

42nd International Chemistry Olympiad Japan, 2010

Preparatory Problems Solutions

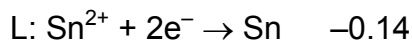
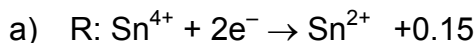


Chemistry : the key to our future



Solutions of Theoretical Problems

Problem 1

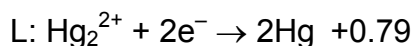
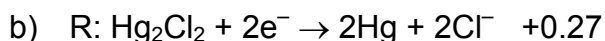


$$E^\circ = +0.29 \text{ V}$$

$$\ln K = -\Delta_r G^\circ / RT = nFE^\circ / RT = 2 \times F \times 0.29 / (R \times 298) = 22.59$$

$$K = \frac{[b_e(\text{Sn}^{2+})]^2}{b_e(\text{Sn}^{4+})} = \exp(22.59) = 6.4 \times 10^9.$$

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$$E^\circ = -0.52 \text{ V}$$

$$\ln K = -\Delta_r G^\circ / RT = nFE^\circ / RT = 2 \times F \times (-0.52) / (R \times 298) = -40.50.$$

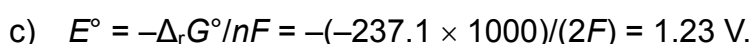
$$K = b_e(\text{Hg}_2^{2+}) [b_e(\text{Cl}^-)]^2 = \exp(-40.50) = 2.58 \times 10^{-18}$$

let $x = b_e(\text{Hg}_2^{2+})$, then $b_e(\text{Cl}^-) = 2x$. Therefore, $K = x(2x)^2 = 4x^3$

Solving this equation for x gives $x = (K/4)^{1/3} = 8.6 \times 10^{-7}$

$$S = x = 8.6 \times 10^{-7} \text{ mol} \cdot \text{kg}^{-1}.$$

$$S = 8.6 \times 10^{-7} \text{ mol} \cdot \text{kg}^{-1}$$



$$E^\circ = 1.23 \text{ V}$$

Problem 2

a) Since the flight energy is zero at 0 K and it increases by $\frac{3}{2}R$ per unit temperature

(per mol), the energy should be $\frac{3}{2}RT$ (per mol) at temperature T .

Thus, the total kinetic energy of one mole of gas is $\frac{1}{2}Mv^2 = \frac{3}{2}RT$.



This equation is solved for v : $v = \sqrt{\frac{3RT}{M}}$

$$v = \sqrt{\frac{3RT}{M}}$$

- b) From the solution to problem a), v , and therefore, v_s should be proportional to $M^{-1/2}$.

Therefore, the speed of sound in Ne can be estimated as

$$v_s(\text{Ne}) = 1007 \times (20.18/4.003)^{-1/2} = 448 \text{ m}\cdot\text{s}^{-1}$$

$$\text{or, } v_s(\text{Ne}) = 319 \times (20.18/39.95)^{-1/2} = 449 \text{ m}\cdot\text{s}^{-1}$$

$$v_s(\text{Ne}) = 448 [449] \text{ m}\cdot\text{s}^{-1}$$

Problem 3

- a) The areas of the hexagon and pentagon (S_6 and S_5) in the fullerenes are

$$S_6 = 0.14 \times 0.14 / 2[\text{nm}] \times \tan\left(\frac{180 - 360/6}{2}\right) / 2 = 0.0509[\text{nm}^2]$$

$$S_5 = 0.14 \times 0.14 / 2[\text{nm}] \times \tan\left(\frac{180 - 360/5}{2}\right) / 2 = 0.0337[\text{nm}^2]$$

respectively. Therefore, the total area of a fullerene with n carbon atoms is

$$S_{\text{total}} = 0.0337 \times 12 + 0.0509 \times \left(\frac{n}{2} - 10\right) = 0.0255n - 0.1046[\text{nm}^2].$$

- b) Since the total area of a perfect sphere is

$$S_{\text{sphere}} = 4\pi r^2,$$

and this area is equal to the area of the fullerene, the radius of the fullerene would be

$$r = \sqrt{\frac{0.0255n - 0.1046}{4\pi}}[\text{nm}].$$

- c) The weight of the fullerene with n carbon atoms is

$$m = 12.01 / N_A n.$$

Since the volume of a sphere with radius r is

$$V_{\text{sphere}} = \frac{4}{3} \pi r^3$$

which is also the volume of the fullerene, the density would be

$$d = \frac{12.01 / N_A n}{\frac{4}{3} \pi \left(\frac{0.0255n - 0.1046}{4\pi}\right)^{\frac{3}{2}}} = \frac{12.0\sqrt{\pi}}{\left(0.0255 - \frac{0.1046}{n}\right) \times \sqrt{0.0255n - 0.1046}} \times 10^{-23} [\text{g}\cdot\text{nm}^{-3}]$$



The density of air under standard conditions is

$$d_{\text{air}} = \frac{M}{V} = \frac{28.0 \times 0.8 + 32.0 \times 0.2}{RT/p} = \frac{28.8}{8.314 \times 298 / 101325} \times \frac{1}{(10^9)^3} = 1.18 \times 10^{-24} [\text{g} \cdot \text{nm}^{-3}].$$

This air density is larger than that of the fullerene with n carbon atoms, and n should be large enough so that

$$d_{\text{air}} > d \Rightarrow$$

$$1.18 \times 10^{-24} > \frac{12.0\sqrt{\pi}}{\left(0.0255 - \frac{0.1046}{n}\right) \times \sqrt{0.0255n - 0.1046}} \times 10^{-23} \approx 5.22n^{-1/2} \times 10^{-20} [\text{g} \cdot \text{nm}^{-3}]$$

$$\therefore n > \left(\frac{5.22 \times 10^{-20}}{1.18 \times 10^{-24}}\right)^2 = 1.96 \times 10^9.$$

In this case, the minimum radius of the “molecular balloon” is

$$r = \sqrt{\frac{0.0255n - 0.1046}{4\pi}} = \sqrt{\frac{0.0255 \times 1.96 \times 10^9 - 0.1046}{4\pi}} = 1.99 \times 10^3 [\text{nm}].$$

Problem 4

a) From the figure, the interval between the peaks can be determined to be 500[480–550] cm^{-1} .

The corresponding wavelength $\lambda = 1 \times 10^{-2} / 500[480-550] = 2.0[1.82-2.08] \times 10^{-5} \text{ m}$

Then, the corresponding energy $E_v = N_A hc / 2.0[1.82-2.08] \times 10^{-5} = 6.0[5.7-6.6] \text{ kJ} \cdot \text{mol}^{-1}$.

$$E_v = \quad \mathbf{6.0 [5.7-6.6] \text{ kJ} \cdot \text{mol}^{-1}}$$

Problem 5

a) $\mu = \frac{m_1 m_2}{m_1 + m_2}$; therefore, $\mu_{\text{H}_2} : \mu_{\text{N}_2} : \mu_{\text{O}_2} = \frac{1 \times 1}{1+1} : \frac{14 \times 14}{14+14} : \frac{16 \times 16}{16+16} = 1:14:16$

b) $\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{500 \times 10^{-9} \text{ m}} = 6.0 \times 10^{14} \text{ s}^{-1}$

$$\text{wavenumber} = \frac{1}{500 \text{ nm}} = \frac{1}{500 \times 10^{-9} \text{ m}} = \frac{1}{500 \times 10^{-7} \text{ cm}} = 2.0 \times 10^4 \text{ cm}^{-1}$$

c) According to the energy-conservation principle, the wavenumber of the Raman scattering light should be $20000 - 4160 = 15840 \text{ cm}^{-1}$. The corresponding wavelength is $\sim 631 \text{ nm}$.



$$d) \sqrt{\frac{k_{\text{O}_2}}{\mu_{\text{O}_2}}} = \sqrt{\frac{2k_{\text{H}_2}}{16\mu_{\text{H}_2}}} = \frac{1}{2\sqrt{2}} \sqrt{\frac{k_{\text{H}_2}}{\mu_{\text{H}_2}}}$$

The vibrational energy of the oxygen molecule is $\frac{1}{2\sqrt{2}}$ of the vibrational energy of the hydrogen molecule, that is, $\sim 1475 \text{ cm}^{-1}$. According to energy-conservation principle, the wavenumber of Raman scattering light should be $20000 - 1470 = 18530 \text{ cm}^{-1}$.

The corresponding wavelength is $\sim 540 \text{ nm}$.

Problem 6

According to the simple model (a rigid rotator model), the allowed frequencies for absorption ($J' = J'' + 1$) are

$$\nu = \frac{E_{J'} - E_{J''}}{h} = \frac{h}{8\pi^2 \mu R_e^2} [(J'' + 1)(J'' + 2) - J''(J'' + 1)] = \frac{h}{4\pi^2 \mu R_e^2} (J'' + 1).$$

Hence, frequency of microwave resonant to the $J' = 1 \leftarrow J'' = 0$ transition is $6.26 \times 10^{11} \text{ s}^{-1}$. As reduced mass of HCl^{35} is $1.61 \times 10^{-27} \text{ Kg}$,

$$R_e = \sqrt{\frac{h}{4\pi^2 \mu \nu}} = \sqrt{\frac{6.63 \times 10^{-34}}{4\pi^2 \times 1.61 \times 10^{-27} \times 6.26 \times 10^{11}}} = 1.29 \times 10^{-10} \text{ [m]}$$

Problem 7

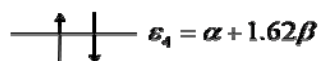
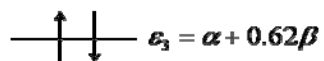
- The upper curve (2) in Fig. 1 shows the energy of the anti-bonding orbital, ϕ_a as a function of the internuclear distance.
- The lower line in Fig. 1 shows the energy of the bonding orbital, ϕ_b . From the minimum of the energy curve, we are able to obtain the internuclear distance of stable H_2^+ to be 0.085 nm .
- The two energy curves in Fig. 1 converge at E_1 as the internuclear distance becomes infinity. Here, H_2^+ is regarded as totally separated one hydrogen atom and one proton. Hence, $|E_1|$ is the same as the ionization potential of the hydrogen atom.

Problem 8

a)

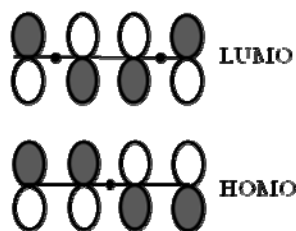
$$\text{————— } \varepsilon_1 = \alpha - 1.62\beta$$

$$\text{————— } \varepsilon_2 = \alpha - 0.62\beta$$



b) $\Delta\varepsilon = \varepsilon_2 - \varepsilon_3 = \alpha - 0.62\beta - (\alpha + 0.62\beta) = -1.24\beta$

c)



d) $E_k(\text{max}) = \alpha - 2\beta$

$$E_k(\text{min}) = \alpha + 2\beta$$

Therefore, the energy width between $E_k(\text{max})$ and $E_k(\text{min})$ is -4β or $|4\beta|$

e) LUMO is destabilized due to proximity of two $2p_z$ orbitals with opposite signs.

HOMO is stabilized due to proximity of two $2p_z$ orbitals with same signs.

Answer: (b)

f) Br_2



Problem 9

- a) Since one eigenstate is occupied by two electrons with opposite spin directions (up-spin and down-spin), the quantum number n of the highest occupied level is $N/2$ for even N and $(N+1)/2$ for odd N . The length of the chain L is expressed as $a_0(N-1)$. On the basis of the given eigenenergy, the energy of the highest occupied level is written as

$$E_{\frac{N}{2}} = \frac{N^2 h^2}{32ma_0^2(N-1)^2} \quad \text{for even } N \quad \text{and} \quad E_{\frac{N+1}{2}} = \frac{(N+1)^2 h^2}{32ma_0^2(N-1)^2} \quad \text{for odd } N.$$

- b) The number of Na atoms present in 1.00 mg of Na is

$$N = 6.02 \times 10^{23} \times \frac{1.00 \times 10^{-3}}{23.0} = 2.617 \times 10^{19}.$$

The energy width is expressed as $E_{\frac{N}{2}} - E_1 = \frac{h^2}{32ma_0^2} \left\{ \frac{N^2 - 4}{(N-1)^2} \right\}$ for even N

and $E_{\frac{N+1}{2}} - E_1 = \frac{h^2}{32ma_0^2} \left\{ \frac{(N+1)^2 - 4}{(N-1)^2} \right\}$ for odd N .

Since N is extremely large, the energy width is calculated as

$$\frac{h^2}{32ma_0^2} = 1.16 \times 10^{-19} \text{ J} \quad \text{for the both cases.}$$

- c) The energy gap for even N is $\Delta E = E_{\frac{N+1}{2}} - E_{\frac{N}{2}}$; using the equation obtained in (a), the

equation for energy gap is rewritten as

$$\Delta E = \frac{h^2}{32ma_0^2} \left\{ \frac{(N+2)^2 - N^2}{(N-1)^2} \right\} = \frac{h^2}{8ma_0^2} \frac{(N+1)}{(N-1)^2}.$$

We solve the equation $\Delta E = \frac{h^2}{8ma_0^2} \frac{(N+1)}{(N-1)^2} = E_{\text{Thermal}} \quad (25 \text{ meV}).$

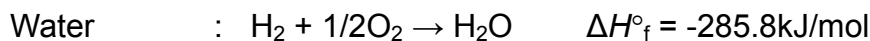
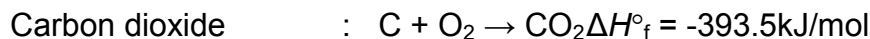
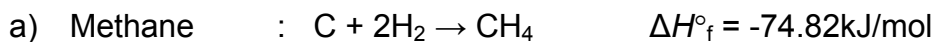
This equation is rewritten as $\frac{(N-1)^2}{N+1} = \frac{h^2}{8ma_0^2 E_{\text{Thermal}}} = 116.2.$

Thus, we obtain the quadratic equation $N^2 - 118.2N - 115.2 = 0$, and solve the equation to obtain $N = 119.2$.

Therefore, at least 120 Na atoms are required when the energy gap is smaller than the thermal energy 25 meV.



Problem 10



$\Delta H^\circ = -890.3 \text{ kJ/mol}$



The amount of generated carbon dioxide: 0.0250mol

Calculation by use of an equation of state for ideal gas, $V=nRT/p$

$$V = 0.0250(\text{mol}) \cdot \frac{8.31(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = \text{N} \cdot \text{m} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \times (298)(\text{K})}{1013 \times 100(\text{Pa} = \text{N} \cdot \text{m}^{-2})}$$
$$= 6.11 \times 10^{-4}(\text{m}^3) = 611(\text{mL})$$

$V=611\text{mL}$

Problem 11

a) CO_2 (M=44.0): face-centered cubic lattice, 4 molecules per one unit lattice:

$$\rho = \frac{\frac{44.0 \text{ g}}{6.02 \times 10^{23}} \times 4}{(0.56 \times 10^{-9} \text{ m})^3} = \frac{44.0 \times 4}{6.02 \times (0.56)^3 \times 10^{(23-27)}} = \frac{176}{1.057 \times 10^{-4}} = 1.67 \times 10^6 \text{ g/m}^3$$



$$\rho = 1.67 \times 10^6 \text{ g} \cdot \text{m}^{-3}$$

b)

$$\begin{aligned} N &= \frac{(0.20 \times 0.10 \times 0.050) \times \rho_{\text{dry ice}}}{44.0} \times N_A \\ &= \frac{(0.20 \times 0.10 \times 0.050) \times 1.67 \times 10^6}{44.0} \times 6.02 \times 10^{23} \\ &= 2.28 \times 10^{25} \end{aligned}$$

$$N = 2.3 \times 10^{25} \text{ molecules}$$

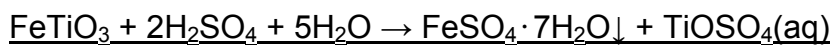
Problem 12

a) Molecular weight, Ilmenite $M(\text{FeTiO}_3) = 151.7$, Titania $M(\text{TiO}_2) = 79.9$

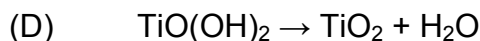
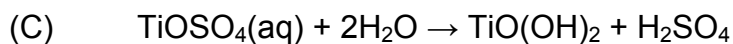
$$m_{\text{FeTiO}_3} = \frac{m_{\text{TiO}_2}}{79.9} \times 151.7 = \frac{1000 \times 1000 \times 0.35}{79.9} \times 151.7 = 664518 \text{ g} = 665 \text{ kg}$$

$$m = 665 \text{ kg}$$

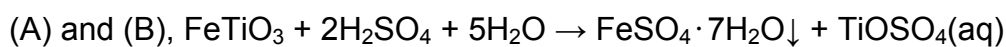
b) Processes (A) and (B):



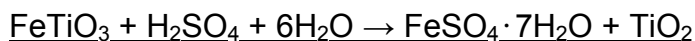
c)



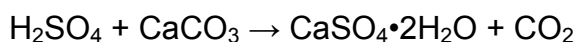
From the answer of b):



Processes (A)-(D):



c) Chemical formula of neutralization:



Sulfuric acid: $M(\text{H}_2\text{SO}_4)=98.08$, Calcium carbonate: $M(\text{CaCO}_3)=100.1$

The necessary amount of sulfuric acid for the reaction:

$$n_{\text{H}_2\text{SO}_4} = \frac{m_{\text{FeTiO}_3}}{151.7} \times 2 = \frac{10.0 \times 2}{151.7} = 0.132 \text{ mol}$$

The amount of surplus sulfuric acid:

$$p_{\text{H}_2\text{SO}_4} = 18.00 \times \frac{25.0}{1000} - 0.132 = 0.318 \text{ mol}$$

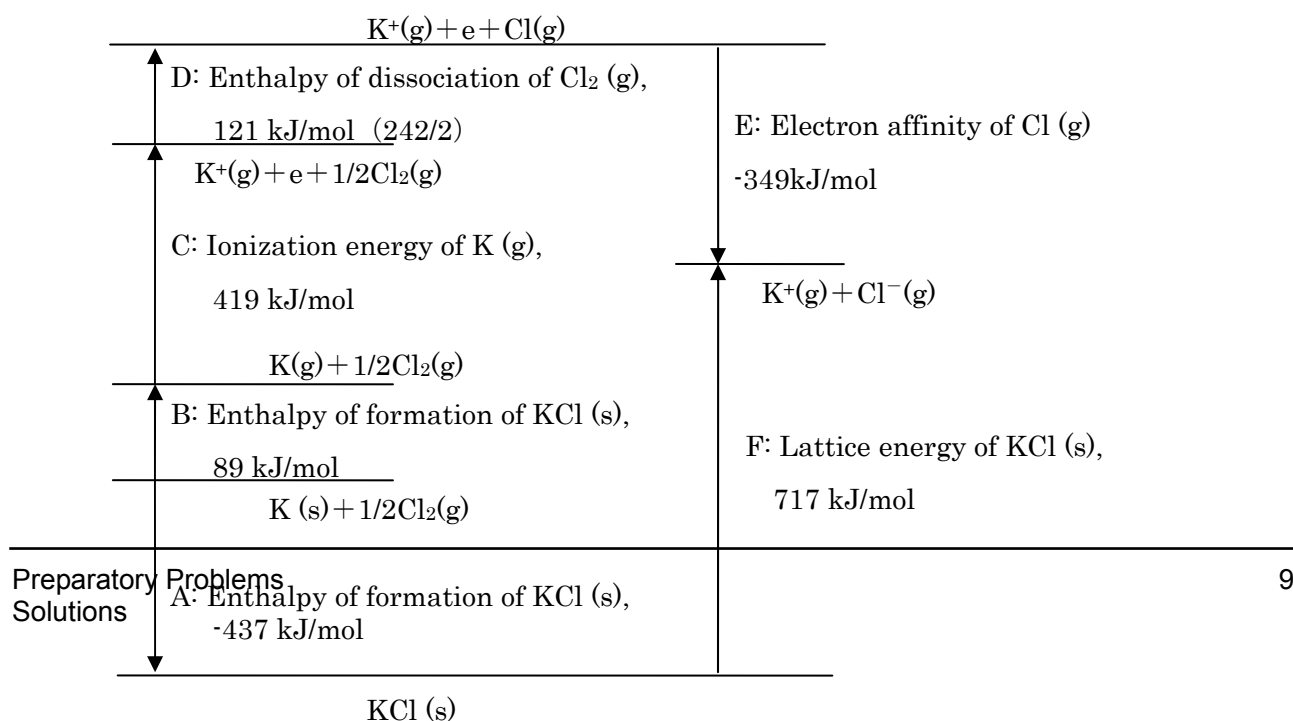
The necessary amount of calcium carbonate for the neutralization:

$$x_{\text{CaCO}_3} = 0.318 \text{ mol} \times 100.1 = 31.8 \text{ g}$$

$$m=31.8 \text{ g}$$

Problem 13

a) $B+C+D-A+E=89 + 419 + 121 - (-437) + (-349) = \underline{717 \text{ kJ/mol}}$



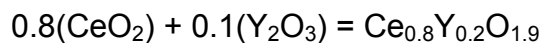


Problem 14

a)

Cations: 4 Anions: 8

b)

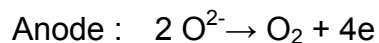
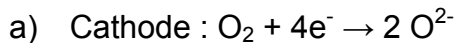


$$0.1/2.0 = 0.05 \quad 5\%$$

c)

$$1/(1.36 \times 10^{-22}) \times 8 \times 0.05 = 2.94 \times 10^{21}$$

Problem 15



b) 1/4 mol O_2 moves when 1 mol electron flows.

$$\text{Moved } \text{O}_2 : n = (1.93 \times 500 / 96485) \times (1/4) = 2.5 \times 10^{-3} \text{ mol}$$

$$V = nRT/P = 2.5 \times 10^{-3} \times 8.314 \times 1073 / 1.01 \times 10^5 = 2.208 \times 10^{-4} \text{ (m}^3\text{)}$$

$$= 2.208 \times 10^2 \text{ (cm}^3\text{)} \quad \text{Ans. } 2.2 \times 10^2 \text{ mL}$$

c) In an oxygen concentration cell, ΔG° and E° are 0 and $z = 4$.

$$E = - (RT/4F) \ln (P_{\text{ox}}/ P_{\text{red}}) = (RT/4F) \ln (P_{\text{cathode}}/ P_{\text{anode}})$$

$$= (2.303RT/4F) \log(P_1/ P_2)$$

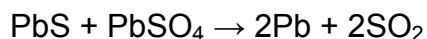
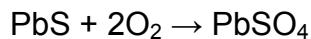
$$= \{(2.303 \times 8,314 \times 1073 / (4 \times 96485))\} \times 2 = 0.1064$$

$$\text{Ans. } 1.1 \times 10^{-1} \text{ V}$$

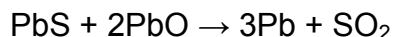
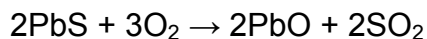


Problem 16

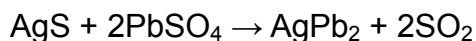
a) **Route 1**



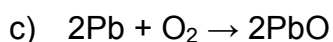
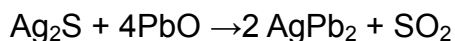
Route 2



b) **Route 1**



Route 2



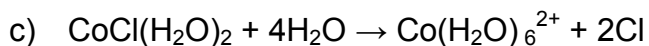
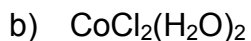
d) B

e)

Problem 17

a) **Coordination number: 4**

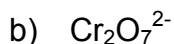
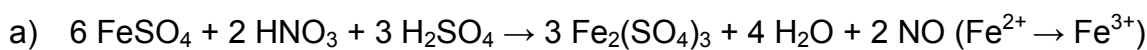
Coordination structure: tetrahedral



d) **Coordination number: 6**

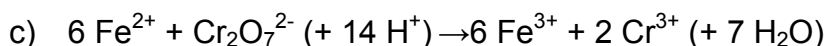
Coordination structure: octahedral

Problem 18

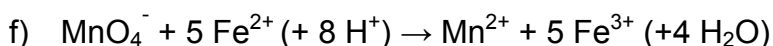
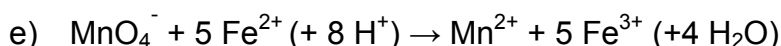




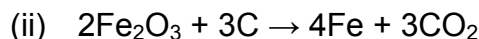
(When the ammonium persulfate is not completely decomposed,) the function of AgNO_3 (oxidation of the solution) will be prevented.



The color changes from orange to (light) blue green.



Problem 19



b) Mass of Fe_2O_3 required to obtain 1.00kg of pig iron is ; $955 \times (159.6 / 111.6) = 1365.75$ (g). And the amount of the slag generated from iron ore is 17/90, namely 257.98(g). 392.29 (g) of coke also produces slag from the gangue 0.17 times as much as the coke, namely 66.69(g). Accordingly, the total amount of the slag generated becomes 324.67(g).

0.325kg

c) Half of the carbon (45 g) in the 1 kg of pig iron is oxidized into CO_2 and the rest into CO. Hence, 3/4 times of 45/12 mole of O_2 gas is required. Using $PV = nRT$, V can be obtained as 34.6 L.

$V = 34.6 \text{ L}$

d) Considering 1 kg of pig iron, the molar amount of C required for the reduction is 1.5 times as much as that of Fe. Then, $955/55.8 \times 3/2 \times 12.0 = 308.06$ g, which becomes 353.06 g together with the carbon dissolved in pig iron, 45 g.

As derived in the question b), 324.67 g of the slag containing 7/17 of CaO is generated.



When this amount of CaO is produced from CaCO₃, CO₂ is generated as much as 44/56.1 of CaO in weight bases. Hence, the total amount of CO₂ generation becomes 353.06×44/12 + 324.67 × 7/17 × 44/56.1 = 1399.41 g.

Then, divided by 0.955, a value per 1 kg of iron can be obtained.

1.47 kg

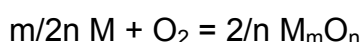
e) The atomic radius of the bcc is $\sqrt{3}/4$ times of the unit length, a. The volume of the unit structure, $a^3 = 55.8/7.90 \times 2 / N_{AV} = 23.4543 \times 10^{-24} \text{ cm}^3$. Hence, $a = 2.8625 \times 10^{-8} \text{ cm}$.

1.24×10⁻¹⁰ m

Problem 20

a)

(i)



(ii)

$$\Delta H^\circ - T\Delta S^\circ$$

(iii)

enthalpy

(iv)

entropy

(v)

$$e^{(\Delta G^\circ/RT)}$$

(vi)

oxidized

b) In all the reactions except for the two C oxidations, 1 mole of the gas (oxygen), namely its entropy, is lost. This is why the slopes are almost identical. However, there are almost no changes in the entropy of the gas in the case of CO₂ gas formation, making the line horizontal, and causing the increase in 1mole of the gas in the case of CO formation showing the different sign with the same slope.



d) The heat generated (or absorbed) by the reaction per 1 mole of oxygen gas can be read from the difference in the values of the intercepts of the lines for Cu and Al. Hence, the value per 1 mole of Al can be obtained by multiplying 3/4. Then, the ΔH° of the reaction can

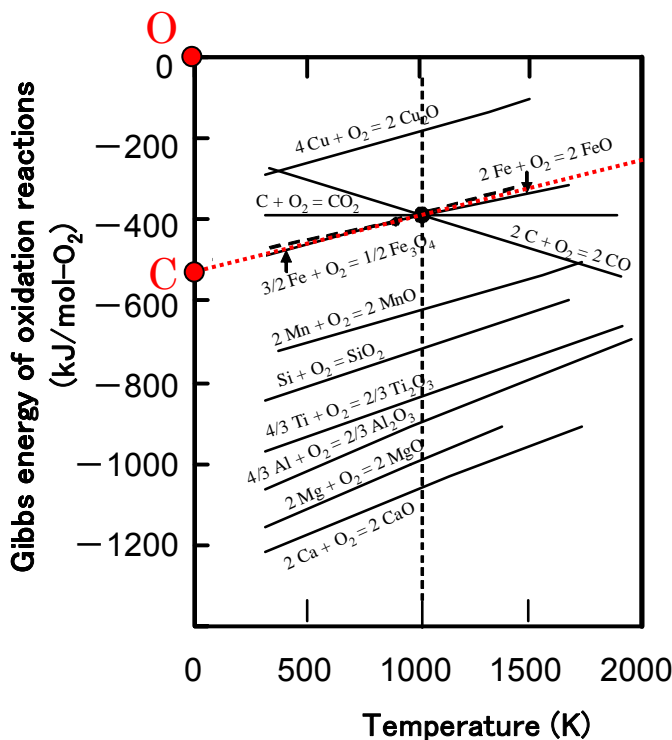
be read as $-1130 - (-350) = -780$ kJ per 1 mole of oxygen gas, and it will become -585 kJ per mole of Al.

Heat of 585 kJ will be generated by the reaction. (exothermic reaction)

e) Since the vertical axis shows $RT \ln p_{O_2}$ value, any straight lines drawn through point “O” have the slope of $R \ln p_{O_2}$. Hence, the value of p_{O_2} is identical on such lines.

On the other hand, the line of the reaction: $2CO + O_2 = 2CO_2$ can be drawn by the two oxidation reactions of C mentioned in the question b), and the intercept of the derived line is assumed to be “C” through which the line of constant p_{CO}/p_{CO_2} value will go.

They are plotted in the figure as “O” and “C”, respectively.



f) Two lines of $2Fe+O_2=FeO$ and $2CO + O_2 = 2CO_2$ happen to cross at 1000 K, which means the ratio of p_{CO}/p_{CO_2} is considered to be unity when Fe and FeO coexist. Accordingly, the consumed fraction becomes 50%.

50%



Problem 21

a) This corresponds to 1 mol of water.

The volume is 22.4 L in the standard condition.

$$22.4 \times 1000 / (22.4 \times 1000 + 50.0 + 109.8 + 28.0) = 0.992$$

$$0.992 \times 100 = 99\%$$

b) Precipitation is BaSO_4 .

The formula weight is

$$\text{BaSO}_4 = 137.3 + 32.1 + 16.0 \times 4 = 233.2$$

0.30 gram of BaSO_4 corresponds to

$$0.30 \div 233.2 = 1.29 \times 10^{-3} \text{ mol}$$

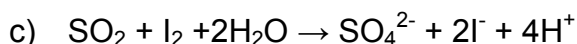
This number corresponds to mole number of sulfur.

Total sulfur in the initial solution is

$$1.29 \times 10^{-3} \times 38.0 \div 10.0 = 4.90 \times 10^{-3} \text{ mol}$$

The volume of the gas is

$$22.4 \text{ L} \times 4.90 \times 10^{-3} \text{ mol} = 109.8 \text{ mL} = 1.1 \times 10^2 \text{ mL}$$



Problem 22

a)



b)



Problem 23

a) Let χ be the molar quantity of the ester, then $K = 4.20 = \chi^2 / (1.00 - \chi)^2$, $\chi = 0.672_{066} \text{ mol}$.

The molecular weight of ester = $12.01 \times 4 + 1.01 \times 8 + 16.00 \times 2 = 88.12$, therefore the



quantity of the ester = $88.12 \times 0.672_{066} = 59.2_{225} \approx 59.2(\text{g})$

b) $K = p n_w / (1 - p)^2$

c) From b), $\beta p^2 - (2\beta + 1)p + \beta = 0$. As $p \leq 1$, then,

$$p = [(2\beta + 1) - \{(2\beta + 1)^2 - 4\beta^2\}^{0.5}] / 2\beta = [(2\beta + 1) - (4\beta + 1)^{0.5}] / 2\beta.$$

Since $\beta \gg 1$, $2\beta + 1 \approx 2\beta$ and $4\beta + 1 \approx 4\beta$, therefore, $p = (2\beta - 2\beta^{0.5}) / 2\beta = 1 - \beta^{-0.5}$.

Put this answer into the Carothers eq.[eq.(6)], $X = 1 / (1 - p) = \beta^{0.5}$

d) In order to realize $X \geq 100$, $\beta^{0.5} = (K / n_w)^{0.5} \geq 100$. At $K = 4.00$, $n_w \leq 4.00 \times 10^{-4} (\text{mol})$

or $4.00 \times 10^{-2} \text{ mol\%}$.

NOTE: The relation between n_w and X was estimated (at $K = 4.00$) and illustrated in

Fig.1. In order to produce PET with $M = 4.00 \times 10^4$ ($X \approx 416.3$), the same degree of polymerization discussed before, n_w should be less than $9.20 \times 10^{-3} \text{ mol\%}$. Careful removal of water is understood to be the key point.

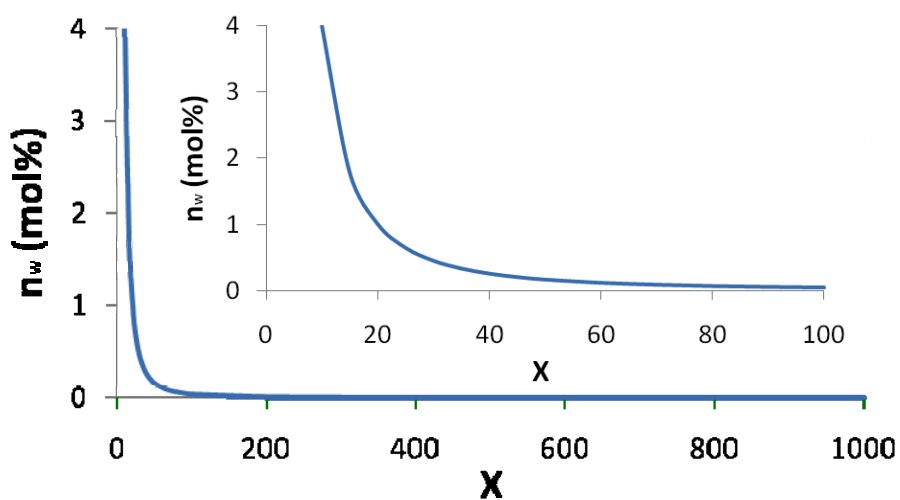
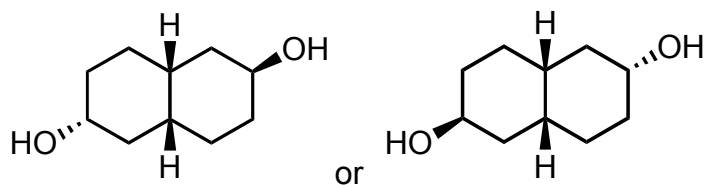


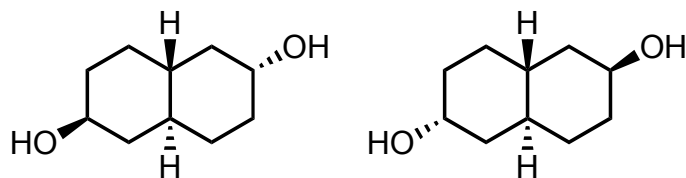
Figure 1. Relation between the (number-average) degree of polymerization X and the amount of residual water n_w

Problem 24

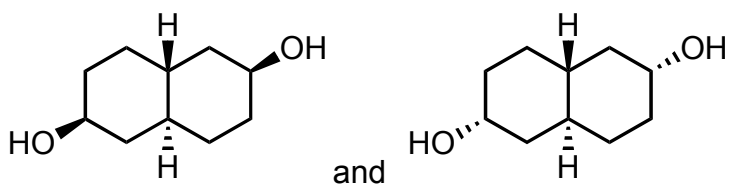
a)



b)

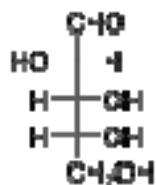


c)

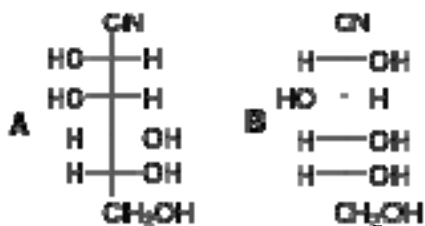


Problem 25

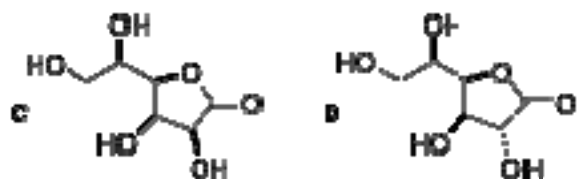
a)



b)

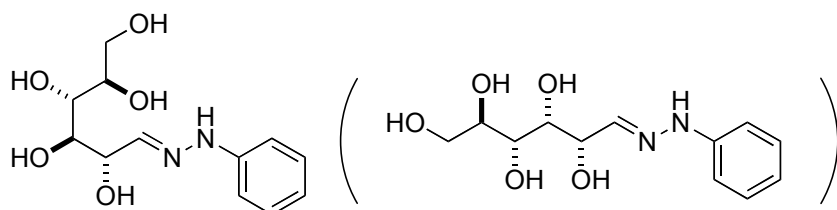


c)

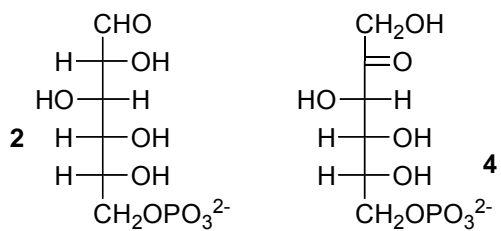


Problem 26

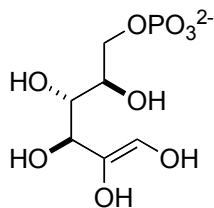
a)



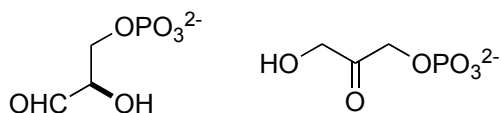
b)



c)



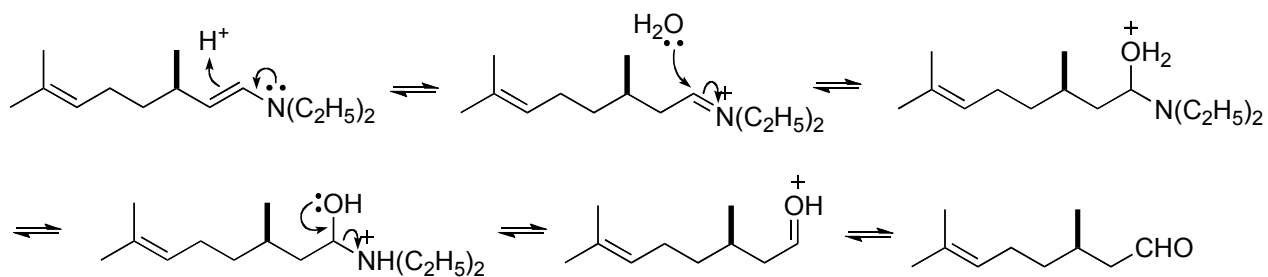
d)



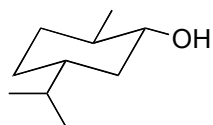
Problem 27

a) E, H

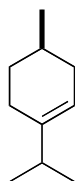
b)



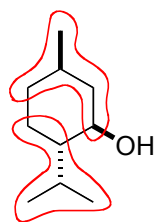
c)



d)

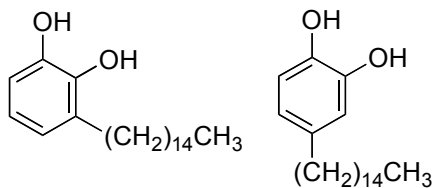


e)

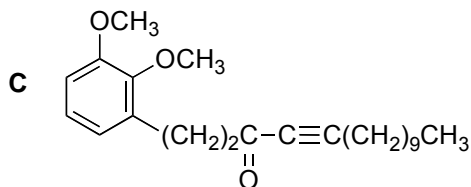
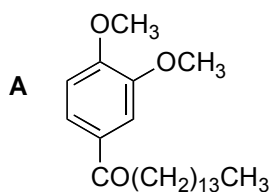


Problem 28

a)



b)

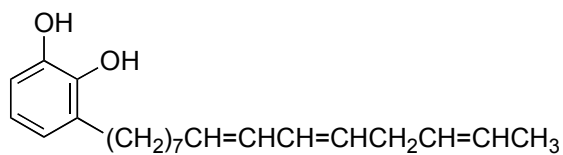
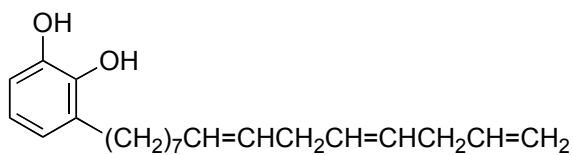
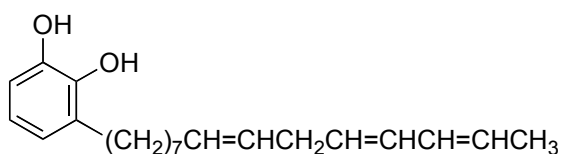
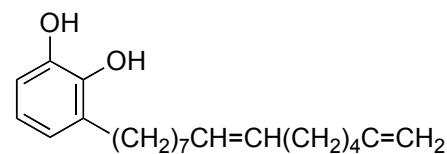


c) **E** CH₃CHO

F CO₂

G CH₃COOH

d)

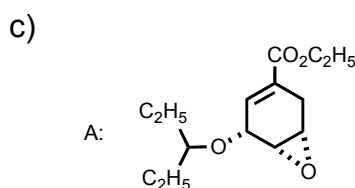
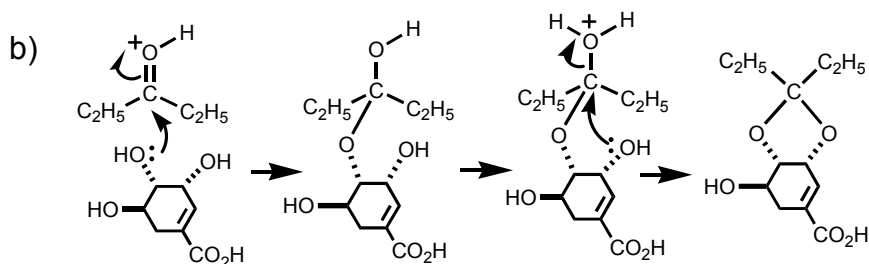


etc

Problem 29

a) **a:** EtOH / SOCl₂ **b:** 3-pentanone / H⁺ **c:** MeSO₂Cl / Et₃N

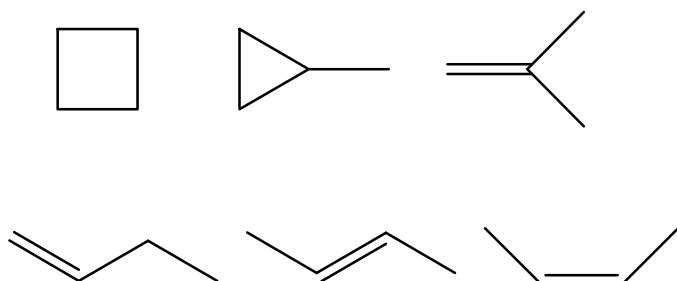
d: NaHCO_3 e: $\text{NaN}_3 / \text{NH}_4\text{Cl}$ f: $\text{NaN}_3 / \text{NH}_4\text{Cl}$



d) 8 isomers

Problem 30

a)



b) All the protons in this isomer are magnetically equivalent. Thus, the answer is cyclobutane.

c) This isomer has only two magnetically non-equivalent protons without spin-spin coupling. Thus, the answer is methylpropene (or isobutene, isobutylene). The numbers of two non-equivalent protons in methylpropene are two and six. Thus, the intensity ratio = $6/2 = 3$ (or $2/6 = 1/3$).

Problem 31

a) [18]Annulene has 6 H_{in} and 12 H_{out} . Therefore, the larger resonance at 9.3 ppm can be



assigned to H_{out} , while the smaller resonance at -3.0 ppm can be assigned to H_{in} .

$$\text{Thus, } A(9.3 \text{ ppm})/A(-3.0 \text{ ppm}) = 12/6 = 2$$

Note:

The ring current from the aromatic 18π system of [18]annulene enhances the magnetic field outside the ring and diminishes the field inside the ring. This phenomenon is also responsible for the clear peak assignments. The downfield peaks (9.3 ppm) and the upfield peaks (-3.0 ppm) are assigned to H_{out} and H_{in} , respectively.

- b) The conformational mobility of [18]annulene allows the exchange of H_{in} and H_{out} by ring inversion. At 213 K, the slow exchange of H_{in} and H_{out} does not show any effect on the NMR spectra. Therefore, the H_{in} and H_{out} resonances are observed at -3.0 ppm and 9.3 ppm, respectively. In contrast, at 383 K, this exchange occurs rapidly and repeatedly; therefore, the resonance is observed at the weighted average of the chemical shifts of H_{in} and H_{out} .
- c) $[9.3 \text{ ppm} \times 12 + (-3.0 \text{ ppm}) \times 6] / [12 + 6] = 5.2 \text{ ppm}$
Notice the difference in the numbers of H_{in} and H_{out} .



Solutions of Practical Problems

Problem 32

- When the PVSK poly anion aqueous solution is added to the Zeph cation aqueous solution, both ions associate quantitatively through electrostatic interaction and yield nonpolar ion pair species. In the early stage of titration with a large amount of free Zeph cations (known as a surfactant), the ion pairs are surrounded by Zeph cations to form cationic micelles. Near the equivalence point, the solution becomes cloudy due to generation of a precipitate of aggregates of the ion pairs, since the amount of free Zeph cations is not sufficient to maintain the micelles.

Beyond the equivalence point, when an excessively large number of PVSK anions is present in the solution, the solution becomes clear again, since the ion pairs are surrounded by PVSK anions and can be dispersed into the solution once more as anionic colloids.

Problem 33

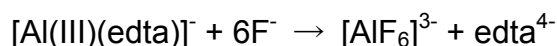
- It makes it possible to avoid the formation of Al(III)-hydroxyl complex ions upon a reaction between EDTA and Al^{3+} .

In this procedure, all Al^{3+} and Zn^{2+} in the sample solution should be reacted with EDTA to obtain the total metal content using the back titration technique in step 1-2. To this end, adjusting the pH of the solution to around 5.5 is required to allow a quantitative reaction between Zn^{2+} and EDTA. At around pH 5.5, on the other hand, formation of an Al(III)-EDTA chelate complex is considerably suppressed by the formation of various Al(III)-hydroxyl complex ions, and the formation of the Al(III)-EDTA chelate complex would be incomplete (Al^{3+} forms various highly stable hydroxyl complex ions, even in weakly acidic media). Multi-nuclear complexes such as $[\text{Al}_2(\text{OH})_2]^{4+}$ or $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$, especially, which are kinetically highly inert, are formed at pH 4 or above. In fact, only a limited amount of the Al(III)-EDTA chelate complex could be expected to be formed in this pH region in a reaction at room temperature. Al^{3+} must therefore be reacted with EDTA under boiling conditions after the pH is carefully adjusted to less than 4.

Hence, a lower aluminum content would be estimated due to incomplete formation of Al(III)-EDTA chelate if the pH of the sample solution was adjusted to pH 5.5 in one step.



2. Ammonium fluoride is used for the quantitative recover of Al^{3+} from the Al(III)-EDTA chelate complex. Fluoride ions react readily with aluminum ions to create a highly stable complex, $[\text{AlF}_6]^{3-}$. Adding a large amount of ammonium fluoride to the titration mixture and heating result in a quantitative exchange of EDTA ligands in the Al(III)-EDTA chelate with fluoride ions, as follows:



(The change in color of the XO indicator upon heating indicates that the free EDTA was released from the Al(III)-EDTA chelate complex by the reaction.)

Hence, the contents of Al^{3+} in the mixture can be determined by titrating the released free EDTA ligands with the Zn^{2+} standard solution.

3. The total molar amount of Al^{3+} and Zn^{2+} in a 10 mL sample solution is given by equation 33-1:

$$\text{Al}^{3+} + \text{Zn}^{2+} [\text{mol}] = 0.01 [\text{mol L}^{-1}] \times f_{\text{edta}} f_{\text{Zn}} \times (6.00 - A) [\text{mL}] \times 0.001 \quad (\text{eq. 33-1})$$

where f_{edta} and f_{Zn} are the factors for the standard solutions of 0.01 mol L^{-1} EDTA and 0.01 mol L^{-1} Zn^{2+} used, respectively.

The concentration of Al^{3+} in the sample solution is given by equation 33-2:

$$\text{Conc. of Al}^{3+} [\text{mol}] = 0.01 [\text{mol L}^{-1}] \times f_{\text{Zn}} \times B [\text{mL}] \times 0.001 / 0.010 [\text{L}] \quad (\text{eq. 33-2})$$

The concentration of Al^{3+} in the sample solution is given by equation 33-3:

$$\begin{aligned} \text{Conc. of Zn}^{2+} [\text{mol}] = & 0.001 \times 0.01 [\text{mol L}^{-1}] \times f_{\text{Zn}} \{ f_{\text{edta}} (6.00 - A) [\text{mL}] \\ & - 0.01 [\text{mol L}^{-1}] \times B [\text{mL}] \} / 0.010 [\text{L}] \end{aligned} \quad (\text{eq. 33-3})$$



Problem 34

- $\text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}_2 \rightarrow \text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$
- (weight of urea [g]/60.06 [g mol⁻¹]) X 94.07 [g mol⁻¹]

Problem 35

I. TLC results

- Dye **A** (rhodamine B) is red, dye **B** (brilliant blue) is blue and dye **C** (berberine chloride) is yellow.
- Judging from their structural formulae, dyes **A** and **B** have relatively larger numbers of dissociable sites than dye **C**. Obviously, dye **A** comprises cationic molecules and dye **B** anionic molecules, on the whole. Dye **C** also comprises cationic molecules but it should have weaker hydrophilicity than the others.

The TLC results indicate that (1) the red dye is strongly retained on the cation-exchange plate, (2) the blue dye is strongly retained on the anion-exchange plate, and (3) the yellow dye is strongly retained on both the cation-exchange and ODS-modified plates.

The conclusion entered in answer 2 was reached based on these observations.

II. Absorption spectra

- According to the Beer–Lambert law, the absorbance, A , is given by following formula:

$$A = \varepsilon [\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}] c [\text{mol dm}^{-3}] l [\text{cm}]$$

The molar absorption coefficient of the dye at 545 nm is:

$$\begin{aligned} \varepsilon &= 0.380 / (3.30 \times 10^{-6} [\text{mol dm}^{-3}] \times 1.0 [\text{cm}]) \\ &= 1.15 \times 10^5 [\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}] \\ &= 1.15 \times 10^4 [\text{m}^2 \text{mol}^{-1}] \end{aligned}$$

- According to Beer–Lambert law, the relationship between % transmittance and absorbance is given as follows:

$$\%T = 10^{-A} \times 100$$

Hence, the % T for the original dye solution, is 41.7 % and 79.4% at 545 and 503 nm, respectively.



When the concentration of dye is decreased to 50%, on the other hand, the absorbance will be decreased to 50%, since absorbance is proportional to the concentration of the species which absorbs the light. Hence, the absorbance will be 0.190 and 0.0500 at 545 and 503 nm respectively, and the %*T* calculated from the absorbance will be 64.6% and 89.1% at 545 and 503 nm, respectively.

Thus, by diluting the dye solution by 50%, the intensity of the transmitted light is increased by 1.55-fold and 1.12-fold at 545 nm and 503 nm, respectively. The above results suggest that wavelengths that show larger absorptivity are more sensitive to changes in the concentrations of species that absorb the light.

3. Since absorbance is proportional to the absorption pass length, when the pass length is increased 3-fold, the absorbance will be increased 3-fold. Hence, the absorbance will be 1.14, and the %*T* calculated from the absorbance will be 7.24 %.

Problem 37

1. Assume the weighed amounts of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (FW = 287.56 [g mol⁻¹]) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (FW = 278.01) to be *x* and *y* g, respectively. Since all Zn ions are converted to ZnFe_2O_4 (FW = 241.09 [g mol⁻¹]), the amount of

ZnFe_2O_4 produced is $\frac{x}{287.56} \times 241.09$ [g].

The amount of Fe consumed in the formation of ZnFe_2O_4 is $\frac{2x}{287.56}$ [mol]

The amount of Fe ions converted to Fe_3O_4 (FW = 231.55 [g mol⁻¹]) is

$$\left(\frac{y}{278.01} - \frac{2x}{287.56} \right) \text{ (mol)}.$$

Thus, the amount of Fe_3O_4 produced is $\left[\left(\frac{y}{278.01} - \frac{2x}{287.56} \right) \times \frac{231.55}{3} \right]$ (g).

The total theoretical yield of the ferrites is consequently

$$\left[\left(\frac{y}{278.01} - \frac{2x}{287.56} \right) \times \frac{231.55}{3} + \left(\frac{x}{287.56} \times 241.09 \right) \right] \text{ (g)}$$



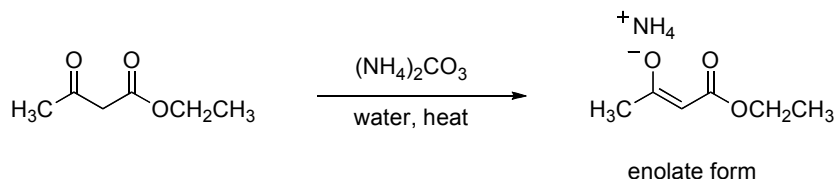
3. Both the species can be detected by coloring test reactions. For Fe(II) ions, addition of a 4,4'-bipyridine or 1,10-phenanthroline solution gives a characteristic red color. For Zn(II) ions, addition of a zincon (1-(2-hydroxycarbonyl-phenyl)-5-(2-hydroxy-5-sulfophenyl)-3-phenylformazan, sodium salt) shows a blue color. Masking of the iron species is necessary for detection of Zn.
4. Cu^{2+} , Mg^{2+} , Ni^{2+}

Problem 38

- (3) Yes. Poly(ethylene imine hydrochloride) (PEI) behaves as a polycation in an aqueous solution, where a polymer chain is positively charged like poly(allyamine hydrochloride). When the PEI solution is mixed with a solution of a polyanion such as poly(sodium 4-styrenesulfonate), a polymer – polymer complex is formed, and a precipitation is observed.

Problem 39

2. $1/2 \times (\text{weight of ethyl acetoacetate [g]}/130.1 [\text{g mol}^{-1}]) \times 253.3 [\text{g mol}^{-1}]$
5. Ethyl acetoacetate becomes more water soluble in its enolate form produced under basic conditions.



6. It is a carbon of formaldehyde generated in water, which is originally from a methylene carbon in hexamine.

Problem 40

1. $(\text{weight of 4-tert-butylcyclohexanone [g]}/154.2 [\text{g mol}^{-1}]) \times 156.2 [\text{g mol}^{-1}]$
4. D