Chemistry: The flavor of life

SOLUTIONS TO

Preparatory Problems

46th International Chemistry Olympiad (IChO - 2014)

Editorial Board

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PART I. THEORETICAL PROBLEMS

Problem 1. Polar and non-polar molecules

1. The net dipole moment μ is calculated as follows:



2.

<u>2.1</u> The geometry of CO_2 :



Because two bond moments of μ_{CO} have opposite directions and cancel each other out, the net dipole moment for CO_2 is zero. Therefore: $\mu_{CO_2} = 0$

<u>2.2</u> The geometry of H_2S :



From the general equation (1),

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$$\mu_{\rm H_2S}^2 = \mu_{\rm HS}^2 + \mu_{\rm HS}^2 + 2\mu_{\rm HS}\mu_{\rm HS}\cos\alpha = 2\mu_{\rm HS}^2(1+\cos\alpha) = 4\mu_{\rm HS}^2\cos^2\frac{\alpha}{2}$$
$$\mu_{\rm HS} = 2\mu_{\rm HS}\cos\frac{\alpha}{2}$$

$$\mu_{\rm H_2S} = 2\mu_{\rm HS} \cos\frac{\alpha}{2}$$

Therefore,

$$\mu_{\rm H_2S} = 2 \times \frac{2.61 \times 10^{-30}}{3.33 \times 10^{-30}} \times \cos \frac{92}{2} = 1.09 \text{ D}$$

3.

3.1



<u>3.2</u> Since $\chi_C > \chi_H$, μ_{C-H} has the direction showed in the above plot, and

$$\mu_{\rm H-C-H} = 2\mu_{\rm C-H} \cos \frac{120}{2} = 2 \times 0.4 \times 0.5 = 0.4 D$$

 $\mu_{C=0}$ also has the direction toward the O atom. Therefore, the net dipole moment μ of the molecule is

$$\mu_{\rm HCH} = \mu_{\rm HCH} + \mu_{\rm C=0} = 0.4 + 2.3 = 2.7 \,\rm{D}$$

4. We can plot the geometry of the three molecules involved in this problem in the following scheme:



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- The dipole moment μ is a vector which can be calculated by adding individual bond moments μ_1 and μ_2

$$\mu^{2} = \mu_{1}^{2} + \mu_{2}^{2} + 2\mu_{1}\mu_{2}\cos\alpha \qquad (1)$$

 α is the angle formed by the individual bond moments.

- The dipole moment μ in the water molecule with the bond angle α formed by the two bond moments of O-H can be calculated as follows.

From equation (1) we have

$$\mu = \left(2\mu_{\text{OH}}^{2} + 2\mu_{\text{OH}}^{2}\cos\alpha\right)^{1/2}$$
$$= \left[2\mu_{\text{OH}}^{2}\left(1 + \cos\alpha\right)\right]^{1/2} = \left[4\mu_{\text{OH}}^{2}\cos^{2}\frac{\alpha}{2}\right]^{1/2}$$
$$= 2\mu_{\text{OH}}\cos\frac{\alpha}{2}$$

Given $\alpha = 105^{\circ}$, the bond moment μ_{OH} in water can be calculated:

$$1.84 = 2\mu_{\rm OH} \cos \frac{105}{2} \rightarrow \mu_{\rm OH} = 1.51 \text{ D}$$

Similarly, we can calculate the bond moment for O-CH₃ in dimethylether:

$$1.29 = 2\mu_{\text{OCH}_3} \cos \frac{110}{2} \rightarrow \mu_{\text{OCH}_3} = 1.12 \text{ D}$$

- In methanol, the individual bond moments are given as $\mu_1 = \mu_{OH}$ and μ_2 $=\mu_{\rm OCH}$ as in water and dimethylether. The bond angle α is formed by the two individual bond moments.

From equation (1), $\cos \alpha$ is:

$$\cos \alpha = \frac{\left(\mu^{2} - \mu_{1}^{2} - \mu_{2}^{2}\right)}{2\mu_{1}\mu_{2}}$$

$$= \frac{\left(1.69^{2} - 1.51^{2} - 1.12^{2}\right)}{2 \times 1.51 \times 1.12} \rightarrow \qquad O \qquad \alpha = ?$$

$$\alpha = 101^{\circ}57 \qquad H$$

Therefore, the bond angle C - O - H in methanol is of $101^{\circ}57$



Problem 2. Calculations of lattice energy of ionic compounds

1.

1.1 Lithium reacts with water:

 $2 \operatorname{Li}(s) + 2 \operatorname{H}_2O(1) \rightarrow 2 \operatorname{Li}^+(aq) + 2 \operatorname{OH}^-(aq) + \operatorname{H}_2(g)$

1.2 Lithium reacts with chlorine:

 $2 \operatorname{Li}(s) + \operatorname{Cl}_2(g) \rightarrow 2 \operatorname{LiCl}(s)$

1.3 Lithium reacts with sulfuric acid:

With dilute sulfuric acid: 2 Li(s) + H₂SO₄(aq) \rightarrow 2 Li⁺(aq) + SO₄²⁻(aq) + H₂(g)

With concentrated acid: $2 \text{ Li}(s) + 3 \text{ H}_2\text{SO}_4(c) \rightarrow 2 \text{ LiHSO}_4 + \text{SO}_2(g) + 2 \text{ H}_2\text{O}(1)$

2.

2.1 To calculate U_o in accordance with Born-Haber cycle, the following cycle is constructed:



2.2 Based on this cycle and Hess's law, we have:

$$\Delta_f H = \Delta_S H + \frac{1}{2} \Delta_D H + I + E + U_0$$

or
$$U_0 = \Delta_f H - \left(\Delta_S H + \frac{1}{2} \Delta_D H + I + E\right)$$

After converting all the numerical data to the same unit, we have:

 $U_0 = -402.3 - 159 - 121 - (5.40 - 3.84) \times 1.6 \times 10^{-19} \times 10^{-3} \times 6.022 \times 10^{23}$ $U_0 = -832.56 \text{ kJ/mol.}$



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3. U₀ = -287.2
$$\frac{Z_+ Z_- \sum v}{r_+ + r_-} \left(1 - \frac{0.345}{r_+ + r_-}\right)$$

For LiCl crystal, we have:

$$U_{0} = -287.2 \frac{1 \times 1 \times 2}{0.62 + 1.83} \left(1 - \frac{0.345}{0.62 + 1.83} \right) = -201.43 \text{ kcal/mol}$$

To conveniently compare the results, we convert the obtained result to SI units:

$$U_o = -201.43 \times 4.184 = -842.78 \text{ kJ/mol}$$

4.

According to the Born-Haber cycle and Kapustinskii empirical formula for lithium chloride crystal structure, both methods are close to the experimental value.

X	

5.

5.1 The geometry diagram for octahedral holes is shown below.



where, R and r are the radii of Cl^{-} and Li^{+} ions, respectively. Based on the diagram, we have:

$$\cos 45^{\circ} = \frac{2R}{2R+2r} = \frac{R}{R+r}$$
$$0.707 = \frac{R}{R+r} \rightarrow R = 0.707(R+r) \rightarrow r = 0.414 R$$

- The body edge length of the unit cell LiCl = 2R + 2r = 5.14 Å

$$2R + 2(0.414 R) = 5.14 \text{ Å} \rightarrow R = 1.82 \text{ Å} (radius of Cl-)$$



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 $2(1.82 \text{ Å}) + 2r = 5.14 \text{ Å} \rightarrow r = 0.75 \text{ Å} (radius of Li^+)$

5.2 Based on the experimental and theoretical data for the radii of Li^+ and Cl^- ions, it is realized that:

• Both calculated radii of lithium and chloride ions are close to the experimental values.

- Only the calculated radius of lithium ion is close to the experimental value.
- Only the calculated radius of chloride ion is close to the experimental value. ×

Problem 3. A frog in a well

1.

<u>1.1</u> The general expression is given by:

$$\Delta E_{\text{LUMO-HOMO}} = \frac{h^2}{8mL^2} \left[\left(\frac{N}{2} + 1 \right)^2 - \left(\frac{N}{2} \right)^2 \right] = \frac{h^2}{8mL^2} (N+1) \qquad \begin{array}{c} E_5 \\ E_4 \\ E_4 \\ AE \\ \hline \\ E_4 \\ AE \\ \hline \\ E_4 \\ AE \\ \hline \\ AE \\ \hline$$

$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2} (N+1) \quad \rightarrow \quad \lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)} \quad (3)$$

2.

2.1

For **BD**:
$$L = (2 \times 2 + 1)0.140 \text{ nm} = 5 \times 0.140 \times 10^{-9} \text{ m} = 7 \times 10^{-10} \text{ m} = 7.0 \text{ Å}$$

For **HT**: $L = (2 \times 3 + 1)0.140 \text{ nm} = 7 \times 0.140 \times 10^{-9} \text{ m} = 9.8 \times 10^{-10} \text{ m} = 9.8 \text{ Å}$

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► For **OT:** $L = (2 \times 4 + 1)0.140 \text{ nm} = 9 \times 0.140 \times 10^{-9} \text{ m} = 12.6 \times 10^{-10} \text{ m} = 12.6 \text{ Å}$ <u>2.2</u> From the general equation (3), the wavelength λ for each of the dyes are given:

$$\lambda = \frac{8\text{mc}}{h} \times \frac{L^2}{(N+1)} = \frac{8(9.11 \times 10^{-31})(3 \times 10^8)}{6.626 \times 10^{-34}} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{L^2}{(N+1)}$$

*** BD:** $\lambda = 3.30 \times 10^{12} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{(7 \times 10^{-10})^2}{(4+1)} = 3.234 \times 10^{-7} \text{ m} = 323.4 \text{ nm}$
*** HT:** $\lambda = 3.30 \times 10^{12} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{(9.8 \times 10^{-10})^2}{(6+1)} = 4.528 \times 10^{-7} \text{ m} = 452.7 \text{ nm}$
*** OT:** $\lambda = 3.30 \times 10^{12} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{(12.6 \times 10^{-10})^2}{(8+1)} = 5.82 \times 10^{-7} \text{ m} = 582.0 \text{ nm}$

3. The box length can be calculated based on the geometry of the C - C- C chain as follows:



The box length is a combination of a number of the length of $\frac{d}{2}$ which is given by

$$\frac{d}{2} = l_{C-C} \times \sin 60 = (0.140 \times 10^{-9}) \times \sin 60 = 1.21 \times 10^{-10} \text{ m}.$$

Therefore, the box length for the three dye molecules can be calculated as follows:

For BD, the box length is consisted of 5 lengths of $\frac{d}{2}$:



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*** BD:**
$$L = 1.21 \times 10^{-10} \text{ m} \times 5 = 6.05 \times 10^{-10} \text{ m} = 6.05 \text{ Å}$$

Similarly, the box length for **HT** has 7 lengths of $\frac{d}{2}$:

*** HT:**
$$L = 1.21 \times 10^{-10} \text{ m} \times 7 = 8.47 \times 10^{-10} \text{ m} = 8.47 \text{ Å}$$

The box length for **OT** has 9 lengths of $\frac{d}{2}$:

• OT:
$$L = 1.21 \times 10^{-10} \text{ m} \times 9 = 10.89 \times 10^{-10} \text{ m} = 10.89 \text{ Å}$$

4.

4.1 From equation (3),
$$\lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)}$$
, and therefore:
$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}}$$

✤ For **BD**:

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}} = \sqrt{\frac{(328.5 \times 10^{-9})(6.626 \times 10^{-34})5}{8(9.11 \times 10^{-31})(3 \times 10^8)}} = 7.06 \times 10^{-10} = 7.06$$
 Å

• For HT:

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}} = \sqrt{\frac{(350.95 \times 10^{-9})(6.626 \times 10^{-34})7}{8(9.11 \times 10^{-31})(3 \times 10^{8})}} = 8.63 \times 10^{-10} = 8.63$$
 Å
• For OT:

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}} = \sqrt{\frac{(586.1 \times 10^{-9})(6.626 \times 10^{-34})9}{8(9.11 \times 10^{-31})(3 \times 10^{8})}} = 12.64 \times 10^{-10} = 12.64$$
 Å

4.2 The following table shows the values of the box length for the



Substance	L=(2k+1)0.140 nm (1)	L calculated based on the bent chain (2)	L calculated from $\lambda_{exp.}$ (3)	Experimental L
BD	7.0	6.05	7.06	7.66
HT	9.8	8.47	8.63	8.64
ОТ	12.6	10.89	12.64	-

investigated dyes calculated with different methods.

- Method (1) is the best fit
- Method (2) is the best fit
- > Method (3) is the best fit
- > All methods (1), (2), (3) are best fit



1.

1.1
$$\Delta E = n^2 \frac{h^2}{8mL^2} - 1^2 \frac{h^2}{8mL^2} = \frac{h^2}{8mL^2} (n^2 - 1^2)$$

<u>1.2</u> According to Planck's equation:

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m/s})}{1.374 \times 10^{-5} \text{ m}} = 1.446 \times 10^{-20} \text{ J}$$

×

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So
$$\Delta E = 1.446 \times 10^{-20} \text{ J} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg})(10.0 \times 10^{-9} \text{ m})^2} (n^2 - 1)$$

 $1.446 \times 10^{-20} \text{ J} = 6.025 \times 10^{-22} (n^2 - 1)$
 $\rightarrow n^2 - 1 = 24.00 \rightarrow n^2 = 25.00 \rightarrow n = 5.00$
 $\mathbf{n} = \mathbf{5}$

2.

<u>2.1</u> The quantum numbers are:

Ground state (E ₁₁)	\rightarrow	$n_x = 1, n_y = 1$
First excited state (E ₂₁)	\rightarrow	$n_x = 2, n_y = 1$
Second excited state (E_{12})	\rightarrow	$n_x = 1, n_y = 2$

Since the energy levels, E_{xy} , are inversely proportional to L^2 , then the $n_x = 2$, $n_y = 1$ energy level will be lower than the $n_x = 1$, $n_y = 2$ energy level since $L_x > L_y$. The first three energy levels, E_{xy} , in order of increasing energy are: $E_{11} < E_{21} < E_{12}$ <u>2.2</u> Calculate the wavelength of light necessary to promote an electron from the first excited state to the second excited state.

$$\begin{split} E_{21} &\rightarrow E_{12} \text{ is transition. } E_{xy} = \frac{h^2}{8 \text{ m}} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \\ E_{12} &= \frac{h^2}{8 \text{ m}} \left(\frac{1^2}{(8.00 \times 10^{-9} \text{ m})^2} + \frac{2^2}{(5.00 \times 10^{-9} \text{ m})^2} \right) = \frac{1.76 \times 10^{17} \text{ h}^2}{8 \text{ m}} \\ E_{21} &= \frac{h^2}{8 \text{ m}} \left(\frac{2^2}{(8.00 \times 10^{-9} \text{ m})^2} + \frac{1^2}{(5.00 \times 10^{-9} \text{ m})^2} \right) = \frac{1.03 \times 10^{17} \text{ h}^2}{8 \text{ m}} \\ \Delta E &= E_{12} - E_{21} = \frac{1.76 \times 10^{17} \text{ h}^2}{8 \text{ m}} - \frac{1.03 \times 10^{17} \text{ h}^2}{8 \text{ m}} = \frac{7.3 \times 10^{16} \text{ h}^2}{8 \text{ m}} \\ \Delta E &= \frac{(7.3 \times 10^{16} \text{ m}^{-2})(6.626 \times 10^{-34} \text{ Js})^2}{8(9.11 \times 10^{-31} \text{ kg})} = 4.4 \times 10^{-21} \text{ J} \\ \lambda &= \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \text{ m/s})}{4.4 \times 10^{-21} \text{ J}} = 4.5 \times 10^{-5} \text{ m} \end{split}$$

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3.

$$\underline{3.1} \quad E = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = \frac{n^2h^2}{8mL^2} = 6.173 \times 10^{-21}J$$
$$n^2 = \frac{8mL^2}{h^2}E$$

If $L^3 = 8.00 \text{ m}^3$, then $L^2 = 4.00 \text{ m}^2$

$$\frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34})^2}{8\left(\frac{0.032}{6.022 \times 10^{23}}\right)4} = 2.582 \times 10^{-43} J$$
$$n^2 = \frac{6.173 \times 10^{-21}}{2.582 \times 10^{-43}} = 2.39 \times 10^{22}; \quad n = 1.55 \times 10^{11}$$

3.2
$$\Delta E = E_{n+1} - E_n = E_{1.55 \times 10^{11} + 1} - E_{1.55 \times 10^{11}}$$

 $\Delta E = (2n+1) \frac{h^2}{8mL^2} = [2(1.55 \times 10^{11}) + 1] \frac{h^2}{8mL^2} = 8.00 \times 10^{-31} J$

4. The energy levels are

$$E_{n_1,n_2,n_3} = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = E_1(n_1^2 + n_2^2 + n_3^2)$$

where E_1 combines all constants besides quantum numbers. The minimum value for all quantum numbers is 1, so the lowest energy is

 $E_{1,1,1} = 3E_1$

The question asks about an energy 21/3 times this amount, namely $21E_1$. This energy level can be obtained by any combination of allowed quantum numbers such that

$$(n_1^2 + n_2^2 + n_3^2) = 21 = 4^2 + 2^2 + 1^2$$

The degeneracy, then is 6, corresponding to $(n_1, n_2, n_3) = (1, 2, 4), (1, 4, 2), (2, 1, 4), (2, 4, 1), (4, 1, 2), \text{ or } (4, 2, 1).$



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Problem 5. Tug of war

1.
$$\Delta_{\text{rnx}} G = \Delta_{\text{rnx}} G^{\circ} + \text{RTln} \frac{P_{SO_2} P_{O_2}^{1/2}}{P_{SO_3}}$$

At equilibrium: $\Delta_{\text{rmx}} G = \Delta_{\text{rmx}} G^{\circ} + \text{RTln} \frac{P_{SO_2} P_{O_2}^{1/2}}{P_{SO_3}} = 0$

$$\Delta_{\rm r} {\rm G}^{\rm o} = - {\rm RTln} \frac{P_{SO_2} P_{O_2}^{1/2}}{P_{SO_3}} = - {\rm RTln} {\rm K}_{\rm p1}$$

T /K = T/°C + 273;

T/ K	800	825	900	953	100
lnK _{p1}	-3.263	-3.007	- 1.899	-1.173	-0.591

2. Plot lnKp against 1/T:



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Assuming that $\Delta_r H^o$ is temperature independent, the slope of this plot is $-\Delta_r H^o/R$, so that $\Delta_{rnx} H^o = 90.2 \text{ kJ/mol}$.

3.
$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$
 (2)

A best-fit equation is $lnK_{p1} = -10851(1/T) + 10.216$ with R-squared value of 0.9967. We can use this equation to estimate the K_{p1} at (651.33 + 273) = 924.33 K because $\Delta_{rnx}H^{o}$ is temperature independent.

 $\ln K_{p1} = -10851(1/924.33) + 10.216 \rightarrow \ln K_{p1} = -1.523313881 \rightarrow K_{p1} = 0.218$ For reaction (2), the equilibrium constant is expressed as:

$$K_{p2} = \frac{P_{SO_2}^2 P_{O_2}}{P_{SO_3}^2} = (K_{p1})^2 = (0.218)^2 = 0.047524$$

Reaction (3): 2 FeSO₄(s) \rightleftharpoons Fe₂O₃(s) + SO₃(g) + SO₂(g)
Decomposition: - - -
Equilibrium: P-a P+a
Reaction (4): 2 SO₃(g) \rightleftharpoons 2SO₂(g) + O₂(g)
Initial P: P P 0
Change -a +a +a/2
Equilibrium P-a P+a a/2
At equilibrium: partial pressure of oxygen = 21.28/760 = 0.028 atm

 $a/2 = 0.028 atm \rightarrow a = 0.056 atm$

Equilibrium constant for (4):

4.

$$K_{p4} = \frac{P_{SO_2}^2 P_{O_2}}{P_{SO_3}^2} = (K_{p1})^2 = (0.218)^2 = 0.047524$$
$$K_{p4} = \frac{P_{SO_2}^2 P_{O_2}}{P_{SO_3}^2} = \frac{(P+a)^2 (a/2)}{(P-a)^2} = \frac{(P+0.056)^2 0.028}{(P-0.056)^2} = 0.047524$$

46th International Chemistry Olympiad Hanoi, Vietnam – 2014 $\frac{(P+0.056)^2 0.028}{(P-0.056)^2} = 0.047524$ $\Rightarrow \frac{(P+0.056)^2}{(P-0.056)^2} = 1.6973$ $\Rightarrow \frac{(P+0.056)}{(P-0.056)} = 1.303 \qquad \Rightarrow P+0.056 = 1.303P - 0.073$ $\Rightarrow 0.303P = 0.12896 \qquad \Rightarrow P = 0.425 \text{ atm}$ Equilibrium constant for (3) 2 FeSO₄(s) = Fe₂O₃(s) + SO₃(g) + SO₂(g) K_{p3} = P_{SO3}P_{SO2} = (P-a)(P+a) = (0.425 - 0.056)(0.425 + 0.056) = 0.177

5. Calculate the percent of FeSO₄ decomposed? Mole number of SO₃ = SO₂ comes from the decomposition of FeSO₄: PV = nRT, $n = PV/PT = (0.425)1 / (0.082 \times 924.33) = 5.6 \times 10^{-3}$ moles Molar number of FeSO₄ decomposed = $2n_{SO3} = 0.0112$ mol Mass of FeSO₄ decomposed = $0.0112 \times 151.91 = 1.70$ grams Percent of FeSO₄ decomposed = 1.70/15.19 = 11.21 %.

Problem 6. Radiochemistry

1.



2. Assume that the mineral initially contained $n_{1,0}$ moles of 238 U, $n_{2,0}$ moles of 206 Pb, and n_3 moles of 204 Pb; and at present, it contains n_1 moles of 238 U, n_2 moles

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of ²⁰⁶Pb, and n_3 moles of ²⁰⁴Pb (this isotope is not generated by the decay of ²³⁸U and ²³⁵U). The age of the zircon mineral is usually very large, and we can consider that the century equilibrium for the decay process has been reached (i.e. loss of 1 mole of ²³⁸U will lead to formation of 1 mole of ²⁰⁶Pb). By conservation of mass, we have the following equation:

$$n_{1} + n_{2} = n_{1,0} + n_{2,0}$$
(1)
Dividing (1) by n₃:

$$n_{1}/n_{3} + n_{2}/n_{3} = n_{1,0}/n_{3} + n_{2,0}/n_{3}$$

$$\rightarrow n_{2}/n_{3} = n_{1,0}/n_{3} - n_{1}/n_{3} + n_{2,0}/n_{3}$$
(2)
In addition, we have $n_{1,2} = n_{1,0}^{\lambda t}$ where λ is the d

In addition, we have $n_{1,0} = n_1 e^{\lambda t}$, where λ is the decay constant of ²³⁸U, and t is the age of the mineral,

$$\rightarrow n_2/n_3 = n_1 e^{\lambda t}/n_3 - n_1/n_3 + n_{2,0}/n_3 = (n_1/n_3)(e^{\lambda t} - 1) + n_{2,0}/n_3$$
(3)

$$\rightarrow e^{-\lambda t} - 1 = \frac{n_2 / n_3 - n_{2,0} / n_3}{n_1 / n_3}$$

$$\rightarrow e^{\lambda t} = 1 + \frac{n_2 / n_3 - n_{2,0} / n_3}{n_1 / n_3}$$

$$\rightarrow t = \frac{1}{\lambda} \ln(1 + \frac{n_2 / n_3 - n_{2,0} / n_3}{n_1 / n_3})$$
(4)

According to the data given:

$$\frac{n_2}{n_3} = \frac{\frac{14.30}{206}}{\frac{0.277}{204}} = 51.12; \quad \frac{n_{2.0}}{n_3} = \frac{\frac{24.10}{206}}{\frac{1.4}{204}} = 17.05$$
$$\frac{n_1}{n_3} = \frac{\frac{99.275}{238}}{\frac{0.277}{204}} = 307.19$$
$$t = \frac{4.47 \times 10^9}{0.693} \ln(1 + \frac{51.12 - 17.05}{307.19}) = 6.78 \times 10^8 \text{ years}$$

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$$m_0(^{235}U) = 0.721 \times e^{\frac{0.693}{7.038 \times 10^8} \times 6.78 \times 10^8} = 1.406 \text{ g}$$
$$m_0(^{238}U) = 99.275 \times e^{\frac{0.693}{4.47 \times 10^8} \times 6.78 \times 10^8} = 110.28 \text{ g}$$
$$m_0(^{235}U) / m_0(^{238}U) = 1.406 / 110.28 = 0.0127$$

3. After 99% of Fe^{3+} precipitated, the concentration of the remaining Fe^{3+} in the solution is:

$$[\mathrm{Fe}^{3^+}] = 2 \times 0.05 \times 10^{-2} = 1 \times 10^{-3} \mathrm{M}$$

The concentration of hydroxide ions necessary to maintain a Fe^{3+} concentration of 10^{-3} M in the solution is:

$$[OH^{-}] = \left(\frac{T_{Fe(OH)_{3}}}{Fe^{3+}}\right)^{\frac{1}{3}} = \left(\frac{3.8 \times 10^{-38}}{10^{-3}}\right)^{\frac{1}{3}} = (38)^{\frac{1}{3}} \times 10^{-12} \text{ M}$$

Thus, the pH value of the solution can be calculated as follows:

pH = $-\log\{10^{-14}/[(38)^{1/3} \times 10^{-12}]\} = 2 + (1/3)\log 38 = 2.53$

At this pH, the reaction quotient of the dissociation of $UO_2(OH)_2$ in 0.01 M of solution is:

 $[\mathrm{UO_2}^{2^+}][\mathrm{OH}^-]^2 = 0.01 \times [(38)^{1/3} \times 10^{-12}]^2 = 1.13 \times 10^{-25} < 10^{-22}$

Since the ionic product is much smaller than the solubility product of $UO_2(OH)_2$,

we can conclude that uranium cannot precipitate under these conditions.

4. Volume ratio of the two phases: $V_{aq}/V_{org} = 1000$: 500 = 2

Let x represent the equilibrium concentration of $UO_2(NO_3)_2$ in the aqueous phase. Let C_0 represent the initial concentration of $UO_2(NO_3)_2$ in the organic phase.



The equilibrium concentration of $UO_2(NO_3)_2$ in the organic phase is calculated as follows:

$$C_{\rm org} = (V_{\rm aq}/V_{\rm org})(C_0 - x)$$

$$D = \frac{C_{\rm org}}{x} = \frac{2(C_o - x)}{x} = 10$$
 (6)

$$x : C_o = 1 : 6 = 16.67\%.$$

5. 500 mL of organic solvent may be divided into n equal portions for extraction. Volume ratio of the two phases: $V_{aq}/V_{org} = 1000$: (500/n) = 2n

- After the first extraction:

$$D = \frac{C_{\text{org}}}{x_1} = \frac{2n(C_{\text{o}} - x_1)}{x_1} = 10$$
(7)

$$\rightarrow x_1 = \frac{2nC_{\text{o}}}{D + 2n}$$
(8)

- For the second extraction, the initial concentration of the aqueous phase is x_1 , while the equilibrium concentration is x_2 . Using equation (8), we replace x_2 with x_1 , and x_1 with C_0 to obtain the following expression:

$$x_2 = \frac{2nx_1}{D+2n} = \left(\frac{2n}{D+2n}\right)^2 C_0$$
 (9)

- After n extractions, the concentration of $UO_2(NO_3)_2$ remaining in the aqueous phase is:

$$\mathbf{x}_{\mathrm{n}} = \left(\frac{2n}{D+2n}\right)^{n} C_{\mathrm{o}} \tag{10}$$

% $UO_2(NO_3)_2$ remaining in the aqueous phase after n extractions is:

$$\frac{x_n}{C_0} 100\% = \left(\frac{2n}{D+2n}\right)^n 100\%$$



Solutions

n =	1	2	3	4	5	6
$\left(\frac{2n}{D+2n}\right)^n 100\% =$	16.67	8.16	5.27	3.9	3.1	2.63
$n = 5 \rightarrow \frac{x_n}{C_0} 100\% = \left(\frac{2n}{D+2n}\right)^n < 4\%$						

Thus, the optimal approach is to divide 500 mL of solvent into 5 portions and extract 5 times.

Other schemes are acceptable, if all calculations and justifications are reasonable.

Problem 7. Applied thermodynamics

1.

1.1 Based on the above data:

 $\Delta G^{o}_{T} = \Delta H^{o}_{T} - T\Delta S^{o}_{T}$ $\Delta G^{o}_{T}(1) = (-112298.8 + 5.94T) - T(54.0 + 6.21\ln T)$ Reaction (1): $\Delta G^{o}_{T}(1) = -112298.8 - 48.06T - 6.21TlnT$

 $\Delta G^{o}_{T}(1)$ decreases with an increase in temperature.

Reaction (2):
$$\Delta G^{o}_{T}(2) = (-393740.1 + 0.77T) - T(1.54 - 0.77lnT)$$

 $\Delta G^{o}_{T}(2) = -393740.1 - 0.77T + 0.77TlnT$

<u>1.2</u> $\Delta G^{o}_{T}(2)$ increases with an increase in temperature.

2.

2.1
$$C(\text{graphite}) + \frac{1}{2} O_2(g) \rightarrow CO(g)$$
 (1)

$$\underline{C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)}$$
(2)

$$(2) - (1) \rightarrow \operatorname{CO}(g) + \frac{1}{2} \operatorname{O}_2 \rightarrow \operatorname{CO}_2(g)$$
(3)

We have, $\Delta G^{o}_{T}(3) = \Delta G^{o}_{T}(2) - \Delta G^{o}_{T}(1)$

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<u>2.2</u> Substitute the values in: $\Delta G^{o}_{T}(3) = (-393740.1 - 0.77T + 0.77TlnT) - (-112298.8 - 48.06T - 6.21TlnT)$ $\Delta G^{o}_{T}(3) = -281441.3 + 47.29T - 6.98TlnT$ At 1673 K: $\Delta G^{o}_{T}(3) = -115650$ J/mol

<u>2.3</u> Since $\Delta G^{\circ} = -RTlnK_p$, the equilibrium constant K_p for reaction (3) can be calculated as follows:

$$\ln K_{p,1673}(3) = -\frac{\Delta G_{1673}^{0}(3)}{RT} = \frac{115650}{8.314 \times 1673} = 8.313457$$

 $\rightarrow K_{p,1673}(3) = 4083$

3.

<u>3.1</u>

$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) \qquad (3)$$

$$\underline{NiO(s) + CO(g) \rightarrow Ni(s) + CO_2(g) \qquad (4)}$$

$$(4) - (3) \qquad NiO(s) \rightarrow Ni(s) + \frac{1}{2} O_2(g) \qquad (5)$$

<u>3.2</u>

At 1673 K, we have:

For reaction (4): $K_p(4) = \frac{p_{CO_2}}{p_{CO}} = \frac{99}{1}$

For reaction (3): $K_p(3) = \frac{p_{CO_2}}{p_{CO}p_{O_2}^{1/2}} = 4083 \text{ or } p_{O_2}^{1/2} = \frac{p_{CO_2}}{p_{CO}4083} = \frac{K_p(4)}{4083} = \frac{99}{4083}$

For reaction (5): $K_p(5) = p_{O_2}^{1/2} = \frac{p_{CO_2}}{p_{CO}K_p(3)} = \frac{K_p(4)}{K_p(3)}$ or

$$K_{p}(5) = p_{O_{2}}^{1/2} = \frac{K_{p}(4)}{K_{p}(3)} = \frac{99}{4083} = 0.024247 = 2.4247 \times 10^{-2}$$

Hence, $p_{O_2} = [K_p(5)]^2 = (2.4247 \times 10^{-2})^2$ and $p_{O_2} = 5.88 \times 10^{-4}$ bar = 58.8 Pa



Problem 8. Complex compound

1. How many atoms of EDTA are capable of binding with the metal ions upon complexation?



2.

<u>2.1</u> Let $[H^+]$ be h and at pH = 10.26:

$$\beta' = \beta \alpha_{Mg^{2+}} \alpha_{Y^{4-}}$$

$$= \beta \frac{1}{1 + {}^*\beta h^{-1}} \frac{K_{a4}}{h + K_{a4}} = 10^{8.69} \frac{1}{1 + 1.58 \times 10^{-13} \times 10^{10.26}} \frac{10^{-10.26}}{10^{-10.26} + 10^{-10.26}}$$

$$\beta' = \beta \alpha_{Mg^{2+}} \alpha_{Y^{4-}} = 10^{8.69} \times 1 \times 0.5 = 2.45 \times 10^{8}$$

2.2 At pH = 10.26:

$$(Mg^{2+})' + (Y^{4-})' \rightarrow MgY^{2-}$$

0.05 0.05

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Solutions

- - 0.05

$$MgY^{2-} \rightleftharpoons (Mg^{2+})' + (Y^{4-})' \qquad (\beta')^{-1} = (2.45 \times 10^8)^{-1}$$
0.05 - x x x

$$C_{Mg^{2+}} = C'_{Mg^{2+}} = x = 1.43 \times 10^{-5} (M)$$

$$C_{Mg^{2+}} \left[OH^{-} \right]^{2} = 1.43 \times 10^{-5} \left(10^{-3.74} \right)^{2} = 10^{-12.32} < K_{s(Mg(OH)_{2})} = 10^{-10.95}$$

-

Hence no Mg(OH)₂ precipitate appears

Precipitation

No precipitation

Х

3.

<u>3.1</u>

$$[CN^{-}] = C_{CN^{-}} \frac{K_{a}}{h + K_{a}} = \frac{1.400 \times 1000}{65 \times 20.00} \frac{10^{-9.35}}{10^{-10.50} + 10^{-9.35}} = 1.00 \text{ (M)}$$

$$\alpha_{Hg^{2+}} = \frac{1}{1 + \beta_{Hg(CN)_{4}^{2-}} [CN^{-}]^{4}} = \frac{1}{1 + 10^{38.97} \times 1^{4}} = 1.00 \times 10^{-38.97}$$

$$\alpha_{Y^{4-}} \approx \frac{K_{a4}}{h + K_{a4}} = \frac{10^{-10.26}}{10^{-10.50} + 10^{-10.26}} = 0.635$$

$$\beta'_{HgY^{2-}} = \beta_{HgY^{2-}} \alpha_{Hg^{2+}} \alpha_{Y^{4-}} = 10^{21.80} (1.00 \times 10^{-38.97}) 0.635 = 4.29 \times 10^{-18}$$

 $\beta'_{HgY^{2-}}$ is very small, Hg^{2+} is cannot be titrated in the experiment 2.

<u>3.2</u> Chemical equations:

Experiment 1:
$$Hg^{2+} + Y^{4-} \rightarrow HgY^{2-}$$

 $Mn^{2+} + Y^{4-} \rightarrow MnY^{2-}$
 $Mg^{2+} + Y^{4-}(excess) \rightarrow MgY^{2-}$
 $(C_{Mn^{2+}} + C_{Hg^{2+}}) \times 20.00 = 25.00 \times 0.040 - 12.00 \times 0.025$ (1)

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Experiment 2:
$$Hg^{2^+} + 4CN^- \rightarrow Hg(CN)_4^{2^-}$$

 $Mn^{2^+} + Y^{4^-} \rightarrow MnY^{2^-}$
 $Mg^{2^+} + Y^{4^-}(excess) \rightarrow MgY^{2^-}$
 $C_{Mn^{2^+}} \times 20.00 = 25.00 \times 0.040 - 20.00 \times 0.025$ (2)

According to (1) and (2): $C_{Mn^{2+}} = 0.025 \text{ M}; C_{Hg^{2+}} = 0.010 \text{ M}$

4.

<u>4.1</u> As $K_{a3}/K_{a4} > 1 \times 10^4$ and $K_{a4} < 10^{-9}$ only one endpoint can be determined for the titration of H_2Y^{2-} :

Titration reaction:
$$H_2Y^{2-} + OH^- \rightarrow HY^{3-} + H_2O$$

$$\underline{4.2} \text{ pH}_{\text{EP}} = \text{pH}(\text{HY}^{3-}) = (\text{pK}_{a3} + \text{pK}_{a4})/2 = 8.21$$

<u>4.3</u> $pH_{EP} = pH_{(phenol red)}$, hence the most suitable indicator is phenol red



4.4

If the final pH is 7.60 the percentage of H_2Y^{2-} that is titrated:

$$\frac{[\text{HY}^{3-}]}{[\text{H}_2\text{Y}^{2-}] + [\text{HY}^{3-}]} = \frac{\text{K}_{a3}}{[\text{H}^+] + \text{K}_{a3}} 100 = \frac{10^{-6.16}}{10^{-6.16} + 10^{-7.60}} 100 = 96.5\%$$

The volume of NaOH solution needed to reach pH of 7.60 is:

$$V_{\text{NaOH}} = V_1 = (0.25 \times 10 \times 0.965)/0.2 = 12.06 \text{ (mL)}$$
$$V_{\text{EP}} = V_2 = (0.25 \times 10)/0.20 = 12.50 \text{ (mL)}$$
$$q = \frac{12.06 - 12.50}{12.50} \times 100\% \approx -3.5\%$$

(As 96.5% of H_2Y^{2-} is titrated, 3.5% of the analyte has not been titrated, or the error q = -3.5%.)



Solutions

Problem 9. Lead compounds



3.

3.1 Condition for precipitation of:

$$PbSO_{4}: C_{Pb^{2^{+}}(1)} \geq \frac{10^{-7.66}}{0.02} = 1.09 \times 10^{-6} \text{ (M)}$$

$$PbC_{2}O_{4}: C_{Pb^{2^{+}}(2)} \geq \frac{10^{-10.05}}{5.0 \times 10^{-3}} = 1.78 \times 10^{-8} \text{ (M)}$$

$$PbI_{2}: C_{Pb^{2^{+}}(3)} \geq \frac{10^{-7.86}}{(9.7 \times 10^{-3})^{2}} = 1.47 \times 10^{-4} \text{ (M)}$$

$$Pb(IO_{3})_{2}: C_{Pb^{2^{+}}(4)} \geq \frac{10^{-12.61}}{(0.001)^{2}} = 2.45 \times 10^{-7} \text{ (M)}$$

$$PbCI_{2}: C_{Pb^{2^{+}}(5)} \geq \frac{10^{-4.8}}{(0.05)^{2}} = 6.34 \times 10^{-3} \text{ (M)}$$

 $C_{Pb^{2+}(2)} < C_{Pb^{2+}(4)} < C_{Pb^{2+}(1)} < C_{Pb^{2+}(3)} < C_{Pb^{2+}(5)} \rightarrow$ The order of precipitation: PbC₂O₄, Pb(IO₃)₂, PbSO₄, PbI₂ and PbCl₂.

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<u>3.2</u> When PbI_2 begins to precipitate (assume I⁻ has not reacted)

$$[SO_4^{2-}] = \frac{K_{s(PbSO_4)}}{C_{Pb^{2+}(3)}} = \frac{10^{-7.66}}{1.47 \times 10^{-4}} = 1.49 \times 10^{-4} \text{ (M)}$$
$$= \sqrt{K_{s(PbSO_4)}} = 1.48 \times 10^{-4} \text{ (M)} = S_{PbSO_4}$$

(S is the solubility of $PbSO_4$ in saturated solution). Hence PbC_2O_4 , $Pb(IO_3)_2$ and $PbSO_4$ have precipitated completely.

$$\rightarrow 21.60 \times C_{Pb(NO_3)_2} = 20.00 \times (C_{C_2O_4^{2-}} + 2 \times C_{IO_3^{-}} + C_{SO_4^{2-}})$$

$$= 20.00(5.0 \times 10^{-3} + 2 \times 0.0010 + 0.020)$$

$$\rightarrow C_{Pb(NO_3)_2} = 0.025 \text{ (M)}$$

4. PbCrO₄
$$\implies$$
 Pb²⁺ + CrO₄²⁻ K_{sp}
C S S
CH₃COOH \implies CH₃COO⁻ + H⁺ K_a = 10^{-4.76}
Pb²⁺ + CH₃COO⁻ \implies Pb(CH₃COO)⁺ $\beta_1 = 10^{2.68}$
Pb²⁺ + 2CH₃COO⁻ \implies Pb(CH₃COO)₂ $\beta_2 = 10^{4.08}$
Pb²⁺ + H₂O \implies PbOH⁺ + H⁺ $^*\beta = 10^{-7.8}$
CrO₄²⁻ + H⁺ \implies HCrO₄ K_a⁻¹ = 10^{6.5}
2CrO₄²⁻ + 2H⁺ \implies Cr₂O₇²⁻ + H₂O K⁻¹ = 10^{14.64}
Let *h* be [H⁺], a conservation of mass requires that:
S = C_{CrO₄²⁻} = [CrO₄²⁻] + [HCrO₄⁻] + 2.[Cr₂O₇²⁻] = [CrO₄²⁻](1 + K_a⁻¹. h) + 2.K⁻¹. h². [CrO₄²⁻]²

$$S = C_{pb^{2+}} = [Pb^{2+}] + [PbOH^{+}] + [Pb(CH_{3}COO)^{+}] + [Pb(CH_{3}COO)_{2}]$$
$$= [Pb^{2+}](1 + {}^{*}\beta h^{-1} + \beta_{1}[CH_{3}COO^{-}] + \beta_{2}[CH_{3}COO^{-}]^{2})$$

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(1)

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$$\rightarrow [Pb^{2^{+}}] = \frac{S}{1 + {}^{*}\beta h^{-1} + \beta_{1}[CH_{3}COO^{-}] + \beta_{2}[CH_{3}COO^{-}]^{2}}$$
(2)

Because S = 2.9×10^{-5} M << $C_{CH,COOH} = 1 \text{ M} \rightarrow \text{ pH}$ of the solution is largely dependent on the dissociation of CH₃COOH:

CH₃COOH
$$\iff$$
 H⁺ + CH₃COO⁻ K_a = 10^{-4.76}
[] 1 − h h h
→[CH₃COO⁻] = [H⁺] = h = 10^{-2.38} (M)

Substitute $[CH_3COO^-] = [H^+] = h = 10^{-2.38} (M)$ and $S = 2.9 \times 10^{-5}$ into (1) and (2), we have:

 $[CrO_4^{2-}] = 2.194 \times 10^{-9} (M) \text{ and } [Pb^{2+}] = 9.051 \times 10^{-6} (M)$ $\rightarrow K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 1.99 \times 10^{-14}$.

2(1.455) $PbO_2 + 4 H^+ + 2e \implies Pb^{2+} + 2 H_2O$ 10 0.0592 **5.** Cathode: $HSO_4^- \implies SO_4^{2-} + H^+$ 10⁻² $Pb^{2+} + SO_4^{2-} \implies PbSO_4$ $10^{7.66}$

Cathode reaction:

PbO ₂	$+ \text{HSO}_4^- + 3\text{H}^+ + 2e \implies \text{PbSO}_4 + 2 \text{H}_2\text{O} \text{ K}$.1 (*)
Anode:	$Pb \implies Pb^{2+} + 2e$	$10^{\frac{-2(-0.126)}{0.0592}}$
	$HSO_4^- \iff SO_4^{2-} + H^+$	10 ⁻²
	$Pb^{2+} + SO_4^{2-} \implies PbSO_4$	$10^{7.66}$
Anode reaction:	$Pb + HSO_4^- \rightleftharpoons PbSO_4 + H^+ + 2e$	K ₂ (**)
Overall reaction	as the battery discharges:	

$$PbO_{2} + Pb + 2 HSO_{4}^{-} + 2 H^{+} \rightleftharpoons 2 PbSO_{4} + 2 H_{2}O \qquad (***)$$

Cell diagram: (a) Pb | PbSO_{4}, H^{+}, HSO_{4}^{-} | PbO_{2} (Pb) (c)



Preparatory Problem Solutions

6.

6.1 According to (*):
$$10^{\frac{2E_{PbO_2/PbSO_4}^0}{0.0592}} = K_1 = 10^{\frac{2(1.455)}{0.0592}} 10^{-2} 10^{7.66}$$

 $\rightarrow E_{PbO_2/PbSO_4}^0 = 1.62 \text{ (V)}$

According to (**):

$$10^{\frac{-2E_{PbSO_4/Pb}^0}{0.0592}} = K_2 = 10^{\frac{-2(-0.126)}{0.0592}} 10^{-2} 10^{7.66} \rightarrow E_{PbSO_4/Pb}^0 = -0.29 \text{ (V)}$$

<u>6.2</u> According to (***):

 $V = E_{(c)} - E_{(a)} = E_{PbO_2/PbSO_4}^0 - E_{PbSO_4/Pb}^0 + \frac{0.0592}{2} \log[HSO_4^-]^2 [H^+]^2$

In which $[HSO_4^-]$, $[H^+]$ are calculated as follows:

$$HSO_{4}^{-} \rightleftharpoons H^{+} + SO_{4}^{2-} K_{a} = 10^{-2}$$
[] $1.8 - x$ $1.8 + x$ x
[SO_{4}^{2-}] = $x = 9.89 \times 10^{-3}$ (M) \rightarrow [H^{+}] = 1.81 (M); [HSO_{4}^{-}] = 1.79 (M)
 $V = 1.62 + 0.29 + \frac{0.0592}{2} \log(1.79)^{2} (1.81)^{2} = 1.94$ (V)

Problem 10. Applied Electrochemistry

1.

<u>1.1</u>

$$0 +7 +2 +4$$

$$C_{6}H_{12}O_{6} + KMnO_{4} + H_{2}SO_{4} \longrightarrow K_{2}SO_{4} + MnSO_{4} + CO_{2} + H_{2}O$$

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$$5 \times \qquad \qquad 6 \stackrel{0}{C} \longleftrightarrow 6 \stackrel{^{+4}}{C} + 24 e^{-}$$

$$24 \times \qquad \qquad \stackrel{^{+7}}{Mn} + 5 e^{-} \longleftrightarrow \stackrel{^{+2}}{Mn}$$

 $5 C_6H_{12}O_6 + 24 KMnO_4 + 36 H_2SO_4 \Longrightarrow 12K_2SO_4 + 24MnSO_4 + 30CO_2 + 66H_2O_2 + 6$ 1.2

$$5 \times | 2Fe^{2+} \longleftrightarrow 2Fe^{3+} + 2e$$

$$2 \times | MnO_4^- + 8H^+ + 5e \longleftrightarrow Mn^{2+} + 4H_2O$$

$$2 MnO_4^- + 10Fe^{2+} + 16H^+ \longleftrightarrow Mn^{2+} + 10Fe^{3+} + 8H_2O$$

Overall reaction:

$$2 \text{ KMnO}_4 + 10 \text{FeSO}_4 + 8 \text{H}_2 \text{SO}_4 \implies 2 \text{MnSO}_4 + 5 \text{Fe}_2 (\text{SO}_4)_3 + 8 \text{H}_2 \text{O}_4 \implies 2 \text{MnSO}_4 + 5 \text{Fe}_2 (\text{SO}_4)_3 + 8 \text{H}_2 \text{O}_4 \implies 2 \text{MnSO}_4 + 5 \text{Fe}_2 (\text{SO}_4)_3 + 8 \text{H}_2 \text{O}_4 \implies 2 \text{MnSO}_4 \implies 2 \text{MnS$$

1.3

- At anode:
$$2 \operatorname{Fe}^{2+} \rightleftharpoons 2 \operatorname{Fe}^{3+} + 2e^{-}$$

At cathode: $MnO_4^- + 8 H^+ + 5e^- \iff Mn^{2+} + 4H_2O$

The cell diagram:

$$Pt |Fe^{3+}, Fe^{2+} || MnO_4^-, Mn^{2+}, H^+ | Pt$$

1.4 Electromotive force E of the cell can be calculated as follows:

$$E = E^{0} - \frac{0.059}{5} \log \frac{\left[Mn^{2+}\right] \left[Fe^{3+}\right]^{5} \left[H_{2}O\right]^{4}}{\left[MnO_{4}^{-}\right] \left[Fe^{2+}\right]^{5} \left[H^{+}\right]^{8}}$$

<u>2.1</u> In order to determine the reduction potential of the pair $\frac{MnO_4^{2-}}{MnO_2}$ we need to use the below diagram:



According to Hess' Law:



<u>3.1</u> According to the standard reduction potential diagram, we have:

$$MnO_{4}^{2-} + 2e + 4H^{+} \implies MnO_{2} + 2H_{2}O \qquad (3) \qquad \Delta G^{0}_{3} \quad (E^{0}_{3} = 2.27 \text{ V})$$

$$2MnO_{4}^{-} + 2e \implies 2MnO_{4}^{2-} \qquad (1) \qquad \Delta G^{0}_{1} \quad (E^{0}_{1} = 0.56 \text{ V})$$

$$\overline{3MnO_{4}^{2-} + 4H^{+}} \implies 2MnO_{4}^{-} + MnO_{2} + 2H_{2}O \qquad \Delta_{r}G^{0}$$

<u>3.2</u> In order to know if the reaction is spontaneous, ΔG must be considered.

The reaction that is considered can be obtained by subtracting (1) from (3): $\Delta_r G^0 = \Delta G^0_3 - \Delta G^0_1$. We have $\Delta G^0 = -nFE^0$ where $\Delta E^0_{reaction} = 1.71$ V, or $\Delta G_3 < 0$ and the reaction is spontaneous.

<u>3.3</u> The equilibrium constant can also be calculated:

$$\log K_3 = \frac{n\Delta E^0}{0.059} \to \log K_3 = \frac{2 \times 1.71}{0.059} \to K_3 = 9.25 \times 10^{57}$$

The large value of K confirms the reaction to be spontaneous.



Problem 11. Phosphoric acid

1. H^+ is used instead of H_3O^+ for clarity. The activities of the ions are ignored. [H⁺] is abbreviated as *h* in all calculations and acid constants for H_3PO_4 are written as K_1 , K_2 and K_3 .

As $K_1 \gg K_2 \gg K_3$, only first dissociation step is considered.

$$H_3PO_4 \implies H^+ + H_2PO_4^-$$

As

$$K_{1} = \frac{[H^{+}][H_{2}PO_{4}^{-}]}{[H_{3}PO_{4}]} = \frac{h^{2}}{C_{o} - h} = 10^{-2.14} = \frac{(10^{-1.14})^{2}}{C_{o} - 10^{-1.46}}$$

Solving for C_o gives $C_o = 0.200$ M

The concentrations of the forms:

$$[H_{3}PO_{4}] = \frac{h^{3}C_{o}}{h^{3} + h^{2}K_{1} + hK_{1}K_{2} + K_{1}K_{2}K_{3}} (hK_{1}K_{2} + K_{1}K_{2}K_{3} \text{ is ignored})$$
$$= \frac{h^{3}C_{o}}{h^{3} + h^{2}K_{1}} = \frac{hC_{o}}{h + K_{1}} = \frac{10^{-1.46} \times 0.2}{10^{-1.46} + 10^{-2.14}} = 0.1653 \text{ M}$$

Similarly, we have:

$$[H_{2}PO_{4}^{-}] = \frac{h^{2}K_{1}C_{o}}{h^{3} + h^{2}K_{1}} = \frac{K_{1}C_{o}}{h + K_{1}} = \frac{10^{-2.14} \times 0.2}{10^{-1.46} + 10^{-2.14}} = 0.0346 \text{ M}$$

$$[HPO_{4}^{2-}] = \frac{hK_{1}K_{2}C_{o}}{h^{3} + h^{2}K_{1}} = \frac{K_{1}K_{2}C_{o}}{h^{2} + hK_{1}} = \frac{10^{-2.14} \times 10^{-7.20} \times 0.2}{(10^{-1.46})^{2} + 10^{-1.46} \times 10^{-2.14}} = 6.29 \times 10^{-8} \text{ M}$$

$$[PO_{4}^{3-}] = \frac{K_{1}K_{2}K_{3}C_{o}}{h^{3} + h^{2}K_{1}} = \frac{10^{-2.14} \times 10^{-7.20} \times 10^{-12.38} \times 0.2}{(10^{-1.46})^{2} \times 10^{-2.14}} = 7.56 \times 10^{-19} \text{ M}$$

2. We have:

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 $n_{_{\rm H_3PO_4}}=0.2\!\times\!0.050\!=\!0.010\ mol$

 $n_{_{\rm NH_3}} = 0.4 \times 0.050 = 0.020 \text{ mol}$

Hence the following reaction occurs: $H_3PO_4 + 2 NH_3 \rightarrow (NH_4)_2HPO_4$

And
$$[(NH_4)_2HPO_4] = \frac{0.010}{0.100} = 0.1 \text{ M}$$

In solution **B**: $(NH_4)_2HPO_4 \rightarrow 2 NH_4^+ + HPO_4^{2-}$

We have the following equilibria:

$$NH_{4}^{+} \rightleftharpoons NH_{3} + H^{+}$$

$$HPO_{4}^{2^{-}} + H^{+} \rightleftharpoons H_{2}PO_{4}^{-}$$

$$H_{2}PO_{4}^{-} + H^{+} \rightleftharpoons H_{3}PO_{4}$$

$$HPO_{4}^{2^{-}} \rightleftharpoons H^{+} + PO_{4}^{3^{-}}$$

A conservation of protons requires:

$$[H^{+}] + 2[H_{3}PO_{4}] + [H_{2}PO_{4}^{-}] = [OH^{-}] + [PO_{4}^{3-}] + [NH_{3}]$$
(1)
which $[NH_{3}] + [NH_{4}^{+}] = 0.2 \text{ M}$

$$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = 0.1 M$$

We also have:

In

$$[NH_{3}] = \frac{K_{NH_{4}^{+}} \times 0.2}{h + K_{NH_{4}^{+}}}$$
$$[H_{3}PO_{4}] = \frac{h^{3} \times 0.1}{h^{3} + h^{2}K_{1} + hK_{1}K_{2} + K_{1}K_{2}K_{3}}$$
$$[H_{2}PO_{4}^{-}] = \frac{h^{2}K_{1} \times 0.1}{h^{3} + h^{2}K_{1} + hK_{1}K_{2} + K_{1}K_{2}K_{3}}$$



Solutions

$$[\text{HPO}_{4}^{2-}] = \frac{hK_{1}K_{2} \times 0.1}{h^{3} + h^{2}K_{1} + hK_{1}K_{2} + K_{1}K_{2}K_{3}}$$
$$[\text{PO}_{4}^{3-}] = \frac{K_{1}K_{2}K_{3} \times 0.1}{h^{3} + h^{2}K_{1} + hK_{1}K_{2} + K_{1}K_{2}K_{3}}$$

As pH of the solution is of about 7 - 9 so we can ignore the [H⁺], [OH⁻], [H₃PO₄] and $[PO_4^{3-}]$ in the equation (1):

$$[H_2PO_4^{-1}] = [NH_3]$$

$$\frac{h^2 K_1 \times 0.1}{h^3 + h^2 K_1 + hK_1 K_2 + K_1 K_2 K_3} = \frac{K_{NH_4^+} \times 0.2}{h + K_{NH_4^+}}$$

$$\frac{h \times 0.1}{h + K_2} = \frac{h \times 0.1}{h + 10^{-7.20}} = \frac{10^{-9.24} \times 0.2}{h + 10^{-9.24}} \ (h^3 + K_1 K_2 K_3 \text{ is ignored})$$

Solving for *h* gives $h = 8.81 \times 10^{-9}$ M and pH = 8.06.

3. Mixing of **B** and $Mg(NO_3)_2$ solution leads to precipitation reaction:

$$\mathrm{NH_4^+}(\mathrm{aq}) + \mathrm{Mg^{2+}}(\mathrm{aq}) + \mathrm{PO_4^{3-}}(\mathrm{aq}) \to \mathrm{NH_4MgPO_4}(\mathrm{s})$$

 $[Mg^{2+}] = 0.2/2 = 0.1 M$

As **B** is a buffer solution when it is diluted to twice the original volume, pH is virtually unchanged and is 8.06.

$$[\mathrm{NH}_{4}^{+}] = \frac{hC}{h + K_{\mathrm{NH}_{4}^{+}}} = \frac{10^{-8.06} \times 0.1}{10^{-8.06} + 10^{-9.24}} = 0.094 \mathrm{M}$$
$$[\mathrm{PO}_{4}^{3-}] = \frac{K_{1}K_{2}K_{3} \times C_{o}}{h^{2}K_{1} + hK_{1}K_{2}} = \frac{K_{2}K_{3}C_{o}}{h^{2} + hK_{2}} = \frac{10^{-7.20} \times 10^{-12.38} \times 0.05}{(10^{-8.06})^{2} + 10^{-8.06} \times 10^{-7.20}} = 2.06 \times 10^{-8} \mathrm{M}$$

The ionic product:

 $[NH_4^{+}][Mg^{2+}][PO_4^{-3-}] = 0.1 \times 0.094 \times 2.06 \times 10^{-6} = 1.93 \times 10^{-8} > 2.5 \times 10^{-13}$

Therefore, the precipitation occurs.

4. We have: $Ca_3(PO_4)_2 \implies 3Ca^{2+} + 2PO_4^{3-}$

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Assume that the hydrolysis of PO_4^{3-} can be ignored, the solubility S_0 of $Ca_3(PO_4)_2$ can be calculated as follows:

$$K_{\rm sp} = [{\rm Ca}^{2+}]^3 [{\rm PO}_4^{3-}]^2 = (3{\rm S}_0)^3 (2{\rm S}_0)^2 = 108{\rm S}_0^{-5} = 2.22 \times 10^{-25}$$

Solving for S_o to gives $S_o = 4.6 \times 10^{-6} M$

However, the hydrolysis of PO_4^{3-} cannot be ignored due to its rather strong basicity $(pK_b = 14 - pK_a = 14 - 12.38 = 1.62)$

$$PO_4^{3-} + H_2O \implies HPO_4^{2-} + OH^-(1)$$

We can ignore the hydrolysis of HPO_4^{2-} (p $K_b = 14 - 7.20 = 6.80$) and $\text{H}_2\text{PO}_4^{-}$ (p K_b = 14 - 2.14 = 11.86).

According to (1): $[HPO_4^{2-}] + [PO_4^{3-}] = 2S(2)$

As $[PO_4^{3-}]$ is very small (the calculation above), it can be ignored in (2). It can alternatively be calculated as follows:

Let x be the concentrations of HPO₄²⁻ and OH⁻, [HPO₄²⁻] = [OH⁻] = x

We have: $\frac{x^2}{2 \times 4.6 \times 10^{-6} - r} = 10^{-1.62} = 0.024$

Solving for x gives $x = 9.19 \times 10^{-6} \rightarrow [PO_4^{3-}] = 0.01 \times 10^{-6} M$

Therefore we can assume that $[HPO_4^{2-}] = [OH^{-}] = 2S$ and $[PO_4^{3-}]$ is determined based on K_3 :

$$K_{3} = 10^{-12.38} = \frac{[\mathrm{H}^{+}][\mathrm{PO}_{4}^{3-}]}{[\mathrm{HPO}_{4}^{2-}]} = \frac{10^{-14}}{[\mathrm{OH}^{-}]} \times \frac{[\mathrm{PO}_{4}^{3-}]}{[\mathrm{HPO}_{4}^{2-}]}$$
$$\implies [\mathrm{PO}_{4}^{3-}] = \frac{10^{-12.38} \times 2\mathrm{S} \times 2\mathrm{S}}{10^{-14}} = 167\mathrm{S}^{2}$$

The solubility S of Ca₃(PO₄)₂: $K_{sp} = 2.25 \times 10^{-25} = (3S)^3 (2 \times 167S^2)^2 = 3012012S^7$ \Rightarrow S = 3.6 × 10⁻⁵ M.

We can see that solubility of Ca₃(PO₄)₂ increases about 10 times due to the hydrolysis of PO_4^{3-} .

Note: Students may use logarithmic concentration diagram to get the relationship $[HPO_4^{2-}] = [OH^{-}] = 2S.$



Preparatory Problem Solutions

Problem 12. Kinetic Chemistry

1. To determine $t_{1/2}$, the time taken from the initial concentration of N₂O₅ (3.80×10⁻³ mol.dm⁻³) to fall to one-half of its value: $t_{1/2} \approx 180$ s corresponding to [N₂O₅] $t_{1/2} = 1.90 \times 10^{-3}$ mol/dm³

2.

<u>2.1</u>



Figure 2. A re-plot of the data in Figure 1 as function of ln $\{[N_2O_5]_0/[N_2O_5]t\}$ versus time

The plot of $\ln \{ [N_2O_5]_0/[N_2O_5]t \}$ versus time is linear for a first order reaction.

 $\underline{2.2} \quad \mathbf{r} = \mathbf{k} \left[\mathbf{N}_2 \mathbf{O}_5 \right]$

The form of integrated rate equation:

$$\ln \frac{[N_2 O_5]_0}{[N_2 O_5]_t} = kt$$
 or $[N_2 O_5]_t = [N_2 O_5]_0 e^{-kt}$

3. The 1st order reaction:

$$k = ln2/t_{1/2} = ln2/180 s = 3.85 \times 10^{-3} s^{-1}$$



Solutions

4.

E_a is independent of temperature:

$$\ln\frac{k_{336.6K}}{k_{318K}} = \frac{E_a}{R} \left[\frac{1}{318} - \frac{1}{336.6} \right] \Longrightarrow \ln\frac{3.85 \times 10^{-3}}{5.02 \times 10^{-4}} = \frac{E_a}{8.314J / mol.K} \left[3.145 \times 10^{-3} - 2.97 \times 10^{-3} \right]$$

 $E_a = 97.46 \text{ kJ}$

Pre-exponential factor (A):

 $k = A. e^{-Ea/RT}$ at 336.3 K, $A = k. e^{Ea/RT} = 3.85 \times 10^{-3} e^{97460/8.3145 \times 336.3} = 5.28 \times 10^{12} s^{-1}$.

5. The intermediate concentrations can be treated by the steady-state approximation:

$$r_{NO} = \frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \quad \rightarrow \quad [NO] = \frac{k_2[NO_2]}{k_3}$$
(Eq.1)

Substituting this equation into the below equation:

$$r_{NO_{3}} = \frac{d[NO_{3}]}{dt} = k_{1}[N_{2}O_{5}] - k_{-1}[NO_{2}][NO_{3}] - k_{2}[NO_{2}][NO_{3}] - k_{3}[NO][NO_{3}] = 0 \quad (Eq. 2)$$

$$\rightarrow k_{1}[N_{2}O_{5}] - k_{-1}[NO_{2}][NO_{3}] - k_{2}[NO_{2}][NO_{3}] - k_{3}\frac{k_{2}[NO_{2}]}{k_{3}}[NO_{3}] = 0$$

$$\rightarrow k_{1}[N_{2}O_{5}] - k_{-1}[NO_{2}][NO_{3}] - 2k_{2}[NO_{2}][NO_{3}] = 0$$

$$\rightarrow \frac{k_{1}[N_{2}O_{5}]}{k_{-1} + 2k_{2}} = [NO_{2}][NO_{3}] \quad (Eq. 3)$$

The reaction rate:

$$r_{2} = r_{N_{2}O_{5}} = -\frac{d[N_{2}O_{5}]}{dt} = k_{1}[N_{2}O_{5}] - k_{-1}[NO_{2}][NO_{3}]$$
$$= k_{1}[N_{2}O_{5}] - k_{-1}\frac{k_{1}[N_{2}O_{5}]}{k_{-1} + 2k_{2}}$$
$$= \frac{2k_{1}k_{2}}{k_{-1} + 2k_{2}}[N_{2}O_{5}]$$
$$= k[N_{2}O_{5}]$$



Problem 13. Kinetics of the decomposition of hydrogen peroxide

1. Chemical reaction: $2 H_2O_2 \rightarrow 2 H_2O + O_2$

The reaction rate is proportional to the volume of oxygen gas released in a unit of time.

In experiments #1, #2, and #3 when the volume of H_2O_2 solution doubles while keeping the same volume of KI solution, the reaction rate also doubles. Therefore, the rate is directly proportional to the concentration of H_2O_2 . Hence, the reaction is the first-order with the respect to H_2O_2 .

Similarly, from experiments #2, #4, and #5 the rate is directly proportional to the concentration of Γ . Hence, the reaction is the first-order with the respect to Γ .

2. Chemical reaction: $2 H_2O_2 \rightarrow 2 H_2O + O_2$

The rate law: $v = kC_{H_2O_2}C_{I^-}$

3. In the experiment #4, the solution of H_2O_2 is diluted three times; therefore, the concentration of H_2O_2 was reduced three times.

 $C_0 = 10 \text{ g H}_2O_2/1 \text{ L} = 10/34 = 0.294 \text{ M}.$

Because the reaction proceeds slowly, the reaction rate (or the rate of releasing oxygen gas) is considered to be unchanged after of short period of time (4 min). The volume of oxygen released after 4 min is equal to $4.25 \times 4 = 17$ (mL O₂).

Hence,
$$n_{O_2} = \frac{PV}{RT} = \frac{(1)(17 \times 10^{-3})}{(0.082)(298)} = 0.695 \times 10^{-3} \text{ (mol)}$$

At the beginning, $n_{H_2O_2} = (0.294)(0.15) = 44.1 \times 10^{-3} \text{ (mol)}$
After 4 min, $n_{H_2O_2} = 44.1 \times 10^{-3} - 2(0.695 \times 10^{-3}) = 42.71 \times 10^{-3} \text{ (mol)}$
Therefore, after 4 min $C_{H_2O_2} = \frac{0.04271}{0.15} = 0.285 \text{ M}.$
4. The overall reaction: $2 \text{ H}_2\text{O}_2 \Rightarrow 2 \text{ H}_2\text{O} + \text{O}_2$ (*)
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$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt}$$

Consider three different cases:

a) If step (1) is slow and determines the overall rate, the rate of the overall reaction (*) will be the same as the rate of step (1):

$$v = -\frac{1}{2} \frac{d[H_2 O_2]}{dt} = k_1 [H_2 O_2] [I^-]$$

which corresponds to the overall rate law as determined in section 2.

b) If step (2) is slow, hence

$$v = -\frac{1}{2} \frac{d[H_2 O_2]}{dt} = k_2 [H_2 O_2] [IO^-] \quad (a)$$

Assume that the steady-state approximation is applied for IO⁻, we have

$$\frac{d[IO^{-}]}{dt} = k_1[H_2O_2][I^{-}] - k_2[IO^{-}][H_2O_2] = 0 \rightarrow [IO^{-}] = \frac{k_1}{k_2}[I^{-}] \qquad (b)$$

Replace $[IO^-]$ from (b) in (a), we have:

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = k_1 [H_2O_2][I^-]$$

which is also appropriate to the overall rate law.

c) If the two steps have similar rates:

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = \frac{1}{2} \left(k_1 [H_2O_2] [I^-] + k_2 [H_2O_2] [IO^-] \right)$$

Let us assume that the concentration of IO⁻ is in steady-state condition. Similar to the case b), we have:

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = k_1[H_2O_2][I^-]$$

which corresponds to the overall rate law.

Among the three cases, case a) is the most appropriate to the overall rate law because no assumption is made. Besides, in the case b) the assumption of the steady-state IO⁻ is not valid since the step (2) is considered slow.

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Problem 14. Magnetism of transition metal complexes

1. Two compounds are octahedral complexes of Mn^{2+} (d⁵).

<u>1.1</u> K_4 [Mn(CN)₆].3H₂O is low spin, 1 unpaired electron.

 $K_4[Mn(SCN)_6]$ is high spin, 5 unpaired electrons.

<u>1.2</u> CN⁻ is strong field ligand, electronic configuration is $(t_{2g})^5 (e_g)^0$

SCN⁻ is weak filed ligand, electronic configuration is $(t_{2g})^3 (e_g)^2$

2. Ni²⁺ (d⁸) in octahedral field has electronic configuration of $(t_{2g})^6(e_g)^2$ with two unpaired electrons. The spin only χ_{eff} is 2.83 MB.

3.
$$\mu_{\text{eff}} = 2.83 \times \left(1 - \frac{4(-315)}{8500}\right)$$
 (BM)

Thus, μ_{eff} is 3.25 MB

4.

<u>4.1</u> d^8 in square planar field is diamagnetic.

<u>4.2</u> **C** is neutral, DBM is monoanionic form. $M_c = 504$ (g/mol). A should be hydrate form of **C**, $M_A = M_B / 0.932 = 540.8$ (g/mol), corresponding to two molecules of H₂O per [Ni(DBM)₂]. Thus, the formula is [Ni(DBM)₂].2H₂O

<u>4.3</u> Water should coordinate to Ni center due to the change of color and magnetic property. μ_{eff} value of **A** is close to that of $[Ni(H_2O)_6]Cl_2$. So, an octahedral complex is expected for **A**.

4.4 There are three isomers, the *trans* isomer and two optical *cis* isomers.

<u>4.5</u> **B** should be an octahedral complex, due to the color and magnetic moment are similar to those of **A**. Octahedral geometry can be formed by oligomerization / polymerization of **B** on heating, the DBM may play as bridging ligand.



Problem 15. Structure and synthesis of Al-Keggin ion

1.

<u>1.1</u> Al₂Cl₆ has sp³ hybridization

1.2
$$Al - Al = \frac{2x(Al - Al)}{2} = 2(Al - Cl)\cos(39.5^{\circ}) = 2 \times 221 pm \times 772 = 325.63 pm$$

2.

2.1 n = 7+

<u>2.2</u> The Al_{octahedral}/Al_{tetrahedral} is estimated ~ 12/1. The center Al atom at number 7 is tetrahedral; the other atoms are octahedral.

<u>2.3 and 2.4</u> The Al-Keggin cation structure is composed of one Al_{tetrahedral} cation surrounded by four oxygens. This Al atom is located centrally and caged by 12 octahedral AlO₆-units linked to one another by the neighboring oxygen atoms. There are a total of 24 bridging oxygen atoms that link the 12 adjacent atoms. The cations centered in the 12 octahedra are arranged on a sphere almost equidistant from each other. The formula can be expressed as $(AlO_4Al_{12}(OH)_{24}(H_2O)_{12})^{7+}$.



<u>2.5</u>

 $13AlCl_3 + 32 NaOH + 8 H_2O = [(AlO_4Al_{12}(OH)_{24}(H_2O)_{12})^{7+}]Cl_7 + 32NaCl_{12}(H_2O)_{12})^{7+}]Cl_7 + 32NaCl_{12}(H_2O)_{12}(H_2O)_{12})^{7+}]Cl_7 + 32NaCl_{12}(H_2O)_{12}(H_2O)_{12})^{7+}]Cl_7 + 32NaCl_{12}(H_2O)_{12}(H_2O)_{12})^{7+}]Cl_7 + 32NaCl_{12}(H_2O)_{12}(H_2O)_{12})^{7+}]Cl_7 + 32NaCl_{12}(H_2O)_{12}(H_2O)_{12})^{7+}]Cl_7 + 32NaCl_{12}(H_2O)_{12}($



3.

$$\frac{3.1}{13\text{Al}[(\text{H}_2\text{O})_6]\text{Cl}_3 + 16(\text{NH}_4)_2\text{CO}_3 + 24\text{H}_2\text{O}} = \\ [(\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12})^{7+}]\text{Cl}_7 + 32 \text{ NH}_4\text{Cl} + 16 \text{ CO}_2 \uparrow + 54 \text{ H}_2\text{O}$$

3.2 Volume of a ball =
$$(4/3) \pi r^3 = (4/3) \times 3.14 \times (0.542)^3 = 0.667 \text{ cm}^3$$
.
Volume of 3 balls = $3 \times 0.667 = 2.00 \text{ cm}^3$.
Inner volume of crucible = 15 cm^3
Volume of gas = $13 - 2 = 13 \text{ cm}^3$.
PV = nRT \rightarrow n = $1 \times 13 \times 10^{-3} / 0.082 \times 298 = 5.32 \times 10^{-4} \text{ mol.}$
After reaction:
 $\sum n_{gases} = n_{before} + n_{CO_2}$

 $PV = n_{gases}RT \rightarrow n = (2.50 \text{ atm}) \times (13.10^{-3} \text{ L}) / (0.082 \text{ L.atm.mol}^{-1} \text{.K}^{-1}) \times (298 \text{ K}) = 1.33 \times 10^{-3} \text{ mol}$

 $n_{CO_2} = n_{after} - n_{before} = 1.33 \times 10^{-3} - 5.23 \times 10^{-4} = 8 \times 10^{-4} mol$

Molar number of Al₁₃-Keggin cation = $8 \times 10^{-4} / 16 = 5 \times 10^{-5}$ mol.

Number of Al₁₃-Keggin cations

= 5×10^{-5} mol $\times 6.023 \times 10^{23}$ = 3×10^{19} ionic molecules



Problem 16. Safrole

1.

Reaction	Balanced equation
1	$K[PtCl_{3}C_{2}H_{4}] + C_{10}H_{10}O_{2} \rightarrow K[PtCl_{3}(C_{10}H_{10}O_{2})] + C_{2}H_{4}$
2	$2 \text{ K}[\text{PtCl}_{3}(\text{C}_{10}\text{H}_{10}\text{O}_{2})] \rightarrow [\text{Pt}_{2}\text{Cl}_{2}(\text{C}_{10}\text{H}_{9}\text{O}_{2})_{2}] + 2 \text{ KCl} + 2 \text{ HCl}$
3	$[Pt_2Cl_2(C_{10}H_9O_2)_2] + 2 C_5H_5N \rightarrow 2 [PtCl(C_{10}H_9O_2)(C_5H_5N)]$

2.

	in A	in B	in C	
From the IR	C9 and C10 bond	C9 and C10 bond	C9 and C10 bond	
data	with Pt	with Pt	with Pt	
From the ¹ H	safrole coordinated	safrole lost H5,	safrole lost H5,	
NMR data	with Pt	C5 bonds with Pt	C5 bonds with Pt	

3.



4.

Reaction	Driving force
1	$K[PtCl_{3}C_{2}H_{4}] + C_{10}H_{10}O_{2} \rightarrow K[PtCl_{3}(C_{10}H_{10}O_{2})] + C_{2}H_{4}\uparrow$



	Ethylene (C_2H_4 , gas) is more volatile than safrole ($C_{10}H_{10}O_2$, liquid).
2	$2 \text{ K}[\text{PtCl}_{3}(\text{C}_{10}\text{H}_{10}\text{O}_{2})] \rightarrow [\text{Pt}_{2}\text{Cl}_{2}(\text{C}_{10}\text{H}_{9}\text{O}_{2})_{2}] + 2 \text{ KCl} + 2 \text{ HCl}$
	The chelate complex $[Pt_2Cl_2(C_{10}H_9O_2)_2]$ is more stable.
3	$[Pt_2Cl_2(C_{10}H_9O_2)_2] + 2 C_5H_5N \rightarrow 2 [PtCl(C_{10}H_9O_2)(C_5H_5N)]$
	In the dinuclear complex $[Pt_2Cl_2(C_{10}H_9O_2)_2]$, two bridging Cl weakly
	bond with Pt but in $[PtCl(C_{10}H_9O_2)(C_5H_5N)]$ the ligand C_5H_5N strongly
	bonds with Pt.

5. This reaction was controlled by steric effects rather than the *trans* effect.



Problem 17. Imidazole

1.

	Structure	aromatic or not
Imidazole (C ₃ H ₄ N ₂)		aromatic
Imidazol-1-ide anion (C ₃ H ₃ N ₂)		aromatic
Imidazolium cation $(C_3H_5N_2)$	⊕ NH N H	aromatic
Oxazole (C ₃ H ₃ NO)		aromatic
Thiazole (C ₃ H ₃ NS)	<i>√</i> ^N S	aromatic

2.

Imidazole > Thiazole > Oxazole
Imidazole is the first because of intermolecular hydrogen
bonding. Thiazole is placed before oxazole because
thiazole's molecular mass and polarizability are lager than
those of oxazole.
Imidazole > Thiazole > Oxazole
Imidazole is the first because of intermolecular hydrogen
bonding. Thiazole is placed before oxazole because
thiazole's molecular mass and polarizability are lager than
those of oxazole.



3.

Equation for	$ \sqrt{N} + H_{-OH} \implies \sqrt{N} + H_{-OH} = 1000 \text{ m}^{-1} $
the ionization	N H HO H H
	$ \sqrt[N]{0} + H-OH \implies \sqrt[N]{NH} + HO^{-} $
	$\sqrt[]{N}$ + H-OH $\implies \sqrt[]{N}$ + HO
	s s
K _b	Imidazole > Thiazole > Oxazole
Justification	Conjugate acid of imidazole is symmetrical delocalized, forms
	stronger hydrogen bonding with water, i.e. more stable, thus
	imidazole more basic than oxadiazole and thiazole. Atom O is
	more electronegative than N and S, it decreased electron
	density at N of oxazole, decreased stability of oxazole's
	conjugate acid making oxazole less basic than thiazole.

4.







6.



 $4 C_3H_4N_2 + COCl_2 \rightarrow (C_3H_3N_2)_2CO + 2 [C_3H_5N_2]Cl$ (1) 2 mol of imidazole react with 1 mol of phosgene to form 1 mol of CDI and 2 mol of HCl; the other 2 mol of imidazole are used to react with the HCl. $2 C_3H_4N_2 + COCl_2 + 2 NaOH \rightarrow (C_3H_3N_2)_2CO + 2 NaCl + 2 H_2O$ (2) In imidazolyl groups of CDI the pair of electrons from N-1 and four electrons of the remaining four atoms form a sextet of π-electron of aromatic system. They do not conjugate with C=O. Two electron-withdrawing imidazolyl groups make C=O more active, the imidazole is good leaving group, hence CDI readily reacts with water from reaction (2): (C₃H₃N₂)₂CO + H₂O → 2 C₃H₄N₂ + CO₂ (3)



8.

8.1



<u>8.2</u>





Problem 18. Small heterocycles

1.

Scheme 1:



Scheme 2:



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2. Reaction mechanism for the transformation from **B** to **C**:



3. Reaction mechanism for the transformation from F to G:



Problem 19. Vitamin H

1. The chloride acid was reacted with the amino group of the "bis(L-cystein)" (**A**) to give amide (**B**). Zn powder in acetic acid solution reduced the S-S bond of (**B**) to give an intermediate containing a thiol (-SH) group. Under normal condition, the -SH group added spontaneously to the terminal alkyne group to yield (**C**) with a ten-membered ring, of which the newly formed C=C double bonds had (Z) configuration.



2. Diisobutyl aluminium hidride (DIBAL) partially reduced ester (C) into aldehyde (D) which was condensed with benzylhydroxylamine to give nitrone (E) with (*E*) configuration. In the intramolecular [4+2] cyclization reaction of (E) (*note that '4' and '2' are the numbers of* π *electron of the nitrone and the double bond involved in the cyclization, respectively*), the configuration of the double bonds C=C and C=N remained unchanged. The resulting compound (F) had three new chiral centers, two of which were (3a*S*, 4*R*). They were the configurations of the corresponding C3 and C4 in the skeleton of (*D*)-(+)-Biotin. The third chiral carbon which was attached to the oxygen atom had an (*R*) configuration.



3. (F) was reduced by Zn in acetic acid to give (G) containing one -OH group and a second-order amino group. The amino group was reacted with chlorofomate in the

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presence of Na₂CO₃ in THF solution produce (**H**). Under basic condition, the tenmembered ring of (**H**) was opened to give δ -hydroxy acid (I). The configuration (6a*R*) of (**I**) resulted from the (*R*) configuration of the chiral carbon in L-cysteine. Therefore, Lcystein is chosen as the starting material for the synthesis.



4. The sulfur atom caused an anchimeric effect by which the configuration of the carbon attached to the –OH in compound (I) remained unchanged as this –OH group was replaced by the halogen atom to yield (**K**). The halogen atom was then replaced when (**K**) was reduced with NaBH₄ in which the "pentanoic acid" branch of (D)-(+)-biotin was formed. The hydrolysis of ester (**M**) in the aqueous solution of HBr, followed by the removal of the benzyl group resulted in the formation of the target molecule, (D)-(+)-Biotin.



Problem 20. No perfume without jasmine

1. In a [4+2] cycloaddition reaction (Diels-Alder reaction), the configuration of the dienophine (**B**) remained unchanged: the two ester groups –COOLac of compound (**C**) were placed in different sites in comparison to the six-membered ring. The hydrolysis of these two ester groups in LiOH solution gave the two corresponding *trans* carboxyl groups.



2. When dicarboxylic acid (**D**) was treated with I_2/KI , it was transformed into γ -iodolactone (**E**) of the *endo* –COOH. This lactone then underwent a decarboxylation-cyclization in basic solution step to give lactone (**F**) containing a three-membered ring. The secondary –OH group which resulted from the hydrolysis of (**F**) was oxidized by NaIO₄ to form a carbonyl group.



3. The addition-ring opening step of the cyclopropane ring with HI oriented by the (-C) conjugation effect of the carbonyl resulted in the formation of γ -iodo acid (H) containing only five-membered rings. The reductive elimination of the iodine atom by Zn in acetic acid produced ketoacid (I) which underwent a Bayer-Viiliger oxidation to yield lactone (K) (the main product) with one carboxyl group. The carboxyl group was treated under Rosenmund reduction condition in which lactone (L) with an aldehyde functional group was obtained. Vinyl ether (M) was separated from the Wittig reaction between the aldehyde and the ylide Ph₃P=CHOMe.



4. Methyl vinyl ether (**M**) was hydrolyzed in acidic medium to give lactone (**N**) containing an aldehyde functional group. From the Wittig reaction between (**N**) and the ylide $Ph_3P=CHCH_2CH_3$, lactone (**O**) with a *cis* carbon-carbon double bond was separated. The hydrolysis of the lactone (**O**) followed by treatment with diazomethane produced ester (**P**) which was oxidized with pyridine dichromate to give the target compound (*Z*)-(*3R*, *7S*)-methyl jasmonate.



(Z)-(3R, 7S): methyl jasmonate



Problem 21. Vietnamese cinnamon

1. Give the structure for A, B, C.



2. Assign ¹H NMR signals in first spectrum to appropriate proton groups of **C**.

С	9.0	7.4-7.3	5.5	4.2	2.8 ppm,	2.6 ppm,
	ppm, s	ppm, m	ppm, s	ppm, t	dd	dd
H _d N~NH _e H _c H _b H _a	H _e	C ₆ H ₅	H _d	H _c	H _a	H _b

3. Propose a reaction mechanism for the formation of C from B.





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4. Among four given below structures, select one for **D** and give the reasons for your selection.

The structure for D	Reasons for your selection.
	D3 derives from C and corresponds with the given ¹ H NMR
	spectrum.
	D1 and D4 do not derive from C.
(D3)	D1 does not correspond with second ¹ H NMR spectrum (For
	example in the spectrum there are not two ethylenic
	protons).
	D2 and D4 seem corresponding to the given ¹ H NMR
	spectrum, but D2 contains three members and D4 contains
	four members cycles, which cannot exist after reflux for 12
	h.

5. Assign ¹H NMR signals in second spectrum to appropriate proton groups of **D**.

D	9.6	8.3	7.6	7.4-	3.0	2.9	2.6
	ppm, s	ppm,	ppm,	7.3	ppm, t	ppm,	ppm,
		d	d	ppm,		dd	dd
				m			
$\begin{array}{c} \begin{array}{c} \begin{array}{c} e & f \\ H_{d} & -C & - \end{array} \\ \hline \\ H_{d} & -C & - \end{array} \\ \hline \\ H_{d} & - \end{array} \\ H_{b} & H_{a} \end{array} \\ \begin{array}{c} \begin{array}{c} \\ \end{array} \\ H_{b} & H_{a} \end{array} \end{array}$	H _d	2 H _f	2 H _e	C ₆ H ₅	H _c	H _a	H _b



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Problem 22. Cinnamic acid

1.

1.1

Reaction mechanism for the isomerization COOH 🕂 -соон = HOOĆ

1.2



1.3

	Ph HOOC Ph H COOH H H	Ph HOOC Ph H H H COOH	Ph HOOC H H COOH Ph H
β-truxinic acid		Has an enantiomer	Has an enantiomer
Ph HOOC H H H Ph COOH	Ph Ph H H COOH		
Has an enantiomer	Has an enantiomer		



Solutions

1.4



In solution all molecules of cinnamic acid were solvated and randomly arranged. 2.

2.1

Α	В	С
COOH NMe OH		NMe
Optically active since A	Optically active since B has	Optically inactive since
has four asymmetric	three asymmetric carbons	C has symmetrical
carbons and has no	and has no symmetrical	plane although has two



symmetrical plane and no	plane and no symmetrical	asymmetric carbons.
symmetrical center.	center.	

2.2



Problem 23. Tris(trimethylsilyl)silane and azobisisobutyronitrile

The products from the each reaction:

2.1 A, B and C from the compound (I):



2.2 **D** from the compound (**II**):



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<u>2.3</u> E from the compound (III):



<u>2.4</u> I from the compound (IV) through radicals F and G:



Problem 24. (-)-Menthol from (+)-δ-3-Carene

Catalytic isomerisation of δ -3-Carene provides (+)- δ -2-Carene (A) which then was pyrolysed to cleave the cyclopropane ring forming diene (B):





Treatment of the unconjugated diene (2,8-menthadiene, **B**) with HCl to give **C** and then, dehydrochlorination led to a conjugated diene ((+)-2,4(8)-*p*-menthadiene, **D**). Treatment of (+)-2,4(8)-*p*-menthadiene with hydrogen chloride affords 8-chloro-3-*p*-menthene (**E**):



E reacted with sodium acetate and acetic acid to give mixed (*cis/trans*) pulegol esters (**F**) via allylic displacements. Hydrolysis **F** affords (-)-cis and (+)-transpulegol (**G**). Reduction of either pulegol isomer provides menthol isomers which can be readily equilibrated to predominently (-)-menthol.



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Problem 25. Cefalotin

1. Synthetic scheme:





2. Reaction mechanism for the transformation from K to L



3. There are two asymmetric carbon atoms on cefalotin, so we should expect to have four optical isomers.





Problem 26. Heterocyclic compounds

1. Synthesis of A from levunic acid:



The purpose of 1.3-dioxolan formation was to protect the carbonyl group from the reaction with NH₂NH₂.

TsOH preparation from toluene:



2. Synthesis of **B** from **A**:





The reaction of A and PhNCS is nucleophilic addition of the -NHNH₂ group to the -NCS group.

PhNCS preparation from aniline:

 $PhNH_2 + CS_2 + NH_4OH \longrightarrow PhNHCSNH_4 + H_2O$ $PhNHCS_2NH_4 + Pb(NO_3)_2 \longrightarrow PhNCS + NH_4NO_3 + HNO_3 + PbS$

3. Synthesis of **C** from levunic acid:



3-O₂NC₆H₄SO₃Na is a dehydrogenation (or oxidation) reagent to convert dihydropiridazine into piridazine ring.

3-O₂NC₆H₄SO₃Na preparation from benzene:



¹H-NMR spectrum:

Before the reaction, the heterocyclic should provide 2 resonant signals with 2H intensity in the strong field of the two CH₂ groups (experimental: 2.57 ppm and

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2.83 ppm). After the reaction, these 2 signals should disappear, and two new signals in with 1H intensity the weak field of the two CH groups should appear (experimental: 7.01 ppm and 7.64 ppm).

4. Reaction mechanism of R-CONHNH₂ with PhCHO:

$$R \xrightarrow{O} \text{PhCHO} R \xrightarrow{O} R \xrightarrow{O} N \xrightarrow{Ph} Ph$$

First, the hydrazide -NHNH₂ group performed nucleophilic addition to the C=O group of benzaldehyde, then the dehydration step occurred:



The electron-withdrawing group $-NO_2$ facilitates the reaction, while the electrondonating group $-NH_2$ retards the reaction.

$$4-Me_2NC_6H_4CH=O < C_6H_5CH=O < 4-NO_2C_6H_4CH=O$$



Problem 27. Lotus



2. Reaction mechanism:

a. A_1 from 3,4-dimethoxibenzaldehyde: aldol condensation, the water elimination, (crotonation).



b. Reaction mechanism for the formation of X_1 : Addition-cyclization as Pictet-Spengler reaction mechanism.



3. Structural formule for Y_{1a} , Y_{1b} , Y_2 :





Problem 28. NMR Spectroscopy

1. A molecule can undergo fluxional process by interchanging two or more sites. If the rate of exchange is faster than the NMR time scale, the two different groups will appear at an average shift. As temperature decreases the rate becomes lower and separate shift can be obtained.

Rapid equilibration at room temperature between chair conformations leads to one peak. As one lowers the temperature, the interconversion is slowed down until, at temperatures below -66.7 °C, peaks due to the axial and equatorial hydrogens are observed. Axial and equatorial hydrogens have different chemical shifts under these conditions.



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2. The *t*-butyl-substituted rings are conformationally locked. The hydrogen at C1 has different chemical shifts, depending upon whether it is axial or equatorial. 4-Bromocyclohexanes are conformationally mobile. No difference between axial and equatorial hydrogens is observed until the rate of chair–chair interconversion is decreased by lowering the temperature.

Problem 29. Infrared Spectroscopy (IR)

1. Resonance (conjugation) effect: the amino group pushes electron density into the ring and into the carbonyl group resulting in a lower frequency carbonyl group (more single bond character). A nitro group withdraws electrons resulting in higher frequency carbonyl absorption (more double bond character).

2. Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single-bond character (through resonance, as the following example shows), a lower force constant *K*, and thus a lower frequency of vibration. For example, the vinyl double bond in styrene gives absorption band at 1630 cm⁻¹. Esters show a very strong band for the C=O group that appears in the range of 1750–1735 cm⁻¹ for simple aliphatic esters. The C=O band is shifted to lower frequencies when it is conjugated to a C=C or phenyl group.



(*Hint*: $\overline{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$, μ : reduced mas $\mu = m_1 m_2 / (m_1 + m_2)$, c: speed of light).

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Therefore,

Spectrum A: Methyl acrylate. The absorption band appears at 1726 cm⁻¹ belong to the C=O group that conjugates to double carbon-carbon double bond. Similarly, the C=C bond in this molecule has the absorption bond at 1639 cm⁻¹ due to the stretching vibration.

Spectrum B: Allyl acetate. The stretching vibrations of C=O and C=C double bonds appear at the normal positions for these vabrations, at 1743 and 1650 cm⁻¹, respectively.

There are only the separated C=C and C=O double bonds in vinyl propionate and allyl acetate, so the stretching bands appear at the normal positions.



PART 2. PRACTICAL PROBLEMS

Problem 30. Condensation between vanillin and benzylamine

2. Mechanism



3. Na_2SO_4 is a water-adsorbing substance. It removes water preventing H₂O attack to the product (imine).

Problem 31. Synthesis of eugenoxy acetic acid



1. Reactions in steps 1a, 1b and 2:

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3. The reaction in step 2 follows a S_N 2 substitution:



4. In alkaline media, eugenol is transformed into eugenolate which has adequate nucleophilicity to replace the chlorine atom of monochloroacetic acid. An excess amount of alkaline, however, should not be used as the hydroxide ions can compete with the eugenolate ions to form the hydroxide derivative of acetic acid.

5. The carboxyl group, on the one hand, provides for an (-I) effect to increase the positive charge density at the alpha carbon, facilitating the attack of nucleophiles. On the other hand, the carboxyl can delocalize the negative charges appearing in the transition state of the S_N2 reaction.



6. Crystallized water in the product re-crystallized from hot water lowers down its melting point. Re-crystallization of the product from dry benzene helps eliminate water and increase the melting point. Titration or TGA can be used to determine the amount of water crystallized in the product
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7. In basic condition, eugenoxyacetic acid is subjected to isomerization in which the terminal C=C double bond is moved in and conjugated with the benzene ring to yield isoeugenoxyacetic acid as shown in the scheme below:



H₃C

(E)

(Z)



Problem 32. Complexometric titration of iron, aluminum, and magnetism in the aqueous solution

1. The chemical equations of the reactions used in the titration:

1.1 Titration of Fe^{3+}

The stability constant of FeY⁻ is much larger (= $10^{25.1}$) >> The constants of complex of Al^{3+} ($10^{16.13}$) and of Mg²⁺($10^{8.7}$) therefore in the solution with pH of 2 only ion Fe^{3+} totally titrated:

 $Fe^{3+} + Na_2H_2Y \rightarrow FeY^- + 2Na^+ + 2H^+$

1.2 In the solution with pH of 4.7 only ions Fe^{3+} and Al^{3+} are totally titrated:

$$Fe^{3^{+}} + Na_{2}H_{2}Y (extra) \rightarrow FeY^{-} + Na_{2}H_{2}Y$$
$$Al^{3^{+}} + Na_{2}H_{2}Y (extra) \rightarrow AlY^{-} + Na_{2}H_{2}Y$$

1.3 Separate and titration of Mg^{2+} :

In the buffer $NH_3 + NH_4^+$ (pH = 9.2) only Al(OH)₃ and Fe(OH)₃ are precipitated and total Mg²⁺ ions are existed in the solution. After the filtration of Al(OH)₃ and $Fe(OH)_3$ we can titrate Mg^{2+} in the filtrate:

$$Mg^{2+} + Na_2H_2Y \longrightarrow MgY^{2-} + 2Na^+ + 2H^+$$

2. The formulae for calculation of ion concentrations (in mol / L)

$$C_{Fe(III)} = V_1 \ 0.05 / 25.0$$

$$C_{Al(III)} = [(50.0 - V_2 - V_1) \ 0.05] / 25.0$$

$$C_{Mg(II)} = V_3 \ 0.05 / 25.0$$

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Problem 33. Determination of zinc and lead in zinc oxide powder 1.

1.1 $ZnO_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_2O_{(1)}$ $PbO_{(s)} + 2 HNO_{3 (aq)} \rightarrow Pb(NO_{3})_{2 (aq)} + H_2O_{(l)}$ $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 (white ppt.)$ 1.2 $PbSO_{4(s)} + 4 NH_4CH_3COO_{(aq)} \rightarrow Pb(CH_3COO)_4(NH_4)_{2(aq)} + (NH_4)_2SO_4$ 1.3 $2Pb(CH_3COO)_4(NH_4)_2$ (ag) + $K_2Cr_2O_7$ (ag) + $H_2O_{(1)} \rightarrow 2PbCrO_4$ (vellow ppt.) + $2KCH_{3}COO_{(aq)} + 4NH_{4}CH_{3}COO_{(aq)} + 2 CH_{3}COOH_{(aq)}$ 1.4 $2PbCrO_{4(s)} + 4NaCl_{(aq)} + 4HCl_{(aq)} \rightarrow 2Na_2PbCl_{4aq)} + H_2Cr_2O_{7(aq)} + H_2O_{(l)}$ 1.5 $Cr_2O_7^{2-}$ + 6 Fe^{2+} + 14H⁺ \rightarrow 2Cr³⁺ + 6Fe³⁺ + 7H₂O $\mathrm{H_2Cr_2O_7} + \mathrm{I^-} + 12\mathrm{H^+} \rightarrow 2\mathrm{Cr^{3+}} + 3 \mathrm{I_2} + 7\mathrm{H_2O}$ $I_2 + 2 \operatorname{Na}_2 S_2 O_{3 \text{ (aq)}} \rightarrow 2 \operatorname{Na}_{4 \text{ (aq)}} + \operatorname{Na}_2 S_4 O_{6 \text{ (aq)}}$

2.

Mass of zinc oxide powder = a (g). The volume of standard solution is recorded in mL.

$$\sqrt[6]{Pb} = (V_{EDTA} \times C_{EDTA}) \times 10 \times 100$$

 $\sqrt[6]{Pb} = \frac{1}{3} \times 207.02 \times (V_{Fe^{2+}} \times C_{Fe^{2+}}) \times 100$



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3.

The half reactions
$$Cr_2O_7^{2^-} + 14H^+ + 6e^- \rightarrow 2Cr^{3^+} + 7H_2O$$
 $E^\circ = 1.33 V$
 $I_2 + 2e \rightarrow 2 I^ E_{I_2/2I^-}^0 = +0.54 V;$
 $S_4O_6^{2^-} + 2e \rightarrow 2S_2O_3^{2^-}$ $E_{S_4O_6^{2^-}/S_2O_3^{2^-}}^0 = +0.08 V$

As $K_2Cr_2O_7$ is a strong oxidant, it can oxidize $S_2O_3^{2-1}$ to form $S_4O_6^{2-1}$ and SO_4^{2-1} . The reactions are not stoichiometry.

4.

4.1

$$\begin{split} & Pb(OAc)_{2}(aq) + K_{2}CrO_{4}(aq) \rightarrow PbCrO_{4}(s) + 2KOAc(aq) \\ & Then \ PbCrO_{4}(s) \Leftrightarrow \ Pb^{2+} + CrO_{4}^{2-} \\ & [Pb^{2+}] = 0.1 \times 10^{-5} / 0.12 = 8.3 \times 10^{-6} \ mol/L \\ & [CrO_{4}^{2-}] = 0.02 \times 1.0 \times 10^{-3} / 0.12 = 1.7 \times 10^{-4} \ mol/L \\ & Therefore \ Q = 8.3 \times 10^{-6} \times 1.7 \times 10^{-4} = 1.4 \times 10^{-9} > K_{sp.} \ So \ a \ precipitate \ will \ occur. \end{split}$$

4.2

Since $[Pb^{2+}] = 8.3 \times 10^{-6}$ and $[CrO_4^{2-}] = 1.7 \times 10^{-4}$ and there is a 1:1 stoichiometry, Pb^{2+} is completely reacted.

 $PbCrO_4(s) \iff Pb^{2+} + CrO_4^{2-}$ I. (after ppt.) 8.3×10^{-6} 1.7×10^{-4} -8.3×10^{-6} $= 1.7 \times 10^{-4}$ C. Х x $1.7 \times 10^{-4} + x$ E. Х $K_{sp} = [x][1.7 \times 10^{-4} + x] = 1.8 \times 10^{-14}$ Solving for x gives $x = 1.1 \times 10^{-10}$, so the concentration of Pb²⁺ remaining in solution is very small.



Problem 34. Preparation of copper(II) acetylacetonate

1. $Cu(acac)_2$

2. There are four main equilibria involved the complex formation:

Hacac (aq) + H₂O
$$\longrightarrow$$
 H₃O⁺ (aq) + acac⁻ (aq)
H₃O⁺ (aq) + OH⁻ (aq) \longrightarrow 2H₂O (l)
Cu²⁺ (aq) + 2acac⁻ (aq) \implies [Cu(acac)₂] (s)
Cu²⁺ (aq) + 2OH⁻ (aq) \implies Cu(OH)₂ (s)

At a low pH, acac⁻ is not sufficiently concentrated to precipitate complex or to form the complex with a high yield. On the contrary, at high pH regions, $Cu(OH)_2$ can be competitively precipitated and an impure product can be obtained.

3. Square planar complex with two six-membered chelate rings.

Problem 35. Kinetic analysis of the hydrolysis of aspirin

1.

The theoretically obtained amount of aspirin is: $n_{(\text{salicylic acid})} = 2.00\text{g}/138.1 = 0.0145 \text{ mol}$ $m_{(\text{aspirin})} = 0.0145 \text{ mol} \times 180.2 = 2.6129 \text{ g}$ Experimentally, the amount of aspirin obtained is 2.0132 g \rightarrow The yield of the reaction is: $(2.0132/2.6129) \times 100 = 77.04 \%$

2. Magnesium hydroxide, magnesium carbonate and aluminum glycinate, when mixed into the formulation of the aspirin will reduce the irritation.



3.

Ignoring the volume change upon mixing and supposing that aspirin occupies only negligible volume:

In the 5×10^{-4} M solution of acetylsalicylic acid, the concentration of NaOH = $(5.0 \times 10^{-3} \text{ mol } \text{L}^{-1} \times 40 \text{ mL})/50 \text{ mL} - 5.0 \times 10^{-3} \text{ mol } \text{L}^{-1} = 3.5 \times 10^{-3} \text{ mol } \text{L}^{-1}$

4. Determine the order with respect to the concentration of aspirin and the pseudo - order rate constant of the reaction.

Time/minute	5	10	20	30	40	50	60	00
Absorbance	0.549	0.829	1,178	1.389	1.506	1.569	1.602	1.653
А	0.0	0.023	11170	1.003	1.000	1.003	1.002	1.000

The UV-Vis absorption obtained in the experiments is given below:





Figure 1. Plot of $(A_{\infty} - A)$ *versus time*

Figure 2. Plot of ln(A_{\infty} - A) vs. t



5. Experimental results showed that the reaction obeyed the pseudo-first-order rate law (figure 2 and 4), but not the second-order (figure 3). Based on the equation $\ln \frac{A_{\infty} - A_{t_1}}{A_{\infty} - A_{t_2}} = kt$ and the results in figure 4, as well as in figure 2, we can easily calculate $k_{obs} = 0.056 \text{ min.}^{-1}$. Hence, the half-life is 17.85 minutes and the reaction time is 3.36 times greater than the half-life.

6. From the obtained experimental results the reaction is first order with respect to both [asp] and [OH⁻], therefore the rate law may be given as

Rate =
$$k [asp]^1 [OH^-]^1$$
.

According to this mechanism, in step 1, the hydroxide nucleophile attacks at the electrophilic C of the ester C=O, breaking the σ bond and creating the **tetrahedral intermediate**. In step 2, the intermediate collapses, reforming the C=O and, the last step (step 3) is an acid-base reaction which takes place very fast, a very rapid equilibrium. Hence, it is not the rate-determining step of the reaction.

Let denote the **tetrahedral intermediate** as I and $(2-HOC_6H_4COO^-)$, a product in step (2) as **P**. The rate of formation of product may be given as



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$$Rate = \frac{d[P]}{dt} = k_2[I]$$

With regard to the stability of the intermediate I, the two possibilities, which may be considered, are

i) If $k_{1} \gg k_{2}$, means the rate of reconversion of **I** into asp and OH⁻ is significantly greater than the rate with which it undergoes to give the **P**, the concentration of intermediate **I**, [I] can be calculated by considering equilibrium (1) alone

$$[I] = K[asp][OH^{-}]$$

Where equilibrium constant $K = k_l/k_{-l}$ and, therefore

Rate of the reaction = $k_2 K[asp][OH^-]$

which is matching well with experimental results.

ii) If intermediate complex I is much less stable species, means the rate of its conversion to product (step 2) is not small compared with the reverse rate in step 1. In this case, the concentration of I must be calculated by using steady-state treatment. By applying the steady state with respect to [I], we get

$$k_{1}[asp][OH^{-}] = k_{-1}[I] + k_{2}[I]$$
$$[I] = \frac{k_{1}[asp][OH^{-}]}{k_{-1} + k_{2}}$$

or

and, therefore

Rate of reaction =
$$\frac{k_1 k_2 [asp][OH^-]}{k_{-1} + k_2}$$

However, when $k_{-1} \gg k_2$, the rate law becomes same as case 1. Thus, the steady state treatment is the general one, and reduces to the equilibrium treatment when $k_{-1} \gg k_2$.

Conclusion: if the equilibrium in step 1 is controlled throughout the reaction process (step 1 is very fast and represents rapid pre-equilibrium to the rate), the



given mechanism agrees with the rate law and in this case the step 2 is ratedetermining step of the reaction.

The obtained rate laws clearly show the rate is dependent on the NaOH concentration. For a given concentration of NaOH, we may write

Rate of reaction = k_{obs} [asp]

Where
$$k_{obs} = \frac{k_1 k_2 [OH^-]}{k_{-1} + k_2}$$
 or $k_2 K [OH^-]$ (when $k_{-1} \gg k_2$)

Constant k_{obs} is proportional to [OH⁻] and is known as catalytic coefficient for the catalyst.

Problem 36. Complex formation of ferric ion and salicylic acid

1. n = 1, thus the empirical formula is $Fe^{3+}(H_2Sal)$

2.

2.1 The chemical equation:

$$H_{2}Sal + Fe^{3+} \longrightarrow [Fe(Sal)]^{+} + 2 H^{+}$$
(1)

$$\underline{2.2} K_{(1)} = K_{f} \times K_{a1} \times K_{a2} = \frac{[Fe(Sal)] \times [H^{+}]^{2}}{[H_{2}Sal] \times [Fe^{3+}]} \text{ or } K_{f} = \frac{K_{eq} \times [H^{+}]^{2}}{K_{a1} \times K_{a2}}$$

[H⁺] need be calculated from initial concentration 0.0025 M and dissociation concentration during complex formation:

 $[H^+]_{eq} = 0.0025 + 2 \times [Fe(Sal)]^+$

2.3 The average value is about 1.4×10^{16}

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2.4 The average K_f value is not the same with literature values which vary from 2.2×10^{16} to 2.7×10^{16} (ref. 2) due to the simplifications of the equilibrium as mentioned, and also using concentrations instead of activities in the K_f equation.

[1]. D. R. Lide. CRC Handbook of Chemistry and Physics (84th Ed). CRC Press, 2003, pp. 1247. [2] Z. L. Ernst; J. Menashi. Complex formation between the Fe³⁺ ion and some substituted phenols. Part 1. Spectrophotometric determination of the stability constant of ferric salicylate. Trans. Faraday Soc., 1963, 59, 1794-1802.



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