

Problem x x% of total	Question	x.1	x.2	x.3	x.4	x.5	x.6	x.7	Total
	Points	13	1	5	1	2	4	2	28

Problem x: An Interesting Equilibria

by Lim Dillion, Singapore

Metal **A** is a silvery-white lustrous metal with a slight golden tinge. It is of great interest in catalytic chemistry, but is pyrophoric when finely divided. Interestingly, metal **A** reacts more slowly with F₂ than most other metals do. It has a notable resistance to attack by aqueous caustic alkali and thus finds use in apparatus for producing NaOH.

Metal **A** is commercially purified by the addition of a colourless, toxic gas to form compound **B** containing 34.38% by mass of metal **A**, before heating it at high temperatures of approximately 230°C to obtain pure metal **A**. Upon dissolving 10.00g of a binary compound containing **A** in excess aqueous HCl, 40.50g of compound **C** was formed. Compound **C** is the most common compound of metal **A**, and is green coloured. Upon passing it through a stream of SOCl₂, yellow crystals **D** are formed.

The blue isomer of compound **E** is prepared by treating compound **C** with triphenylphosphine in alcohols or glacial acetic acid, and water is liberated in this reaction. When allowed to crystallise from chlorinated solvents, the blue isomer **E** converts to the red isomer **F**.

When compound **D** was mixed with KCl and heated strongly under F₂, a ternary red solid **G** was formed which contained 23.39% metal **A** by mass, which was strongly oxidising and liberated O₂ from water. When heated under even higher temperatures and pressures, the compound **H** containing 20.24% metal **A** by mass was formed instead with an elongated ion octahedron.

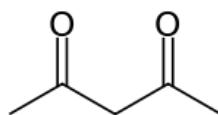
- 1) State the identities of compounds **A** to **H**. Compounds **E** and **F** can be answered with the same molecular formula. Explain your answer clearly.
- 2) State the effect that causes the "elongated ion octahedron" as stated in the last paragraph.
- 3) The blue isomer, **E**, has a tetrahedral geometry, while the red isomer, **F**, has a square planar geometry. By considering the nature of the ligands, explain fully why both isomers co-exist in aqueous solutions, yet one isomer exists in slightly greater excess. Hence, determine if isomer **F** exists as a cis- or trans- molecule.
- 4) State a method to separate the *cis-trans* isomers of isomer **F** from a solution containing a mixture of these isomers.

- 5) Compounds **E** and **F** are sometimes used as a catalyst in organic chemistry for the cross-coupling of an aryl halide and an organoboron species, as reported by Han in 2013. Today, these compounds are sometimes used for the Suzuki–Miyaura cross-coupling reaction, as shown below.



Identify two alternative reagents to compound **E/F** for this reaction.

Metal **A** is, in fact, a highly versatile metal, forming many other compounds. One such compound is a complex with acetylacetone (abbreviated "acac"), the anion of the compound shown below:



- 6) State the denticity of the acac ligand. **A(acac)₂** exists as a green solid, with acac as a ligand. Hence, draw the structure of a single **A(acac)₂** complex. Use $\text{O}^{\wedge}\text{O}$ to represent any acac ligands. State the expected geometry of this complex. However, crystallographic literature shows that it is in fact, octahedral about the **A** centre. Propose a possible reason for this.
- 7) The distinguishing test of the metal ion of **A** involves the addition of reagent **X** to a solution containing the metal ion, forming a famous rose-red precipitate. Identify reagent **X**. Aside from metal ion **A**, reagent **X** is also used as a distinguishing test for other metal ions, one of which forms a deep blue precipitate. What is this metal ion?



Rose-red precipitate on addition of reagent **X**.

Problem x: Solution

- 1) State the identities of compounds **A** to **H**. Compounds **E** and **F** can be answered with the same molecular formula. Explain your answer clearly.

A good starting point for this question would be:

*"Metal **A** is commercially purified by the addition of a colourless, toxic gas to form compound **B** containing 34.38% by mass of metal **A**, before heating it at high temperatures of approximately 230°C to obtain pure metal **A**."*

The colourless, toxic gas is most likely carbon monoxide (CO). Let us try it – it seems reasonable since metal carbonyl compounds do exist.

Let compound **B** be $\mathbf{A}(\text{CO})_n$. Let the atomic mass of **A** be a .

$$\frac{a}{a + 28n} = 0.3438 \Rightarrow a = 14.6699n$$

When $n = 1$, $a = 14.67$, unlikely to be any metal.

When $n = 2$, $a = 29.34$, unlikely to be any metal.

When $n = 3$, $a = 44.01$, unlikely to be any metal.

When $n = 4$, $a = 58.68$, likely to be Ni.

Sanity check: $\text{Ni}(\text{CO})_4$ is indeed a very common carbonyl compound of Ni.

*"Upon dissolving 10.00g of a binary compound containing **A** in excess aqueous HCl, 40.50g of compound **C** was formed."*

Firstly, one would assume that some salt of NiCl_2 would be formed, yet it is discovered that this does not give the correct mass of 40.50g. It is likely a hydrated salt of NiCl_2 , given that it was conducted in an aqueous medium.

[At this point, if one were to leverage on their knowledge that Ni usually forms salts with 6 H_2O , to determine that **C** is $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, that will be perfectly acceptable.]

Assuming 1 mol of Ni reacts to form x mol of **C**,

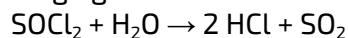
No. of moles of Ni = $10.00 / 58.69 = 0.1704 \text{ mol}$

When $x = 1$, molar mass of **C** = $40.50 / 0.1704 = 237.69 \text{ g mol}^{-1}$

Subtracting away the molar mass of $\text{NiCl}_2 = 129.69 \text{ g mol}^{-1}$, one obtains a remaining mass of 108 g mol^{-1} . The trained eye will notice that this is a multiple of 18, corresponding to our prediction that this is in fact, a hexahydrate.

*"Upon passing it through a stream of SOCl_2 , yellow crystals **D** are formed."*

It is a well known fact that SOCl_2 reacts exothermically with water to form SO_2 and HCl , and thus functions as a dehydrating agent:



Consequently, **D** is anhydrous NiCl_2 .

*"The blue isomer of compound **E** is prepared by treating compound **C** with triphenylphosphine in alcohols or glacial acetic acid, and water is liberated in this reaction. When allowed to crystallise from chlorinated solvents, the blue isomer **E** converts to the red isomer **F**."*

If water is liberated in this reaction, it is likely that it is just a complex formation. The problem now is – what is the coordination number? Reading further down the question, it is stated that **E** and **F** are tetrahedral / square planar respectively. This is a hint that the coordination number is 4, and hence 2 PPh_3 ligands are attached.

"When compound **D** was mixed with KCl and heated strongly under F₂, a ternary red solid **G** was formed which contained 23.39% metal **A** by mass, which was strongly oxidising and liberated O₂ from water. When heated under even higher temperatures and pressures, the compound **H** containing 20.24% metal **A** by mass was formed instead with an elongated ion octahedron."

For a nickel compound to be strongly oxidising, it must take on an oxidation number even higher than its normal +2 oxidation state. Another hint is that an octahedron is formed, indicating that Ni is coordinated to 6 ligands here.

Since heating compound **D** with KCl under F₂ is likely to be a fluorination, a reasonable guess would be that compound **G** contains the [NiF₆²⁻] ion (having the +4 oxidation state) and compound **H** has the [NiF₆³⁻] ion (having the +4 oxidation state too). Verifying the percentage by mass reveals that **G** must hence be K₂NiF₆.

Consequently, **H** must be K₃NiF₆, verifying it with the percentage by mass.

Unknown	Compound	Unknown	Compound
A	Ni	E	NiCl ₂ (PPh ₃) ₂
B	Ni(CO) ₄	F	
C	NiCl ₂ ·6H ₂ O	G	K ₂ NiF ₆
D	NiCl ₂	H	K ₃ NiF ₆

1 point for determining the colourless, toxic gas is CO, either implicitly or explicitly.

1 point for performing the guess-and-check method to determine the metal Ni.

1 point for either using background knowledge or by performing guess-and-check to determine that it is a hexahydrate salt.

1 point for stating that SOCl₂ reacts with H₂O, stating it is a dehydrating agent or something to that effect.

1 point for determining that E and F have PPh₃ ligands, and that the water of crystallisation is lost.

1 point for either stating that Ni should have 6 ligands or has a higher oxidation state.

1 point for each correct compound (from A to H). (Total 7 points, E and F are identical)

- 2) State the effect that causes the "elongated ion octahedron" as stated in the last paragraph.

Jahn-Teller distortion/effect.

1 point for correct effect identified.

0 points if misspelt.

- 3) The blue isomer, **E**, has a tetrahedral geometry, while the red isomer, **F**, has a square planar geometry. By considering the nature of the ligands, explain fully why both isomers co-exist in aqueous solutions, yet one isomer exists in slightly greater excess. Hence, determine if isomer **F** exists as a cis- or trans- molecule.

Weak field ligands favour tetrahedral geometry while strong field ligands generally favour the square planar isomer. According to the spectrochemical series, Cl^- is a weak field ligand while PPh_3 is a strong field ligand. Thus, $\text{NiCl}_2(\text{PPh}_3)_2$ contains a mixture of both geometries.

However, isomer **E** is slightly more favoured. PPh_3 ligands have high steric demand, thus favouring the less crowded tetrahedral geometry.

Isomer **F** exists primarily as a trans- molecule. This ensures that the sterically-demanding PPh_3 ligands are further apart, leading to less repulsion.

0.5 points each for stating the geometrical preferences of strong and weak field ligands. (Total 1 point)

0.5 points for stating Cl^- is a weak field ligand, 0.5 points for stating PPh_3 is a strong field ligand. (Total 1 point)

1 point for stating isomer E is more favoured.

0.5 points for making a relevant justification using steric hindrance.

1 point for stating that isomer F exists primarily as trans.

0.5 points for making a relevant justification using steric hindrance.

- 4) State a method to separate the *cis-trans* isomers of isomer **F** from a solution containing a mixture of these isomers.

Accept any of the following:

- Chromatography (HPLC) - e.g.
<https://www.sciencedirect.com/science/article/abs/pii/S002235491544568X>
- Fractional recrystallisation - e.g.
<https://www.sciencedirect.com/science/article/abs/pii/S1011134416304791>

1 point for stating chromatography or fractional recrystallisation.

- 5) Identify two alternative reagents to compound **E/F** for this reaction.

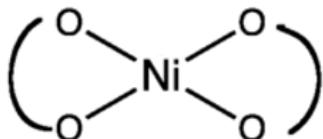
Any of the following:

Ni, Pd, $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{OAc})_2$, $\text{NiCl}_2\cdot\text{diglyme}$, $\text{PCy}_3\cdot\text{HBF}_4$, $\text{NiCl}(\text{1-naphthyl})(\text{PCy}_3)_2$, ($\text{CuI} +$) CsF , Na_2PdCl_4 , $\text{PdCl}_2(\text{PhCN})_2$, $\text{Pd}(\text{dba})_2$, Au nanoparticles, $\text{Pd}(\text{dpff})\text{Cl}_2$, Pd_2dba_3 , etc.

1 point each for each viable alternative reagent for the conversion. (Total 2 points)

- 6) State the denticity of the acac ligand. $\text{A}(\text{acac})_2$ exists as a green solid, with acac as a ligand. Hence, draw the structure of a single $\text{A}(\text{acac})_2$ complex. Use $\text{O} \curvearrowright \text{O}$ to represent any acac ligands. State the expected geometry of this complex. However, crystallographic literature shows that it is in fact, octahedral about the A centre. Propose a possible reason for this.

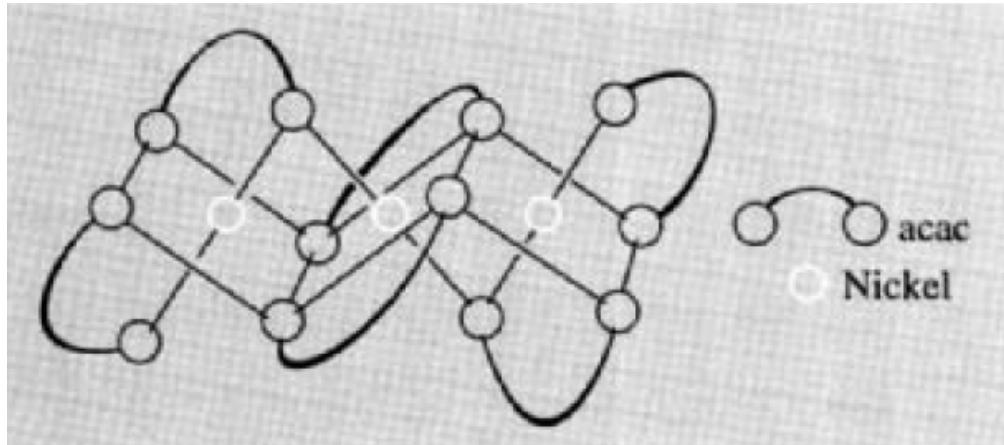
Acac is bidentate (at both carbonyl oxygens).



, expected to be square planar.

Octahedral since it forms a trimer, hence having a coordination number of 6 and forming an octahedral complex.

For the reader's information, here is the structure of the $[\text{Ni}(\text{acac})_2]_3$ trimer:



1 point for stating bidentate.

1 point for drawing the correct structure of $\text{Ni}(\text{acac})_2$.

1 point for stating the correct geometry.

1 point for stating it is octahedral due to formation of polymer / trimer with coordination number 6.

- 7) The distinguishing test of the metal ion of A involves the addition of reagent X to a solution containing the metal ion, forming a famous rose-red precipitate. Identify reagent X . Aside from metal ion A , reagent X is also used as a distinguishing test for other metal ions, one of which forms a deep blue precipitate. What is this metal ion?

Reagent X is dimethylglyoxime.

The metal ion is Co^{2+} / cobalt(II).

1 point for stating dimethylglyoxime.

1 point for stating Co^{2+} ion. [0.5 points for stating "Co ion"]