



29th International Chemistry Olympiad

29e Olympiade Internationale de la Chimie

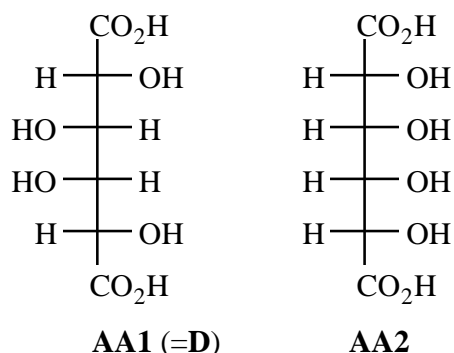
Theoretical Examination

Montreal, Thursday, July 17, 1997

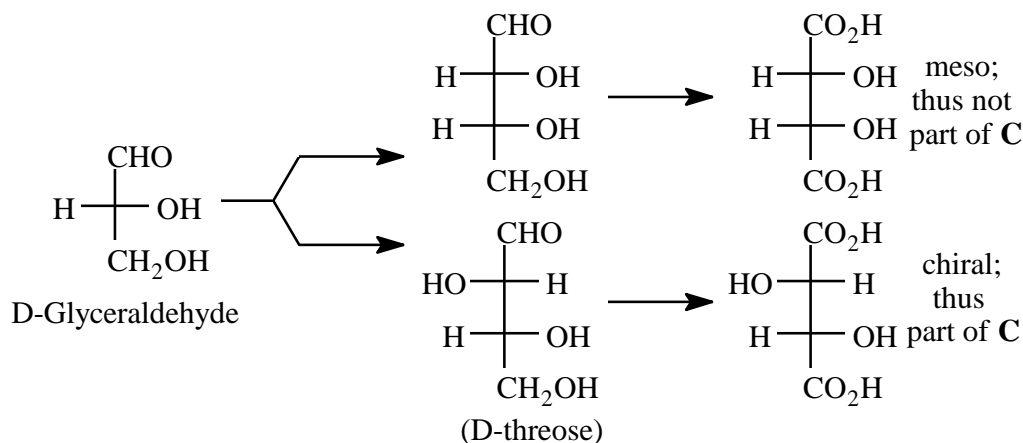
*****DETAILED SOLUTIONS*****

SOLUTION 1

Compound **X** is a trisaccharide which does not react with Benedict's solution nor does it mutarotate. This shows that **X** is a non-reducing sugar and therefore only acetal or ketal linkages exist at all of the anomeric carbons. Of the three monosaccharides, **A** and **B** give the same osazone and therefore have identical stereochemistry at C-3, C-4, and C-5 (and C-6). **A** and **B** are also different from compound **1** (i.e. D-mannose) yet give the same osazone, and thus one of them must be the C-2 epimer of D-mannose (i.e. D-glucose) and the other must be the corresponding keto sugar at C-2 (i.e. D-fructose). (This deduction is confirmed later in the oxidative cleavage reactions.) Compound **C**, after reaction with nitric acid, gives an optically inactive aldaric acid **D**. The two possible aldaric acids which could be **D** are thus:



The aldotetrose which is the precursor of **C** (and thus also of **D**) does not give a meso compound after reaction with nitric acid and therefore must be the D-threose:

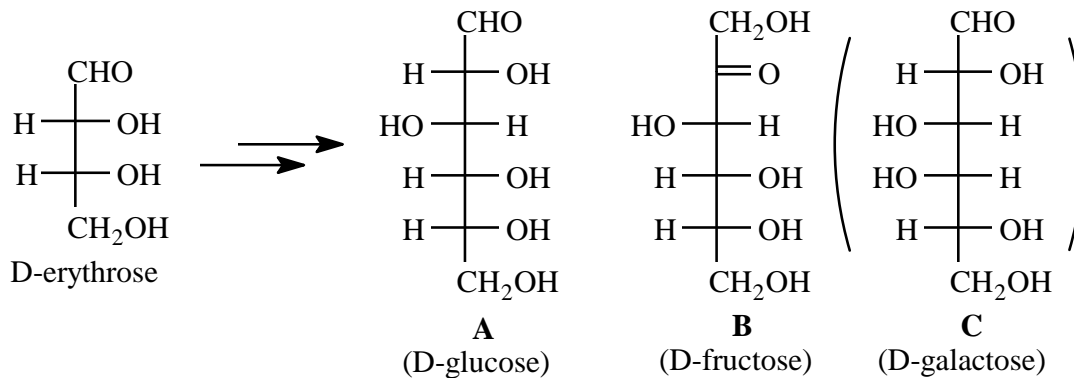


It follows from this that the aldaric acid **D** produced from **C** above is **AA1** and thus that **C** must be D-galactose. Compound **A** reacts with 5 moles of HI to give 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) suggesting that it is an aldohexose while **B** reacts with 5 moles of HI to give 4 moles of methanoic (formic) acid, one mole of methanal (formaldehyde) and one mole of CO₂ suggesting that it is a ketohexose.

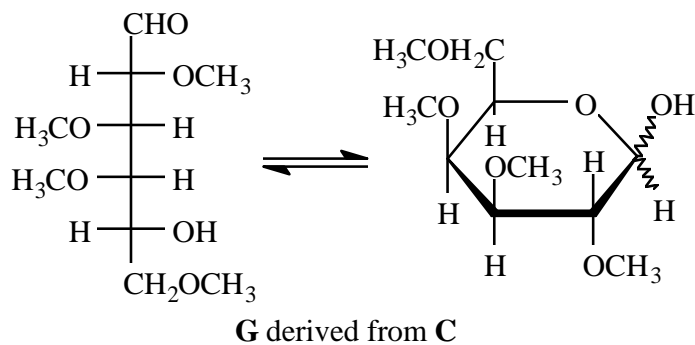
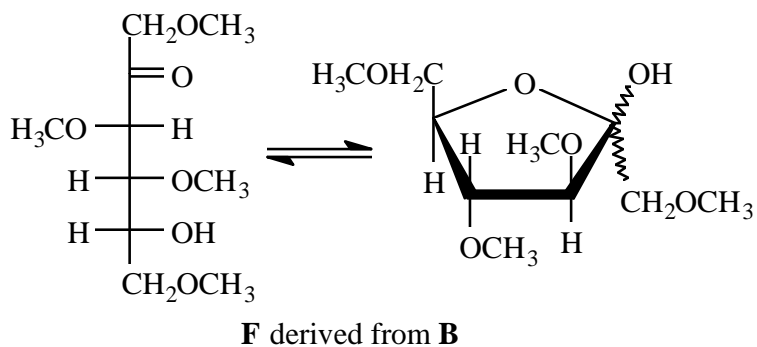
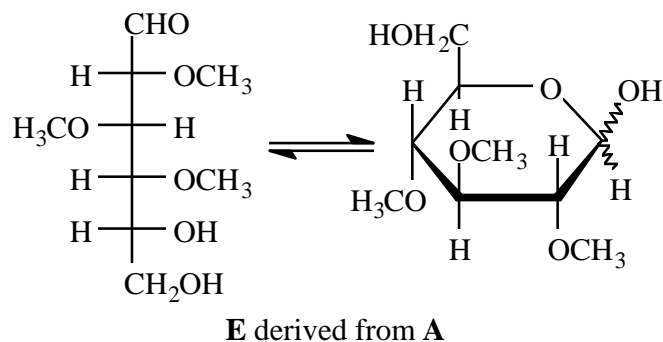
Compounds **A** and **B** are related to the same tetrose which is not the same as that of **C** (i.e.

SOLUTION 1 (continued)

are related to D-erythrose). The tetrose which is related to **A** and **B** must therefore have the following structure and accordingly **A** is D-glucose and **B** is D-fructose.



Methylation of **X** followed by hydrolysis yields **E**, **F** and **G** below:



SOLUTION 1 (continued)

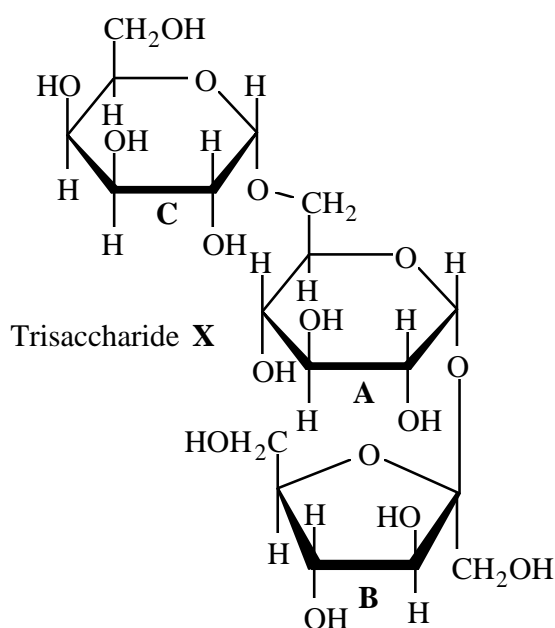
During methylation, only hydroxyl groups not involved in acetal/ketal formation (either intra- or intermolecular) will be etherified. From the methylation data, only **E** has two free hydroxyl groups with which to link to the other carbohydrates. Thus **A** must be the central carbohydrate.

These results indicate that the sequence of monosaccharides in **X** is **C-A-B** (or **B-A-C**).

- If: **A**₅ represents the furanose (5-membered ring) form of carbohydrate **A**.
 A₆ represents the pyranose (6-membered ring) form of carbohydrate **A**.
 B₅ represents the furanose (5-membered ring) form of carbohydrate **B**, etc.

then the trisaccharide **X** would be represented as: **C**₆-**A**₆-**B**₅

One of the 4 possible variations in the structure of **X** is given below.



Note: The nature of the anomeric linkages was not specified in the problem. The linkage arrangement of **A** to **B** and **C** may also be reversed (i.e. a 1,1' linkage between **C** and **A** and a 1,6 linkage between **A** and **B**).

SOLUTION 2

i) Proposal A: $\frac{d[\text{H}_2\text{SO}_4]}{dt} = k[\text{H}_2\text{O}][\text{SO}_3]$

Summing the exponents gives a second order process

Proposal B: $\frac{d[\text{H}_2\text{SO}_4]}{dt} = k[\text{SO}_3][\text{H}_2\text{O}]^2$

Summing the exponents gives a third order process

ii) The steady state approximation gives:

The rate law here will be similar to that found for an enzymatic process which proceeds through a rapid reversible binding step followed by a slower reaction process.

$$\frac{d[\text{SO}_3 \cdot 2\text{H}_2\text{O}]}{dt} = k_1[\text{SO}_3][\text{H}_2\text{O}]^2 - k_{-1}[\text{SO}_3 \cdot 2\text{H}_2\text{O}] - k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = 0$$

$$\text{Thus: } k_{-1}[\text{SO}_3 \cdot 2\text{H}_2\text{O}] + k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = k_1[\text{SO}_3][\text{H}_2\text{O}]^2$$

$$\text{and therefore: } [\text{SO}_3 \cdot 2\text{H}_2\text{O}] = \frac{k_1[\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1} + k_2}$$

$$\text{Also: } \frac{d[\text{H}_2\text{SO}_4]}{dt} = k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] \text{ and substituting from above yields}$$

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = \frac{k_1 k_2 [\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1} + k_2}$$

However, since $k_2 \ll k_{-1}$ the above reduces to:

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = \frac{k_1 k_2 [\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1}} = K_{\text{eq}} k_2 [\text{SO}_3][\text{H}_2\text{O}]^2 = k[\text{SO}_3][\text{H}_2\text{O}]^2$$

which is also third order

SOLUTION 2 (continued)

iii) Knowing the Arrhenius relationship: $k = Ae^{-E/RT}$

for Proposal A: $k = A e^{-E_A/RT} = Ae^{-83.6/RT}$ which increases with increasing T

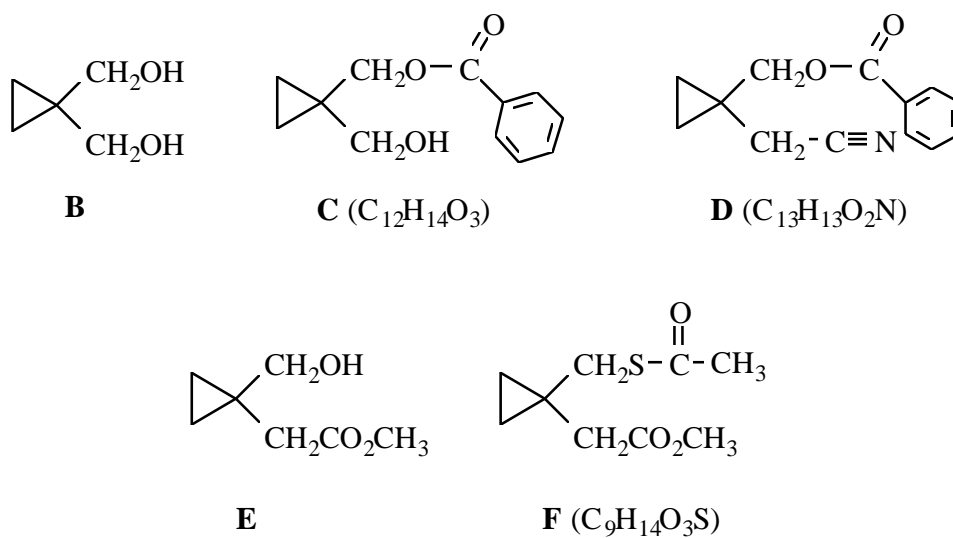
For Proposal B only the slow step is critical in determining the dependence of the rate constant on the temperature. The complexation step is very stable which explains the negative activation energy.

for Proposal B: $k = Ae^{-E_B/RT} = Ae^{+83.60/RT}$ which decreases with increasing T

iv) Assuming that the pre-exponential factors are comparable in magnitude as is usually the case, the reaction will be faster at the lower temperatures found in the upper atmosphere due to the temperature dependence deduced above, and thus Proposal B must be operating. The rationale for Proposal B which involves the relative sizes of the rate constants is nonsense and was included to balance the choices. The rationale for Proposal A involving collision probabilities appears plausible but is not a factor — it is the massive negative activation energy which controls the situation.

SOLUTION 3

i)

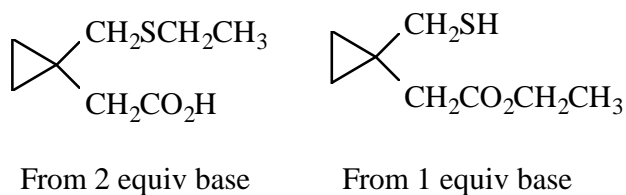


ii) S_N2 Bimolecular Nucleophilic Substitution

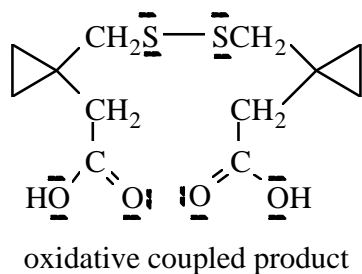
iii) Rate = k[substrate] [nucleophile]

The overall rate is directly dependent on the concentration of both the substrate and the nucleophile. Thus tripling the concentration of both of the reactants will result in a 9-fold increase in the overall reaction rate.

iv)



v)



SOLUTION 4

i) The observed colour will be the complementary colour to that of the absorption maximum.

a) Acidic conditions (pH 1):

The sample absorbs at 490 ± 25 (blue-green) and thus will transmit the complementary colour and will appear to be yellow-orange (625 ± 25 nm).

b) Basic conditions (pH 13):

The sample absorbs at 625 ± 25 (yellow-orange) and thus will transmit the complementary colour and will appear to be blue-green (490 ± 25 nm).

ii) The filter should transmit the colour that the sample will absorb most efficiently. The acidic sample absorbs most strongly in the blue range (490 ± 25 nm) and thus a similar colour filter would be most suitable for the photometric analysis of the sample.

iii) The wavelength range to be used for maximum sensitivity should correspond to that at which the sample absorbs most strongly. The maximum absorbance for the basic form of the indicator in solution occurs at 625 ± 25 nm and this is the most suitable wavelength for the analysis.

iv) From a graph of A versus wavelength, the absorbance of a 5.00×10^{-4} M basic solution at 545 nm is 0.256. From the plot, it is clear that this region of the graph is linear and thus the above value can also be interpolated from the data table.

$A = \epsilon l c$ (Beer's Law)

where, l = length of cell

c = concentration of analyte

ϵ = molar absorptivity

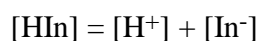
$$\text{therefore, } \epsilon = \frac{A}{lc} = \frac{0.256}{1.0 \times 5.00 \times 10^{-4}} = 5.12 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$$

Absorbance of a 1.00×10^{-4} M basic solution of the indicator using a 2.50 cm cell is:

$$A = 5.12 \times 10^2 \times 2.50 \times 1.0 \times 10^{-4} = 0.128$$

SOLUTION 4 (continued)

v) The dissociation reaction of the indicator is:



accordingly,

$$[\text{H}^+] = [\text{In}^-] \quad (1)$$

and

$$[\text{HIn}] + [\text{In}^-] = 1.80 \times 10^{-3} \text{ M} \quad (2)$$

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad (3)$$

Substitute (1) and (2) into (3)

$$K_a = \frac{[\text{In}^-]^2}{1.8 \times 10^{-3} - [\text{In}^-]} = 2.93 \times 10^{-5}$$

Rearrangement yields the quadratic expression

$$[\text{In}^-]^2 + 2.93 \times 10^{-5}[\text{In}^-] - 5.27 \times 10^{-8} = 0$$

which results in

$$[\text{In}^-] = 2.15 \times 10^{-4} \text{ M}$$

$$[\text{HIn}] = 1.80 \times 10^{-3} \text{ M} - 2.15 \times 10^{-4} \text{ M} = 1.58 \times 10^{-3} \text{ M}$$

The absorbance at the two wavelengths are then:

$$A_{490} = (9.04 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.08 \times 10^2 \times 1 \times 2.15 \times 10^{-4}) = 1.45$$

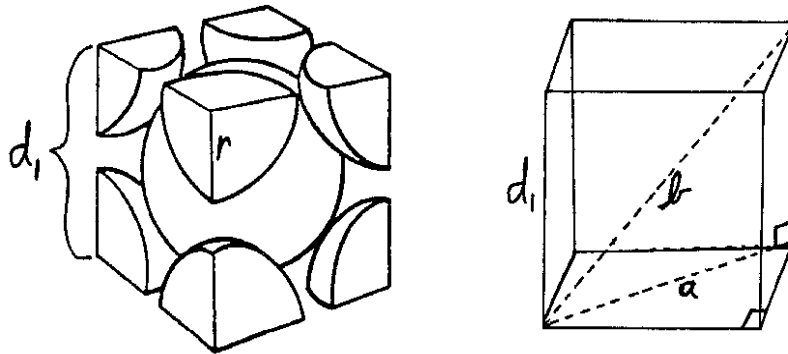
$$A_{625} = (3.52 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.65 \times 10^3 \times 1 \times 2.15 \times 10^{-4}) = 0.911$$

SOLUTION 5

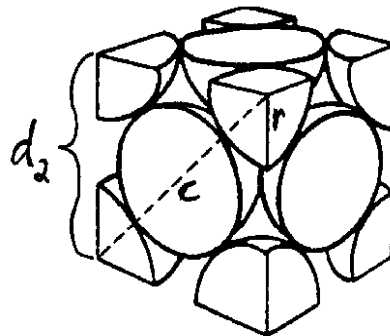
- i) Expected steps of the calculation:
1. Define the length (a , b , c , d_1 , d_2 , and r) and volume (V_1 and V_2) parameters for both bcc and fcc structures of iron (*cf.* Details below).
 2. Calculate the volume (V_1) of the unit cell of α -iron from its density (ρ_{bcc}) at 293 K, the molar weight (M_{Fe}) of iron, and Avogadro's number (N_A).
 3. Calculate the length (d_1) of the edge of the bcc unit cell from its volume (V_1).
 4. Calculate the atomic radius (r) of iron from the length " d_1 ".
 5. Calculate the length (d_2) of the edge of the fcc unit cell (at 1250 K) from the atomic radius (r) of iron.
 6. Calculate the volume (V_2) of the fcc unit cell of γ -iron from the length (d_2) of its edge.
 7. Calculate the mass (m) of the number of iron atoms in a unit cell of γ -iron from the molar weight (M_{Fe}) of iron and Avogadro's number (N_A).
 8. Calculate the density (ρ_{fcc}) of γ -iron from the values of " m " and " V_2 ".

An alternative route to ρ_{fcc} of γ -iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

- 5'. Calculate the percent space filling ratio of the bcc unit cell.
- 6'. Calculate the percent space filling ratio of the fcc unit cell.
- 7'. Calculate the $\rho_{\text{fcc}}/\rho_{\text{bcc}}$ density ratio from the fcc/bcc space filling ratios.
- 8'. Calculate the density (ρ_{fcc}) of γ -iron from the value found in step 7'.



Body centered cubic structure (bcc)



Face-centered cubic structure (fcc)

SOLUTION 5 (continued)

i) Details:

1. At 293 K, α -iron has a bcc crystal structure.
Each unit cell possesses 2 atoms and one of them is in the center of the cell.
At 1250 K, γ -iron has a fcc crystal structure.
Each unit cell possesses 4 atoms and each side has one-half an atom at its center.

r = atomic radius of iron.

a = length of the diagonal on one side of the bcc unit cell.

b = length of the diagonal passing through the center of the bcc unit cell.

c = length of the diagonal on one side of the fcc unit cell.

d_1 = length of the edge of the bcc unit cell of α -iron.

d_2 = length of the edge of the fcc unit cell of γ -iron.

V_1 = Volume of the bcc unit cell of α -iron.

V_2 = Volume of the fcc unit cell of γ -iron.

V_a = Volume of one atom.

V_{a1} = Volume occupied by 2 atoms in one bcc unit cell.

V_{a2} = Volume occupied by 4 atoms in one fcc unit cell.

R_1 = Percent space filling ratio in a bcc unit cell.

R_2 = Percent space filling ratio in a fcc unit cell.

$$V_a = (4/3) \pi r^3 \qquad V_{a1} = 2 V_a \qquad V_{a2} = 4 V_a$$

$$b = 4r; \qquad a^2 = 2d_1^2; \qquad b^2 = d_1^2 + a^2 = 3d_1^2$$

$$d_1 = (b^2/3)^{1/2} = (16r^2/3)^{1/2}; \qquad V_1 = d_1^3 = [(16r^2/3)^{1/2}]^3$$

$$c = 4r; \qquad c^2 = 2d_2^2$$

$$d_2 = (c^2/2)^{1/2} = (16r^2/2)^{1/2}; \qquad V_2 = d_2^3 = [(16r^2/2)^{1/2}]^3$$

2. 1.000 cm³ of iron weights 7.874 g at 293 K (ρ_{bcc}).

1 mole of iron weights 55.847 g (M_{Fe}).

So 0.1410 mol (7.874 g/55.847 g mol⁻¹) of iron occupy a volume of 1.000 cm³ or

1 mol of iron will occupy a volume of 7.093 cm³

1 mole corresponds to 6.02214 x 10²³ atoms

$$V_1 = (7.093 \text{ cm}^3 \text{ mol}^{-1}) \times (2 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$$

$$V_1 = 2.356 \times 10^{-23} \text{ cm}^3 \text{ per unit cell}$$

3. $d_1 = (V_1)^{1/3} = (2.356 \times 10^{-23} \text{ cm}^3)^{1/3}$

$$d_1 = 2.867 \times 10^{-8} \text{ cm}$$

SOLUTION 5 (continued)

4. For a bcc structure, the value of d_1 can be expressed as: $d_1 = [(16r^2)/3]^{1/2}$
so the value of “r” will be: $r = (3d_1^2/16)^{1/2}$
 $r = [3 (2.867 \times 10^{-8} \text{ cm})^2/16]^{1/2}$
 $r = 1.241 \times 10^{-8} \text{ cm}$
5. At 1250 K, in the fcc structure, the value of “ d_2 ” is given by: $d_2 = (16r^2/2)^{1/2}$
 $d_2 = [16 (1.241 \times 10^{-8} \text{ cm})^2/2]^{1/2}$
 $d_2 = 3.511 \times 10^{-8} \text{ cm}$
6. $V_2 = d_2^3 = (3.511 \times 10^{-8} \text{ cm})^3$
 $V_2 = 4.327 \times 10^{-23} \text{ cm}^3$
7. The mass “m” of the 4 iron atoms in the fcc unit cell will be:
 $m = (55.847 \text{ g mol}^{-1}) \times (4 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$
 $m = 3.709 \times 10^{-22} \text{ g per unit cell}$
8. $\rho_{\text{fcc}} = m/V_2 = (3.709 \times 10^{-22} \text{ g}) / (4.327 \times 10^{-23} \text{ cm}^3)$
 $\rho_{\text{fcc}} = 8.572 \text{ g/cm}^3$

Alternative route to ρ_{fcc} of γ -iron:

- 5'. $R_1 = [(V_{a1}) / (V_1)] \times 100\% = [(2 V_a) / (V_1)] \times 100\%$
 $R_1 = [(2 \times (4/3) \pi r^3) / [(16r^2/3)^{1/2}]^3] \times 100\%$
 $R_1 = [(8/3) \pi r^3] / [(16/3)^{3/2} r^3] \times 100\%$
 $R_1 = [(8/3) \pi] / [(16/3)^{3/2}] \times 100\%$
 $R_1 = [(8.378) / (12.32)] \times 100\%$
 $R_1 = 68.02\%$
- 6'. $R_2 = [(V_{a2}) / (V_2)] \times 100\% = [(4 V_a) / (V_2)] \times 100\%$
 $R_2 = [(4 \times (4/3) \pi r^3) / [(16r^2/2)^{1/2}]^3] \times 100\%$
 $R_2 = [(16/3) \pi r^3] / [8^{3/2} r^3] \times 100\%$
 $R_2 = [(16/3) \pi] / [8^{3/2}] \times 100\%$
 $R_2 = [(16.76) / (22.63)] \times 100\%$
 $R_2 = 74.05\%$
- 7'. $\rho_{\text{fcc}} / \rho_{\text{bcc}} = (74.05\%) / (68.02\%)$
 $\rho_{\text{fcc}} / \rho_{\text{bcc}} = 1.089$
- 8'. $\rho_{\text{fcc}} = 1.089 \times \rho_{\text{bcc}}$
 $\rho_{\text{fcc}} = 1.089 \times 7.874 \text{ g cm}^{-3}$
 $\rho_{\text{fcc}} = 8.572 \text{ g cm}^{-3}$

SOLUTION 5 (continued)

ii) Expected Steps of the Calculation:

1. From the percent composition of martensite (by mass), calculate the relative amounts of moles of carbon and iron.
2. Bring the C/Fe molar ratio to one (1) unit cell (Note: 2 Fe atoms per unit cell).
3. Find the smallest whole number of C atoms for the smallest whole number of unit cell (facultative).
4. Calculate the mass of iron per unit cell.
5. Calculate the mass of carbon per unit cell.
6. Calculate the total mass of carbon and iron in one unit cell.
7. Calculate the density of martensite [$\rho(\text{martensite @ 4.3\%C})$] from the total mass of C and Fe and volume (V_1) of α -iron bcc unit cell.

ii) Details:

1. In 100.0 g of martensite at 4.3%C: $(4.3 \text{ g C}) / (12.011 \text{ g mol}^{-1}) = 0.36 \text{ mol C}$
 $(95.7 \text{ g Fe}) / (55.847 \text{ g mol}^{-1}) = 1.71 \text{ mol Fe}$

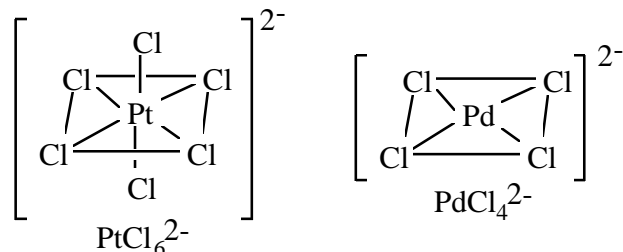
So we have 1 carbon atom for 4.8 iron atoms or
0.21 carbon atoms per iron atom

2. Martensite has a bcc crystal structure (2 iron atoms per unit cell).
[(1 C atom) / (4.8 Fe atoms)] x (2 Fe atoms / unit cell)
or: 0.42 carbon atoms per unit cell
3. 5 carbon atoms [(0.42 C atom/0.42) x 5] in 12 unit cells [(1 unit cell/0.42) x 5].
5 carbon atoms dispersed in 12 unit cells
4. [(55.847 g/mol) / (6.02214 x 10²³ atoms/mol)] x (2 atoms/unit cell of α -Iron)
1.8547 x 10⁻²² g Fe per unit cell of α -Iron
5. (12.011 g/mol) / (6.02214 x 10²³ atoms/mol)
1.9945 x 10⁻²³ g C per atom
6. [1.8547 x 10⁻²² g Fe + (0.42 C at. x 1.9945 x 10⁻²³ g/C at.)] per unit cell
1.938 x 10⁻²² g C and Fe per unit cell
7. Each unit cell of α -Iron occupies a volume, V_1 , of 2.356 x 10⁻²³ cm³
(cf. Question i)
 $\rho(\text{martensite @ 4.3\% C}) = (1.938 \times 10^{-22} \text{ g C and Fe}) / (2.356 \times 10^{-23} \text{ cm}^3)$
 $\rho(\text{martensite @ 4.3\% C}) = 8.228 \text{ g cm}^{-3}$

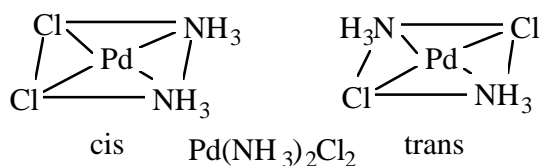
SOLUTION 6

a)

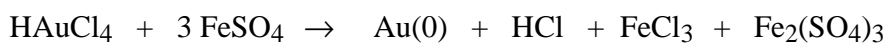
- i) The PtCl_6^{2-} anion consists of a Pt(IV) centered in a regular octahedron of Cl^- ions. The PdCl_4^{2-} anion consists of a Pd(II) centered in a square of Cl^- ions.



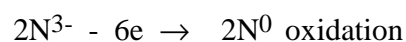
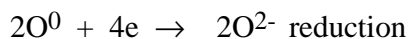
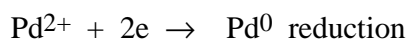
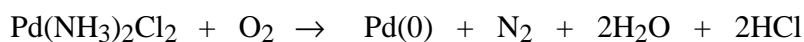
- ii) Like PdCl_4^{2-} , $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is also square planar. However, in this case there are two distinct ways in which the two different substituent groups (ligands) can be arranged. One places the two Cl^- on adjacent corners of the square (and axiomatically, the two NH_3 on the other two adjacent corners). This arrangement is called the *cis* isomer. The second arrangement has the pairs of the same ligand placed on diagonally opposite corners of the square. This arrangement is called the *trans* isomer. There are only these two stereoisomers possible for a monomeric form of the complex.



- iii) The FeSO_4 [i.e. Fe(II)] acts as a reducing agent. Under the conditions used in the process, the Fe(II) is a strong enough reducing agent to reduce Au(III) to Au(0), but not to reduce Pd(II) or Pt(IV).

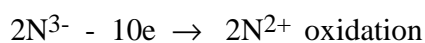
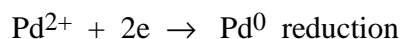
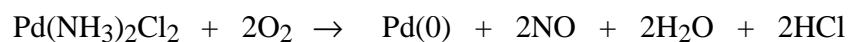


iv)

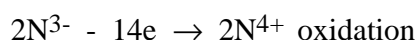
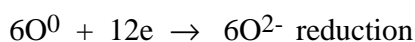
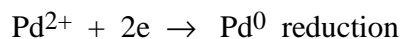
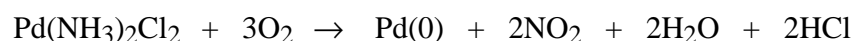


or

SOLUTION 6 (continued)



or



In this reaction the ammonia is oxidized to water and dinitrogen (or nitrogen oxides) and the Pd(II) and dioxygen are being reduced.

Part of the oxidation is due to the Pd(II) acquiring two electrons to go to Pd(0), and part by dioxygen which is reduced to water. In the presence of noble metal catalysts, NH_3 can also be oxidized to $(\text{NO})_x$. Thus other nitrogen species are also in principle possible in the above ignition.

b)

i) **A** = sulfur

All Cl is located in the NH_4Cl , and thus the weight of Cl is found by:

$$53.492 \text{ g } \text{NH}_4\text{Cl} \rightarrow 35.453 \text{ g Cl}$$

$$25.68 \text{ g } \text{NH}_4\text{Cl} \rightarrow ? \text{ g Cl}$$

$$? = 25.68 \times 35.453 / 53.492 = 17.02 \text{ g Cl}$$

Total amount of **A** in the reaction is $24.71 \text{ g Cl} - 17.02 \text{ g Cl} = 7.69 \text{ g A}$

There is 2.57 g free **A** and $(7.69 - 2.57) = 5.12 \text{ g A}$ in the nitride.

The amount of N bound in nitride is therefore

$$7.37 \text{ g nitride} - 5.12 \text{ g A bound in nitride} = 2.25 \text{ g N bound in nitride}$$

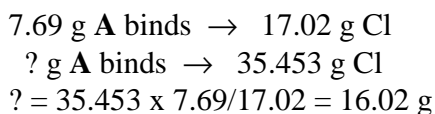
The amount of nitrogen bound in NH_4Cl is $25.68 - 17.02 = 8.66 \text{ g}$

The rule of multiple proportions is applied:

SOLUTION 6 (continued)

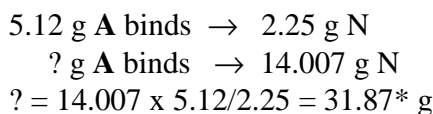
PROPORTIONS OF 1:1

Chloride:



A could be oxygen, but it is a main group element and it is a gas and thus it can be excluded

Nitride

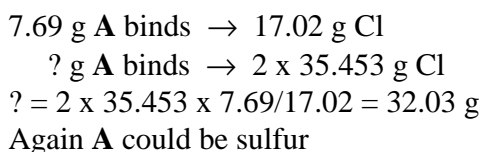


A could be sulfur, fits the physical description and $M_S=32.064$

(*Phosphorus, $M_P = 30.97$, is also possible, but the highest degree of “polymerization” known is 4, in the P_4 molecule and thus P must also be excluded)

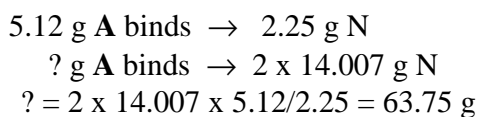
PROPORTIONS OF 1:2

Chloride:



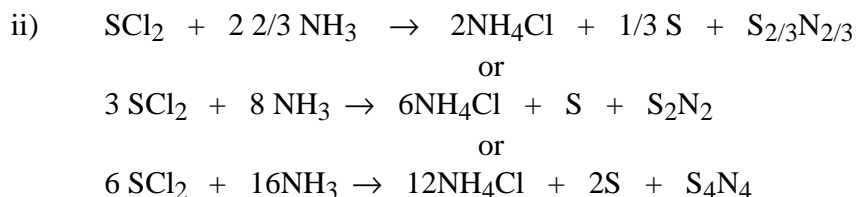
Again A could be sulfur

Nitride



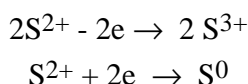
A could be Cu but it is a Group B element and thus can be excluded

Therefore element A must be sulfur.



In fact the elemental S is in the form of S_8 and so the equation should be multiplied by a factor of 8. Although S_2N_2 roughly fits the description of colour and explosive instability, it is actually S_4N_4 that is produced in this reaction. Both of these ring compounds under carefully controlled heating polymerize to give the high molecular weight linear polymer $(SN)_n$, which is one of the rare examples of a metal containing only lighter p-group elements. The tendency of these ring compounds to polymerize is due to the relatively weak S-N bonds and the large amount of strain energy in the ring. The S-S bond is also quite weak and can be broken by heating. For this reason the S_8 ring also undergoes polymerization at high temperature. However, there is hardly any energy stored in the form of ring strain in this ring and so the polymerization is not highly exothermic or explosive. Other sulfur chlorides (S_2Cl_2 and SCl_4 do not fit the stoichiometry of the reaction.)

iii) A disproportionation reaction involving sulfur occurs:

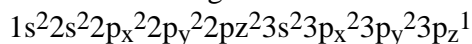


SOLUTION 7

a)

i)

Electronic configuration of a Cl atom:



Significant atomic orbitals (AO) = 1(K) + 4(L) + 4(M) = 9 AO

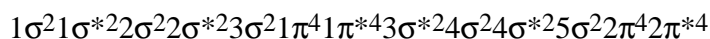
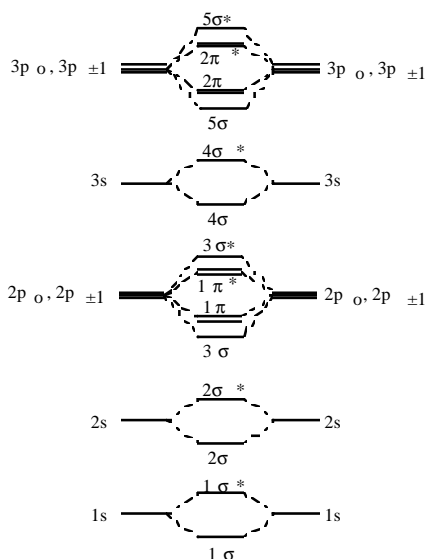
Number of electrons in these AOs: 17

Number of molecular orbitals (MO) equals number of AOs

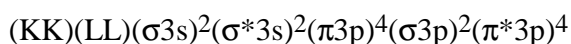
Thus $2 \times [1(K) + 4(L) + 4(M)] = 18$ MOs are present in a Cl_2 molecule

In the formation of Cl_2 : $2 \times 17 = 34$ electrons to go into the 18 MOs.

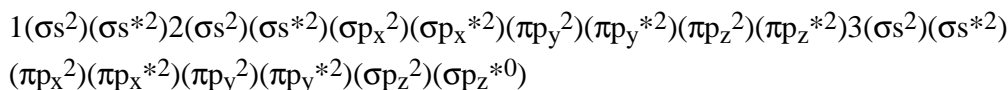
MO description of Cl_2 :



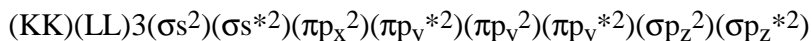
or



or



or



*assumption: - bond formation is along the z-axis
(equivalent formulae for x or y axes are accepted)

Bond order is given by $(n-n^*)/2$:

$$(2-2)/2 \text{ for (KK)} + (8-8)/2 \text{ for (LL)} + (2-2)/2 \text{ for } 3s + (2-2)/2 \text{ for } 3p_x + (2-2)/2 \text{ for } 3p_y +$$

$$(2-0)/2 \text{ for } 3p_z = 0+0+0+0+0+1 = 1 \text{ (}\sigma \text{ bond, not } \pi \text{ bond)}$$

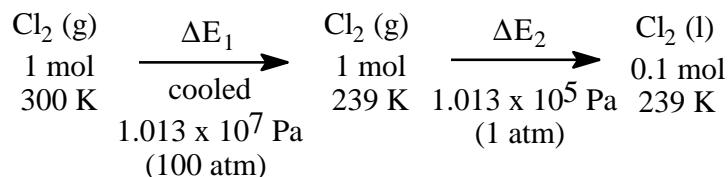
The Cl_2 molecule has a bond order of 1.

The Cl_2 molecule is diamagnetic since there are no unpaired electrons.

SOLUTION 7 (continued)

a)

ii) Summary of the changes involved:



The total process is an expansion plus an isobaric change of phase (gas to liquid) and since the internal energy (E) is a function of state, the total change in the internal energy is $\Delta E = \Delta E_1 + \Delta E_2$.

Process 1:

$$\Delta E_1 = \int nC_v dT = (1)(28.66)(239 - 300) = -1748.3 \text{ J}$$

Note: a) ΔE for a perfect gas is a function only of T

b) C_v is constant

c) “-” sign means a loss of energy due to the work needed for expansion of 1 mole of gas

Process 2: For convenience, the data were manipulated in atm; equivalent procedure in Pa will require the appropriate conversion factor

From an energetic point of view, the liquid formation Process 2 can be split into two separate steps :

- the vaporization heat loss (decreased internal energy, -) from the system into surroundings (since the process takes place at constant pressure, the heat is equal to the change in the enthalpy)
- the work done by the surroundings in compressing the system to a smaller volume (increased internal energy, +).

$$\text{Volume of gas which condensed is } V = nRT/P = (0.1)(0.0820584)(239)/1 = 1.96 \text{ L}$$

$$\text{Volume of liquid Cl}_2: (0.1)(2 \times 35.454)/1.56 = 4.54 \text{ mL}$$

$$\Delta E_2 = \Delta H_2 - \int P_{\text{ext}} \Delta V(\text{phase change}) = \Delta H_2 - P_{\text{ext}}(V_1 - V_g)$$

but V_1 is approximately 0 and can be neglected

(ca. 4.5 mL liquid volume vs. ca. 17.6 L; ca. 0.03% error)

$$\begin{aligned}
 \Delta E_2 &= (0.1)(-\Delta H_{\text{vap}}) + P_{\text{ext}}V_g \\
 &= (0.1)(-20420) + 1(1.96 \text{ L})(101.325 \text{ J L}^{-1} \text{ atm}^{-1}) \\
 &= -2042.0 + 198.5 \\
 &= -1843.5 \text{ J}
 \end{aligned}$$

$$\Delta E = \Delta E_1 + \Delta E_2 = -1748.3 + (-1843.5) = -3591.8 \text{ J}$$

SOLUTION 7 (continued)

Entropy S is a function of two variables of state. Since in Process 1 the known variables are T and P , expression of S is chosen as $S(T,P)$.

$$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2 \quad \text{and} \quad \bar{C}_p = \bar{C}_v + R = 28.66 + 8.314 = 36.97 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta S_1 &= nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} = 1.0(36.97) \ln \frac{239}{300} - 8.314 \ln \frac{1}{100} \\ &= -8.40 + 38.29 = 29.89 \text{ J K}^{-1} \end{aligned}$$

For the phase transition (constant temperature), by definition $\Delta S_2 = Q/T$
Since the pressure is constant in this case, $Q/T = Q_p/T = \Delta H/T$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{(0.1)(-20420)}{239} = -8.54 \text{ J K}^{-1} \quad \Delta S_2 = \frac{\Delta H_2}{T} = \frac{(0.1)(-20420)}{239} = -8.54 \text{ J K}^{-1}$$

$$\Delta S_{\text{sys}} = 29.89 - 8.54 = 21.35 \text{ J K}^{-1}$$

SOLUTION 7 (continued)

- b) Beware of round-off errors in the variations to the solution to this problem: One can get small differences due to conversion into and out of the \ln relationships. It is the approach which matters.

One reverses the signs of $\ln K_c$ and ΔH° for Reaction 1 when it is reversed.

Equilibrium constants are multiplied when equations are added, thus $\ln K$'s will add.

Reaction 3 = Reaction 2 - Reaction 1

Thus $\Delta S_3 = \Delta S_2 - \Delta S_1$ and $\Delta G_3 = \Delta G_2 - \Delta G_1$

$$\Delta G_1^\circ = -RT \ln K_{c1} = -8.314(298)(11.60) = -28740 \text{ J mol}^{-1} = -28.74 \text{ kJ mol}^{-1}$$

$$\Delta H_1^\circ = -33.5 \text{ kJ mol}^{-1}$$

$$\Delta S_1^\circ = (\Delta H_1^\circ - \Delta G_1^\circ)/T$$

$$= (-33.5) - (-28.74)/298 = -0.0161 \text{ kJ K}^{-1} \text{ mol}^{-1} = -16.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Similarly:

$$\Delta G_2^\circ = -44.05 \text{ kJ mol}^{-1}$$

$$\Delta H_2^\circ = -37.2 \text{ kJ mol}^{-1}$$

$$\Delta S_2^\circ = -22.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

Reaction 3 = Reaction 2 - Reaction 1, thus

$$\Delta H_3^\circ = \Delta H_2^\circ - \Delta H_1^\circ = -3.7 \text{ kJ}$$

$$\Delta S_3^\circ = \Delta S_2^\circ - \Delta S_1^\circ = 39.08 \text{ J K}^{-1}$$

$$\Delta G_3^\circ = \Delta H_3^\circ - T\Delta S_3^\circ = -15.35 \text{ kJ mol}^{-1}$$

$$\text{Thus } K_{c3} = e^{\frac{15.35}{RT}} = 4.90 \times 10^2$$

Alternatively:

$$\Delta G_3^\circ = \Delta G_2^\circ - \Delta G_1^\circ = -44.05 - (-28.74) = -15.31 \text{ kJ mol}^{-1} \text{ thus } K = 4.82 \times 10^2$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = (-3700 - (-15311))/298 = 38.96 \text{ J K}^{-1}$$

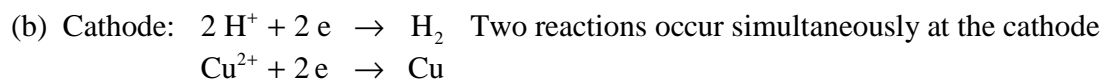
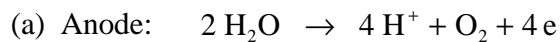
SOLUTION 8

Approach

- Determine the number of H₂ moles generated by the electrolysis
- Calculate the charge required for the H₂ production and the charge of the formation of the Cu deposit and thus the number of moles of Cu in the deposit.
- Calculate the surface concentration of atoms in the Pt (100) face thus the number of Pt atoms per 1 cm²; during an epitaxial growth the number of Cu atoms per 1 cm² equals the number of Pt atoms
- Determine the charge necessary to form one monolayer of Cu and subsequently the number of Cu monolayers on Pt (100)

Calculations

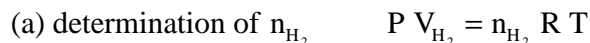
i) Balanced electrode equations



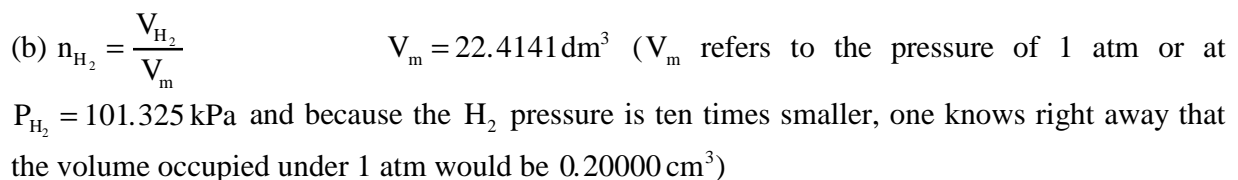
ii)

Determination of the charge necessary to generate 2.0000 cm³ of H₂ gas (T = 273.15 K, P = 10.1325 kPa)

Two approaches to determination of the number of H₂ gas moles



$$n_{\text{H}_2} = \frac{10132.5 \times 2.0000 \times 10^{-6}}{8.314510 \times 273.15} = 8.9230 \times 10^{-6} \text{ mol}$$



$$n_{\text{H}_2} = \frac{0.20000 \times 10^{-3}}{22.4141} = 8.9230 \times 10^{-6} \text{ mol}$$

SOLUTION 8 (continued)

Determination of the charge necessary to generate 8.9230×10^{-6} moles of H_2 gas

Two approaches to determination of the charge

(a) the number of H atoms, N_H , equals twice the number of H_2 molecules; if one multiplies N_H by e , then one gets the sought charge, Q_H

$$Q_H = 2 \times 8.9230 \times 10^{-6} \times N_A \times 1.60218 \times 10^{-19}$$

$$Q_H = 1.7219 \text{ C}$$

(b) one may use the Faraday law

$$m_H = k_H Q_H$$

where k_H is the electrochemical equivalent of H thus the mass of H generated by 1 C; to use this formula one has to calculate k_H ; knowing that the charge of 1 F = 96485.3 C results in formation of 1 mole of H (1/2 mole of H_2), one may easily determine k_H

$$\frac{96485.3}{1.00795} = \frac{1.0000}{k_H}$$

$$k_H = 1.04467 \times 10^{-5} \text{ g C}^{-1}$$

Subsequently

$$Q_H = \frac{m_H}{k_H} = \frac{2 \times 8.9230 \times 10^{-6} \times 1.00795}{1.04467 \times 10^{-5}}$$

$$Q_H = 1.7219 \text{ C}$$

Determination of the Cu deposition charge

$$Q_{Cu} = 2.0000 - Q_H$$

$$Q_{Cu} = 2.0000 - 1.7219 = 0.2781 \text{ C}$$

The moles of Cu is thus $0.2781/2F = 1.4412 \times 10^{-6}$

SOLUTION8 (continued)

iii)

Determination of the charge of formation of 1 monolayer (ML) of the Cu deposit and the number of Cu monolayers on the Pt (100) substrate

Calculate the number of surface Pt atoms in the (100) face

Surface area of the fundamental unit:

$$A_u = a_{Pt}^2 = 1.5395 \times 10^{-15} \text{ cm}^2$$

Number of atoms per fundamental (100) unit: $n_u = 2$

Surface atom concentration:

$$s_{Pt(100)} = \frac{n_u}{A_u} = \frac{2}{1.5395 \times 10^{-15} \text{ cm}^2} = 1.2991 \times 10^{15} \text{ cm}^{-2}$$

The number of Cu atoms per 1 cm^2 equals the number of Pt atoms - *epitaxial growth*

$$\sigma_{Cu(100)} = \sigma_{Pt(100)} = 1.2991 \times 10^{15} \text{ cm}^{-2}$$

The charge of formation of one monolayer (ML) of Cu equals:

$$q_{ML} = 2 \times e \times 1.2991 \times 10^{15}$$

$$q_{ML} = 4.1628 \times 10^{-4} \text{ C}$$

Determination of the number of Cu monolayers on the Pt (100) substrate

$$n_{ML} = \frac{0.2780 \text{ C}}{4.1628 \times 10^{-4} \text{ C}}$$

$$n_{ML} = 668 \text{ ML}$$

One can also calculate the number of Cu atoms (8.6802×10^{17}) formed from the number of moles produced and divide this by the number of atoms (1.2991×10^{15}) on the exposed Pt surface to also arrive at 668 monolayers.