 4.184 \text{ J K}^{-1} \text{ g}^{-1}) = +0.614 \text{ K}$$

As an overall temperature *decrease* from 47.5 °C to 46.4 °C, corresponding to 1.1 K, is observed:

$$\Delta T_{\text{overall}} = \Delta T_{\text{neutralisation}} + \Delta T_{\text{precipitation}}$$
$$\Delta T_{\text{precipitation}} = \Delta T_{\text{overall}} - \Delta T_{\text{precipitation}} = [(-1.1) - (0.614)] = -1.7 \text{ K}$$

The heat change due to precipitation is therefore

$$q_{\text{precipitation}} = mc\Delta T_{\text{precipitation}} = (220.0 \text{ g}) \times (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (-1.7 \text{ K}) = 1570 \text{ J}$$

The number of moles of Ba^{2+} is 0.050 mol so this amount of BaSO$_4$ precipitates. Hence, the molar enthalpy of precipitation is:

$$\Delta_{\text{precipitation}}H^o = (1570 \text{ J}) / (0.050 \text{ mol}) = 320 \text{ kJ mol}^{-1}$$

Hence, for dissolution:

$$\Delta_{\text{solution}}H^o = -320 \text{ kJ mol}^{-1}$$

Answer: **-320 kJ mol^{-1}**

	Marks
• Explain the following phenomena. (a) When O_2 dissolves in water at room temperature, the total entropy of the system decreases.	6

The decrease in entropy of O_2 going from (g) → (aq) outweighs the increase in entropy of pure water going to water with O_2 dissolved in it.

(b) When $MgSO_4$ is dissolved in water, there is a very small but measurable decrease in volume.

The hydration spheres around the dissolved ions (especially the small Mg^{2+} ion) create a denser structure than that of random H_2O molecules in pure water.

(c) A crystal (*e.g.* of NaCl) in its lowest energy configuration (thermodynamic ground state) will always contain defects at finite temperatures.

Defects increase enthalpy, but they also increase entropy. So a small number of defects will lower the total free energy (except at $T = 0$ K).

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

	Marks
• Explain, with the aid of a diagram labelling all the key components, how sodium stearate ($C_{17}H_{35}COONa$) can stabilise long-chain non-polar hydrocarbons ("grease") in water.	**3**

Sodium stearate dissolves in water to give stearate ions which act as surfactants. They have non-polar (hydrophobic) "tails" that associate with grease and charged, polar (hydrophilic) "heads" that associate with water. This leads to the formation of stable spherical micelles in which the grease molecules are contained within a monolayer of stearate anions with their heads pointing outwards.
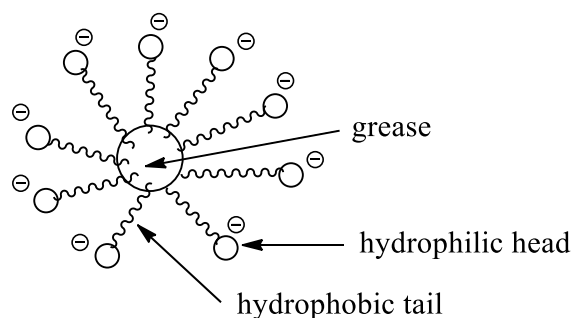
• Consider the complex $K_4[Mn(CN)_6]$. Describe and contrast the origin, strength and directionality of the chemical bonds in this compound (a) between C and N; (b) between the manganese and cyanide ions; and (c) between the complex and the potassium counterions.

6

C–N bonds are covalent. They are relatively short, strong and highly directional.

Mn–CN coordination bonds are due to the donation of the lone pair of electrons on C to the Mn^{2+}. These bonds are weaker, longer and less directional than covalent bonds.

$[Mn(CN)_6]^{4-}$ and K^+ are ionically bonded in the solid state due to coulombic attraction between the oppositely charged ions. These bonds are strong but not directional.

Marks
6

- Equal volumes of carbon monoxide and hydrogen gas are introduced into a sealed 4.5 L flask at 1200 K and the following reaction occurs.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$
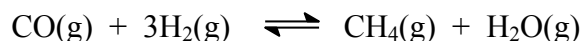
Sometime later, total pressure in the flask is 46.4 atm. Calculate the total amount of gas (in mol) in the flask at this later time.

From the ideal gas law, $PV = nRT$. Hence

    $n = PV / RT = $ **(46.4 atm) × (4.5 L) / ((0.08206 atm L mol^{-1} K^{-1}) × (1200 K))**
      = 2.1 mol

	Answer: **2.1 mol**

When the total pressure in the flask is 46.4 atm, the flask contains 0.22 mol of CH_4. Calculate the amount of $H_2(g)$ (in mol) that was initially introduced into the flask.

From above, equal amounts of CO(g) and H_2(g) were initially added. A reaction table can be used:

	CO(g)	**3H$_2$(g)**	$\rightleftharpoons$	**CH$_4$(g)**	**H$_2$O(g)**
I	$n_{initial}$	$n_{initial}$		**0**	**0**
C	-x	-3x		+x	+x
E	$n_{initial}$ - x	$n_{initial}$ - 3x		x	x

As $n_{CH_4} = 0.22$ mol, $x = 0.22$ mol.

As the total number of moles is 2.1 mol,

    [($n_{initial}$ – 0.22) + ($n_{initial}$ – 3 × 0.22) + (0.22) + (0.22)] mol = 2.1 mol
or

    $n_{initial}$ = 1.3 mol

	Answer: **1.3 mol**
	Answer: **YES** / NO

ANSWER CONTINUES ON THE NEXT PAGE

In a separate experiment, it is determined that the reaction is in equilibrium when the same 4.5 L flask contains 0.18 mol of CH_4, 0.24 mol of H_2O, 0.82 mol of CO and 0.65 mol of H_2 at 1200 K. Was the reaction at equilibrium in the previous part of this question? Show all working.

As $K_c = [CH_4(g)][H_2O(g)] / [CO(g)][H_2(g)]^3$, the equilibrium constant is

    $K_c = (0.18 / 4.5) \times (0.24 / 4.5) / ((0.82 / 4.5) \times (0.65 / 4.5)^3) = 3.88$

Using the answers obtained above, the number of moles in the reaction are

    $n_{CH_4} = 0.22$ mol
    $n_{H_2O} = 0.22$ mol
    $n_{CO} = (1.3 - 0.22)$ mol $= 1.1$ mol
    $n_{CO} = (1.3 - 3 \times 0.22)$ mol $= 0.6$ mol

the reaction quotient for the reaction is

    $Q = (0.22 / 4.5) \times (0.22 / 4.5) / ((1.1 / 4.5) \times (0.6 / 4.5)^3) = 3.88$

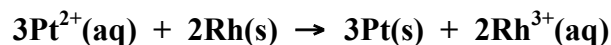**As $Q = K_c$, the reaction *was* at equilibrium**
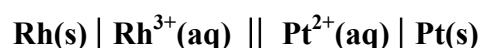
Answer: **YES** / NO

Marks
7

- A voltaic cell is set up at 298 K based on the following half-cell reactions.

$$Pt^{2+}(aq) + 2e^- \rightleftharpoons Pt(s) \qquad E° = +1.18 \text{ V}$$
$$Rh^{3+}(aq) + 3e^- \rightleftharpoons Rh(s) \qquad E° = +0.76 \text{ V}$$

Write the overall chemical reaction that takes place in this cell.

$3Pt^{2+}(aq) + 2Rh(s) \rightarrow 3Pt(s) + 2Rh^{3+}(aq)$

Write the same reaction in shorthand voltaic cell notation.

$Rh(s) \mid Rh^{3+}(aq) \parallel Pt^{2+}(aq) \mid Pt(s)$

Which metal electrode is acting as the cathode in this reaction? | **Pt**

Calculate the potential of this cell at 298 K, in which the concentration of Pt^{2+}(aq) is 0.0544 mmol L^{-1} and the concentration of Rh^{3+}(aq) is 0.0393 mmol L^{-1}.

As the Rh^{3+} / Rh reduction potential is the smallest, it is reversed and becomes the oxidation half cell (as in the chemical reaction above). Hence

$$E° = E°_{reduction} + E°_{oxidation} = (+1.18 \text{ V}) + (-0.76 \text{ V}) = +0.42 \text{ V}$$

At the non-standard concentrations, the Nernst equation can be used to calculate the cell potential for this 6 electron reaction

$$E_{cell} = E° - \frac{RT}{nF} \ln Q = E° - \frac{RT}{6F} \ln \frac{[Rh^{3+}(aq)]^2}{[Pt^{2+}(aq)]^3}$$
$$= (+0.42 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(6)(96485 \text{ C mol}^{-1})} \ln \frac{(0.0393 \times 10^{-3})^2}{(0.0544 \times 10^{-3})^3} = +0.38 \text{ V}$$

Answer: **+0.38 V**