**Dartmouth College**

Illustrative Chemistry Placement test questions and their solutions

As the following examples illustrate, the Chemistry Placement test is, in the main, not a multiple-choice examination, but rather, it consists of a collection of short problems that provide the student an opportunity to display her or his problem-solving abilities. On such questions, major partial credit is awarded for the development of an approach that will lead to a successful answer. So, make sure that your answer shows clearly the approach you are using to solve the problem.

The solutions to these questions are provided, not only for you to check your answers, but also to indicate the depth of answer that is expected. You should not be surprised to find that the depth of understanding expected in your answers to these questions sometimes goes beyond that expected in high school.

To be awarded credit for Chemistry 5, a student must score at least 65% on the Chemistry Placement test.

You will be provided with an information sheet similar to the one included below.

**Information sheet**

\[ R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \]

\[ N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1} \]

\[ g = 9.8066 \text{ m s}^{-2} \quad F = 96,485 \text{ C (mol electrons)}^{-1} \]

\[ 1 \text{ atm} = 760 \text{ torr} = 760 \text{ mm Hg} \quad T(\text{K}) = T(\circ \text{C}) + 273 \quad 1 \text{ L atm} = 101.3 \text{ J} \]

\[ 1 \text{ kg m}^2 \text{s}^{-2} = 1 \text{ V C} \quad 1 \text{ A} = 1 \text{ C s}^{-1} \quad 1 \text{ m}^3 = 1000 \text{ L} \]

For the general reaction: \( aA + bB \rightleftharpoons cC + dD \) \( K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \)

If the initial amounts of \( A, B, C, \) and \( D \) are \( n_A^0, n_B^0, n_C^0, \) and \( n_D^0, \) then

\[ \xi = \frac{n_A^0 - n_A}{a} = \frac{n_B^0 - n_B}{b} = \frac{n_C^0 - n_C}{c} = \frac{n_D^0 - n_D}{d} \]

For the reaction of acid \( HA: \) \( HA + H_2O \rightleftharpoons A^- + H_3O^+ \) \( K_a = \frac{[H_3O^+][A^-]}{[HA]} \)

\[ \text{pH} = -\log_{10} [H_3O^+] \quad K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \]

\[ \text{pH} = pK_a + \log_{10} \frac{[A^-]}{[HA]} \quad pK_a = -\log_{10} K_a \]

For the quadratic equation \( ax^2 + bx + c = 0, \) the solutions are:

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]
\[ P_i = X_i P_i^0 \] (Raoult's Law)

\[ P V = n R T \quad E = (3/2) n R T \]

\[ C_p - C_v = R \quad \text{Ideal monatomic gas: } C_v = (3/2) n R; \quad C_p = (5/2) n R \]

\[ \Delta E = q + w \quad H = E + PV \quad G = H - TS \quad q_p = \Delta H \]

\[ q_v = \Delta E \quad q_x = C_x \Delta T \quad (x = P \text{ or } V) \quad w = - \int P \, dV \]

\[ w = -n R T \ln \left( \frac{V_2}{V_1} \right) \quad \Delta S = n R \ln \left( \frac{V_2}{V_1} \right) \quad dS = \frac{dq_{rev}}{T} \]

\[ dS = C_x \, d\ln T \quad (x = P \text{ or } V) \quad \Delta G = \Delta G^0 + RT \ln Q \quad (Q = \text{reaction quotient}) \]

\[ \Delta G^0 = -RT \ln K \quad \ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^0}{R} \left\{ \frac{1}{T_2} - \frac{1}{T_1} \right\} \quad Q = 1 \text{ t} \]

\[ \Delta E = \Delta E^0 - \frac{R T}{n F} \log_{10} Q \]
**Thermodynamic Data at 298 K**

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_f^o$ (kJ mol$^{-1}$)</th>
<th>$S^o$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(g)</td>
<td>217.96</td>
<td>114.60</td>
</tr>
<tr>
<td>H$_2$(g)</td>
<td>0.0</td>
<td>130.57</td>
</tr>
<tr>
<td>H$^+$ (aq)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H$_3$O$^+$ (aq)</td>
<td>−285.83</td>
<td>69.61</td>
</tr>
<tr>
<td>C(s, graphite)</td>
<td>0.0</td>
<td>5.74</td>
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<tr>
<td>C(s, diamond)</td>
<td>1.895</td>
<td>2.377</td>
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<tr>
<td>C(g)</td>
<td>716.682</td>
<td>157.99</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>−74.81</td>
<td>186.15</td>
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<tr>
<td>C$_2$H$_2$(g)</td>
<td>226.73</td>
<td>200.83</td>
</tr>
<tr>
<td>C$_2$H$_4$(g)</td>
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<td>219.45</td>
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<tr>
<td>C$_2$H$_6$(g)</td>
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<tr>
<td>C$_6$H$_6$(g)</td>
<td>82.93</td>
<td>269.2</td>
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<td>C$_6$H$_6$(l)</td>
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<td>CO(g)</td>
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<td>CO$_2$(g)</td>
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<td>CH$_3$OH(g)</td>
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<td>CH$_3$OH(aq)</td>
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<td>N(g)</td>
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<td>H$_2$O(g)</td>
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<tr>
<td>H$_2$O$_2$(aq)</td>
<td>−191.17</td>
<td>143.9</td>
</tr>
</tbody>
</table>

**Standard Electrode Potentials at 298 K and 1 atm**

(All species are in aqueous solution unless otherwise indicated)

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>$E^o$(volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^+$ + e$^-$ → Cu(s)</td>
<td>0.522</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2 e$^-$ → Cu(s)</td>
<td>0.340</td>
</tr>
<tr>
<td>Cu$^{2+}$ + e$^-$ → Cu$^+$</td>
<td>0.158</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{H}_2(\text{g}) & 0.000 \\
\text{Zn}^{2+} + 2 \text{e}^- & \rightarrow \text{Zn}(\text{s}) & -0.763
\end{align*}
\]
Question 1
A first-year chemistry student learns how aspirin is synthesized and decides to try out the synthesis in her basement laboratory. She obtains 6.22 g of salicylic acid and an excess of acetic acid and runs the following reaction

\[
\text{HOC}_6\text{H}_4\text{COOH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOC}_6\text{H}_4\text{COOH} + \text{H}_2\text{O}
\]

salicylic acid acetic acid aspirin

(a) The molecular weight of aspirin is 180.16 g mol\(^{-1}\). Calculate the maximum mass of aspirin the student could synthesize.

(b) The student collected and purified her aspirin product and wanted to calculate the yield of the reaction. Unfortunately her balance was broken, but her pH meter was in working condition. She dissolved all her product in 1.00 L of water and found that the solution had a pH = 3.19. Calculate her yield, expressed as a percentage of her maximum yield from part (a). You will also need to know that aspirin's \(K_a = 2.75 \times 10^{-5}\).

Question 2
Methanol (CH\(_3\)OH) can be made by passing CO and H\(_2\) at high temperature over a catalyst according to

\[
\text{CO(g)} + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH(g)}.
\]

If 1.00 mol of CO(g) and 2.00 mol of H\(_2\)(g) are introduced over the catalyst at 500 K and at a constant pressure of 1.00 atm, calculate the equilibrium number of moles of CH\(_3\)OH(g) that will be formed. At 500 K, \(K_P = 6.23 \times 10^{-3}\) for this reaction. To simplify your algebra, note that the small value of \(K_P\) indicates that at equilibrium, only a small fraction of the reaction mixture will be methanol.

Question 3
4.52 g of silver sulfate, Ag\(_2\)SO\(_4\), is dissolved in water. Hydrogen sulfide gas (H\(_2\)S) is bubbled through the solution, which causes insoluble silver sulfide Ag\(_2\)S(s) to precipitate from solution according to the net reaction

\[
2\text{Ag}^+(aq) + \text{H}_2\text{S(g)} \rightarrow \text{Ag}_2\text{S(s)} + 2\text{H}^+(aq).
\]

The Ag\(_2\)S is gathered, dried and weighed. The solution left behind is now boiled to remove the last traces of dissolved, excess H\(_2\)S. Next, an excess of a solution of barium nitrate, Ba(NO\(_3\))\(_2\), is added to the solution. A white solid precipitates, which subsequent analysis proves to be a compound containing 58.84% Ba, 13.74% S, and 27.42% O by mass.

(a) Show that the analysis data of the second solid are consistent with the molecular formula BaSO\(_4\).

(b) What are the ions left in solution once the two precipitated solids have been removed?
Question 4
Calculate the concentrations of $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ needed to prepare a pH = 7.40 buffer solution that has a total phosphate concentration ($[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}]$) of 0.100 M. ($\text{H}_2\text{PO}_4^-$ has a $pK_a = 7.18$).

Question 5
The combustion of either hydrazine ($\text{N}_2\text{H}_4$ (l)) or ammonia ($\text{NH}_3$ (g)) results in the formation of $\text{N}_2$ (g) and $\text{H}_2\text{O}$ (l) under standard conditions. Calculate the standard enthalpy of combustion ($\Delta H^\circ_{\text{combust}}$) for each compound, and use these numbers to determine which compound would make a better rocket fuel per mole of compound.

Question 6
Your company makes polyethylene products and you are investigating a plan to use excess ethylene gas ($\text{C}_2\text{H}_4$ (g)) to make benzene ($\text{C}_6\text{H}_6$ (l)) according to the reaction

$$3\text{C}_2\text{H}_4(g) \rightleftharpoons \text{C}_6\text{H}_6(l) + 3\text{H}_2(g).$$

The benzene could be sold, and hydrogen gas, $\text{H}_2$ (g), could be used to provide power at the plant.

Calculate a value of the equilibrium constant for this reaction at 1000 °C.

Question 7
If atmospheric pressure is equal to 1.000 atm it can support a column of Hg which is 760.0 mm tall. Suppose a column of Hg is set up where the bath is open to the atmosphere, and the column height of Hg is 760.0 mm with the top of the enclosed column being a vacuum. Next, suppose some diethyl ether (a volatile liquid) is injected into the top of the vacuum above the Hg column such that the saturation vapor pressure of diethyl ether is achieved. Now, instead of a vacuum at the top of the column, there is the diethyl ether vapor, then a layer of diethyl ether liquid, and then the Hg column. At 25.00 °C the vapor pressure of diethyl ether ($\text{C}_4\text{H}_{10}\text{O}$) is 442 mm Hg.

(a) At 25.00 °C, what would be the new column height of Hg present?

(b) Suppose that $10.00 \times 10^{-3}$ moles of diethyl ether had been injected in part (a), and that $3.000 \times 10^{-3}$ moles of decane (a liquid) are then injected to the top of the column.

(i) Assuming that the number of moles in the vapor phase is small compared to that in the liquid phase, calculate the mole fraction composition of the liquid solution above the Hg column at 25.00 °C.

(ii) The vapor pressure of decane ($\text{C}_{10}\text{H}_{22}$) at 25.00 °C is 1.800 mm Hg. Calculate the composition of the vapor in equilibrium with the solution of part (i). You may assume that both components obey Raoult's Law.

(iii) Calculate the total vapor pressure above the Hg column.
(iv) In light of your answer to part (iii) what would the new height of the Hg column be?

Question 8
One mole of an *ideal, monatomic gas* is put through the following *reversible* processes. In each case the initial state of the gas is at a temperature of 298 K and a pressure of 1 atm.

(a) For each of the following three processes, determine $q$, $w$, $\Delta E$, $\Delta H$ and $\Delta S$.

(i) cooling to 248 K at constant volume

(ii) isothermal (constant T) compression to 50.0 atm

(iii) heating at constant pressure to 323 K.

(b) For which of the processes could one use $\Delta G = \Delta H - T \Delta S$? *State your reasoning.*

Question 9
A zinc-copper battery is constructed as follows:

\[
\text{Zn} / \text{Zn}^{2+} (0.10 \text{ M}) \parallel \text{Cu}^{2+} (2.50 \text{ M}) / \text{Cu}.
\]

The temperature is held constant at 298 K and, initially, the mass of each of the two metal electrodes is 200 g.

(i) What is the cell potential when the battery is first connected?

(ii) Calculate the cell potential after 10.0 A of current has flowed for 10.0 hours? (Assume that each half cell contains 1.00 L of solution).

(iii) Calculate the mass of the metal at the cathode after 10.0 hours.

(iv) If the mass of the anode is the limiting factor, how long can this battery deliver a current of 10.0 A before it goes dead?
Question 10
Consider a solution which has concentrations of [Pb\(^{2+}\)] = 0.01 M and [Ag\(^{+}\)] = 0.01 M. Suppose that a sodium chloride solution is slowly dripped into this mixture. K\(_{sp}\) (PbCl\(_2\)) = 1.6 × 10\(^{-6}\) and K\(_{sp}\) (AgCl) = 1.8 × 10\(^{-10}\).

(i) Write out expressions for each of the two equilibrium constants given above.

(ii) Which salt precipitates first, and what is the minimum chloride ion concentration required for this to happen?

(iii) What is the concentration left in solution of the cation of the salt in part (ii) when the chloride salt of the second cation begins to precipitate?

(iv) Suppose that just enough chloride has been added so that everything has equilibrated. Next, a few mLs of a rather concentrated solution of Hg\(^{+}\) are added to the solution. Given that K\(_{sp}\) (Hg\(_2\)Cl\(_2\)) is approximately 1 × 10\(^{-18}\), would you expect the number of grams of AgCl(s) to (check one)

(a) ______ increase  (b) ______ decrease  (c) ______ stay the same?

Explain your reasoning.
Solutions to Sample Questions

Question 1
(a) Because acetic acid is present in excess, the maximum number of moles of aspirin that can be produced is limited by the number of moles of salicylic acid.

The number of moles of salicylic acid = \( \frac{6.22 \text{ g}}{138.12 \text{ g mol}^{-1}} \) = 0.045 mol.

Thus, from the stoichiometry of the reaction, the maximum number of moles of aspirin that can be produced = 0.045.

Maximum mass of aspirin that can be produced = (0.045 mol) (180.16 g mol\(^{-1}\)) = 8.11 g

(b) If we denote aspirin as the acid HA, then the reaction with water is:

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+
\]

That is, in aqueous solution some HA will dissociate to A\(^-\).

The equilibrium constant, K\(_a\), for this acid dissociation is given by:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = 2.75 \times 10^{-5}
\]

So, if we can determine \([\text{A}^-] = [\text{H}_3\text{O}^+]\), we can obtain the amount of HA that was dissolved in 1.00 L of water.

From the pH of the solution, \([\text{H}_3\text{O}^+] = 10^{-3.19} = 6.46 \times 10^{-4} \text{ M}\).

Let \(C_0\) = the initial concentration of aspirin (HA) -- i.e. the concentration of HA before any dissociation to A\(^-\) has taken place.

Then, at equilibrium \([\text{H}_3\text{O}^+] = [\text{A}^-] = 6.46 \times 10^{-4} \text{ M}\) (these were produced from HA), and \([\text{HA}] = C_0 - [\text{A}^-] = C_0 - 6.46 \times 10^{-4} \text{ M}\).

Thus,

\[
\frac{(6.45 \times 10^{-4} \text{ M})^2}{C_0 - 6.45 \times 10^{-4} \text{ M}} = 2.75 \times 10^{-5}
\]

Solving for \(C_0\), we obtain \(C_0 = 0.0158 \text{ M}\). Thus, in 1.00 L of water there are 0.0158 moles of aspirin.

Mass of aspirin in 1.00 L of water = (0.0158 mol) (180.16 g mol\(^{-1}\)) = 2.88 g.

Thus, the percentage yield is \(\frac{2.88}{8.11} \times 100\% = 35.5\%\).
**Question 2**

Let $P_{tot}$ be the total gas pressure, and $P_{CH_3OH}$, $P_{CO}$, and $P_{H_2}$ be the partial pressures of CH$_3$OH, CO, and H$_2$, respectively. Then, at 500 K

$$KP = \frac{P_{CH_3OH}}{P_{CO} P_{H_2}^2} = 6.23 \times 10^{-3}$$

The partial pressure $P_i = X_i P_{tot}$, where $X_i$ is the mole fraction of species $i$. Here $n_i$ is the number of moles of species $i$ and $n_{tot}$ is the total number of moles. The expression for $KP$ can then be written in the equivalent forms:

$$KP = \frac{X_{CH_3OH}}{X_{CO} X_{H_2}^2 P_{tot}^2} = \frac{n_{CH_3OH} n_{tot}^2}{n_{CO} n_{H_2}^2 P_{tot}^2} = 6.23 \times 10^{-3}.$$ 

We can define the extent of reaction, $\xi$, in any of the following equivalent ways:

$$\xi = \left( n_{CO}^o - n_{CO} \right) = \left( \frac{n_{H_2}^o - n_{H_2}}{2} \right) = \left( n_{CH_3OH} - n_{CH_3OH}^o \right)$$

with $n_{CH_3OH}^o = 0$, $n_{CO}^o = 1.00$ mol, $n_{H_2}^o = 2.00$ mol.

Thus, $n_{CO} = 1.00 - \xi$, $n_{H_2} = 2.00 - 2\xi$, $n_{CH_3OH} = \xi$, and $n_{tot} = 3.00 - 2\xi$. Using these expressions in $KP$ gives:

$$KP = 6.23 \times 10^{-3} = \frac{\xi \left( 3.00 - 2\xi \right)^2}{\left( 1.00 - \xi \right) \left( 2.00 - 2\xi \right)^2} \approx \frac{9\xi}{4} \quad \text{since} \quad \xi \quad \text{is small.}$$

Solving for $\xi$ yields $\xi = n_{CH_3OH} = \frac{4 KP}{9} = 2.77 \times 10^{-3}$ mol = 2.77 mmol.

**Question 3**

(a) 1 mole of BaSO$_4$ has a mass of (1 mol) (233.3876 g mol$^{-1}$) = 233.4 g. This mass has 1 mol of Ba (with mass 137.3 g), 1 mol of S (with mass 32.06 g) and 4 mol of O (with mass 4 $\times$ 16.00 g = 64.00 g). Thus, the mass fractions are:

For Ba: $\frac{137.33 \text{ g}}{233.4 \text{ g}} = 0.5884 = 58.84\%$ Ba

For S: $\frac{32.06 \text{ g}}{233.4 \text{ g}} = 0.1374 = 13.74\%$ S

For O: $\frac{64.00 \text{ g}}{233.4 \text{ g}} = 0.2742 = 27.42\%$ O
as expected.

(b) The H₂S replaces Ag⁺ with H⁺; the Ba(NO₃)₂ replaces SO₄²⁻ with NO₃⁻; and since the barium nitrate was added in excess, there will also be Ba²⁺ in solution.

**Question 4**

The dissociation of H₂PO₄⁻ in water is described by the equation:

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+
\]

The equilibrium constant for this reaction is given by:

\[
K_a = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}
\]

Taking log₁₀ of both sides we obtain:

\[
\log_{10} K_a = \log_{10} [\text{H}_3\text{O}^+] + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}
\]

Noting that pKₐ = −log₁₀Kₐ and pH = −log₁₀ [H₃O⁺], this may be rewritten as:

\[
pH = pK_a + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}
\]

i.e. 7.40 = 7.18 + log₁₀ \( \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \)

Let \([\text{HPO}_4^{2-}] = x \text{ M; then } [\text{H}_2\text{PO}_4^-] = (0.100 - x) \text{ M. Thus,} \)

\[
0.22 = \log_{10} \frac{x}{(0.100 - x)} \quad \text{or} \quad \frac{x}{(0.100 - x)} = 10^{0.22} = 1.66
\]

Solving for x yields, \( x = [\text{HPO}_4^{2-}] = 0.0624 \text{ M} \)

and \([\text{H}_2\text{PO}_4^-] = (0.100 - 0.0624)\text{M} = 0.0376 \text{ M.} \)
Question 5
The first step is to write a balanced stoichiometric equation for each reaction.

\[ \text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O(\text{l})} \]

Note that the balanced reaction involves one mole of hydrazine.

For this reaction the standard enthalpy of combustion is given by:

\[ \Delta H_{\text{combust}}^0 = 2 \Delta H_f^0 (\text{H}_2\text{O(\text{l})}) - \Delta H_f^0 (\text{N}_2\text{H}_4(\text{l})) \]

\[ = 2 \text{ mol} \ (-285.83 \text{ kJ mol}^{-1}) - 1 \text{ mol} \ (50.63 \text{ kJ mol}^{-1}) = -622.3 \text{ kJ} \]

Thus, the standard enthalpy of combustion per mole of hydrazine is –622.3 kJ.

\[ 2 \text{NH}_3(\text{g}) + (3/2) \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3 \text{H}_2\text{O(l)} \]

Note that this balanced reaction involves two moles of ammonia.

\[ \Delta H_{\text{combust}}^0 = 3 \Delta H_f^0 (\text{H}_2\text{O(\text{l})}) - 2 \Delta H_f^0 (\text{NH}_3(\text{g})) \]

\[ = 3 \text{ mol} \ (-285.83 \text{ kJ mol}^{-1}) - 2 \text{ mol} \ (-46.11 \text{ kJ mol}^{-1}) = -765.3 \text{ kJ} \]

Thus, the standard enthalpy of combustion per mole of ammonia is –382.6 kJ.

Therefore, hydrazine is a better rocket fuel, since there is more heat released per mole.

Question 6
The approach here is to use the relation \( K = e^{-\Delta G^{\text{rxn}}/RT} \) and the thermodynamic data provided with the examination to calculate a numerical value for the equilibrium constant \( K \). This requires that we determine \( \Delta G_{\text{rxn}}^0 = \Delta H_{\text{rxn}}^0 - T \Delta S_{\text{rxn}}^0 \). From the thermodynamic data provided, we can calculate \( \Delta H_{\text{rxn}}^0 \) and \( \Delta S_{\text{rxn}}^0 \).

\[ \Delta H_{\text{rxn}}^0 = n_{\text{C}_6\text{H}_6} \Delta H_f^0 (\text{C}_6\text{H}_6(\text{l})) - n_{\text{C}_2\text{H}_4} \Delta H_f^0 (\text{C}_2\text{H}_4(\text{g})) \]

\[ = 1 \text{ mol} \ (49.03 \text{ kJ mol}^{-1}) - 3 \text{ mol} \ (52.26 \text{ kJ mol}^{-1}) = -107.75 \text{ kJ} \]

\[ \Delta S_{\text{rxn}}^0 = n_{\text{H}_2} S^o (\text{H}_2(\text{g})) + n_{\text{C}_6\text{H}_6} S^o (\text{C}_6\text{H}_6(\text{l})) - n_{\text{C}_2\text{H}_4} S^o (\text{C}_2\text{H}_4(\text{g})) \]

\[ = 3 \text{ mol} \ (130.57 \text{ J mol}^{-1} \text{ K}^{-1}) + 1 \text{ mol} \ (172.8 \text{ J mol}^{-1} \text{ K}^{-1}) - 3 \text{ mol} \ (219.45 \text{ J mol}^{-1} \text{ K}^{-1}) \]

\[ = -93.84 \text{ J K}^{-1} \]

Thus, at 1000 °C,
\[ \Delta G_{\text{reaxn}}^0 = \Delta H_{\text{reaxn}}^0 - T \Delta S_{\text{reaxn}}^0 = -107.750 - 1273 \, \text{K} \left( -93.84 \, \text{J} \, \text{K}^{-1} \right) = 11,700 \, \text{J} \]

Using \( \Delta G_{\text{reaxn}}^0 \) in the expression for the equilibrium constant \( K \) yields

\[ K_{1273} = e^{\frac{- \Delta G_{\text{reaxn}}^0}{RT}} = e^{\frac{-11,700}{(8.3145)(1273)}} = 0.33. \]

**Question 7**

(a) The pressure from the diethyl ether vapor together with that from the new height of the Hg column must be balanced by atmosphere pressure -- i.e.

\[ (442 + \text{new height of Hg column}) \, \text{mm Hg} = 760 \, \text{mm Hg}. \]

\[ \therefore \text{new height of Hg column} = 318 \, \text{mm Hg}. \]

(b) Assuming that the number of moles in the vapor phase << the number of moles in the liquid phase, total number of moles in the liquid phase = 13.00 \times 10^{-3}.

Thus, the ether mole fraction in the liquid, \( X_{\text{ether}} = \frac{10.00 \times 10^{-3}}{13.00 \times 10^{-3}} = 0.7692 \)

Then the decane mole fraction, \( X_{\text{decane}} = 1 - X_{\text{ether}} = 1 - 0.7692 = 0.2308. \)

(c) Applying Raoult's law (see the information sheet) \( P_{\text{ether}} = X_{\text{ether}} \, P_{\text{ether}^0} \) and

\[ P_{\text{ether}} = 0.7692 \times 442 \, \text{mm Hg} = 340.0 \, \text{mm Hg}. \]

Similarly, \( P_{\text{decane}} = 0.2308 \times 1.8 \, \text{mm Hg} = 0.4154 \, \text{mm Hg}. \)

With these data in hand we can calculate the composition of the vapor.

The ether mole fraction in the vapor, \( Y_{\text{ether}} = \frac{P_{\text{ether}}}{P_{\text{total}}} = \frac{340 \, \text{mm Hg}}{340.4 \, \text{mm Hg}} = 0.9988 \)

and \( Y_{\text{decane}} = 1 - Y_{\text{ether}} = 1 - 0.9988 = 0.0012. \)

(d) \( P_{\text{total}} = P_{\text{ether}} + P_{\text{decane}} = 340.4 \, \text{mm Hg}. \)
(e) Using the approach followed in part (a),

\[(340.4 + \text{new height of Hg column}) \text{ mm Hg} = 760 \text{ mm Hg}\]

\[\therefore \text{new height of Hg column} = 419.6 \text{ mm Hg}.

Question 8

(i) The initial state of the gas is: 1 mole, \(T_i = 298\text{K}, P_i = 1 \text{ atm}, V_i\). After the reversible process is complete, the final state of the gas is 1 mole, \(T_f = 248\text{ K}, V_f = V_i, P_f = \text{unknown}\).

Since the volume of the gas does not change, \(\Delta V = 0\) and thus, \(w = 0\); no work is done by the gas or on the gas.

From information given with the examination, \(\Delta E = q_v = n \bar{C}_v \Delta T\). Here \(\bar{C}_v\) is the molar heat capacity at constant volume (= \(3R/2\) for a monatomic ideal gas).

Thus, \(\Delta E = (1.00 \text{ mol}) ((3 \times 8.314/2) \text{ J mol}^{-1} \text{ K}^{-1}) (248 \text{ K} - 298 \text{ K}) = -624 \text{ J}\).

From information given with the examination, \(\Delta H = q_p = n \bar{C}_p \Delta T\). Here \(\bar{C}_p\) is the molar heat capacity at constant pressure (= \(5R/2\) for a monatomic ideal gas).

Thus, \(\Delta H = (1.00 \text{ mol}) ((5 \times 8.314/2) \text{ J mol}^{-1} \text{ K}^{-1}) (248 \text{ K} - 298 \text{ K}) = -1039 \text{ J}\).

From information given with the examination, \(\Delta S = n \bar{C}_v \ln \left(\frac{T_f}{T_i}\right)\)

Thus, \(\Delta S = (1.00 \text{ mol}) ((3 \times 8.314/2) \text{ J mol}^{-1} \text{ K}^{-1}) \ln (248 \text{ K}/298 \text{ K}) = -2.29 \text{ J/K}\).

Note that it is incorrect to use the relation \(\Delta S = \frac{q_{rev}}{T}\) here, because the temperature does not remain fixed.

(ii) The initial state of the gas is: 1 mol, \(T_i = 298\text{K}, P_i = 1 \text{ atm}, V_i\). After the reversible, isothermal process is complete, the final state of the gas is 1 mol, \(T_f = 298\text{ K}, V_f = \text{unknown}, P_f = 50 \text{ atm}\).

Because the temperature is fixed, for an ideal gas \(\Delta E = 0\) and \(\Delta H = 0\).

In this case, the gas undergoes a decrease in volume and so work will be done on the gas to achieve such a reduction in volume.

Thus, \(w = -nRT \ln \left(\frac{V_f}{V_i}\right) = -nRT \ln \left(\frac{P_i}{P_f}\right)\). Here, since the gas is ideal and the temperature is fixed, \(\frac{V_f}{V_i} = \frac{P_i}{P_f}\).

\[\therefore w = -(1.00 \text{ mol}) (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (298 \text{ K}) \ln (1.00/50.00) = 9.69 \text{ kJ}\).

From the first law of thermodynamics, \(\Delta E = q + w\). Since \(\Delta E = 0\), \(q = -w = -9.69 \text{ kJ}\).

In this case, since the temperature remains constant, we may use \(\Delta S = \frac{q_{rev}}{T}\).
Thus, $\Delta S = \frac{(-9.69 \times 10^3 \ J)}{298 \ K} = -32.5 \ J \ K^{-1}$.

(iii) The initial state of the gas is: 1 mole, $T_i = 298 K$, $P_i = 1 \ atm$, $V_i$. After the reversible, constant pressure process is complete, the final state of the gas is 1 mole, $T_f = 323 K$, $V_f$ = unknown, $P_f = 1.00 \ atm$.

Following an analogous approach to that employed in parts (i) and (ii),

$\Delta H = q_p = n \overline{C_p} \Delta T = (1.00 \ mol) \left( \frac{5 \times 8.314}{2} \ J \ mol^{-1} \ K^{-1} \right) (323 \ K - 298 \ K)$

$= 520 \ J$;

$\Delta E = q_v = n \overline{C_v} \Delta T = (1.00 \ mol) \left( \frac{3 \times 8.314}{2} \ J \ mol^{-1} \ K^{-1} \right) (323 \ K - 298 \ K)$

$= 312 \ J$;

$w = \Delta E - q = 312 \ J - 520 \ J = -208 \ J$;

and $\Delta S = n \overline{C_p} \ln \left( \frac{T_f}{T_i} \right) = (1.00 \ mol) \left( \frac{5 \times 8.314}{2} \ J \ mol^{-1} \ K^{-1} \right) \ln (323/298 \ K)$

$= 1.67 \ J/K$.

(b) $\Delta G = \Delta H - T \Delta S$ could only be used for process (a) (ii), since use of this expression requires that $T$ remains fixed.

Question 9
(a) From the table of standard electrode potentials provided, the following half-cell reaction may be written:

$\text{Zn}^{2+}(aq) + 2 \ e^- \rightarrow \text{Zn(s)} \quad E^\circ = -0.763 \ V$ - note that Zn(s) is oxidized at the anode

$\text{Cu}^{2+}(aq) + 2 \ e^- \rightarrow \text{Cu(s)} \quad E^\circ = +0.340 \ V$ - note that Cu$^{2+}$ is reduced at the cathode

The equation for the net reaction is:

$\text{Cu}^{2+}(aq) + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(aq) \quad \Delta E^\circ = (0.340 - (-0.763)) = 1.103 \ V$

Here, $\Delta E^\circ$ is the standard potential difference. Also, note that 2 moles of charge are involved in the process.

From information provided, $\Delta E = \Delta E^\circ - \frac{R \ T}{n \ F} \ln Q = \Delta E^\circ - \frac{R \ T}{n \ F} \ln \left[ \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right]$,

where $F$, the Faraday, is the charge corresponding to 1 mole of electrons.
Thus, \[ \Delta E = 1.103 \text{ V} - \left( \frac{8.314 \text{ J mol}^{-1} \text{K}^{-1}}{2 \left( 96,485 \text{ C mol}^{-1} \right)} \right) \ln \left( \frac{0.10 \text{ M}}{2.50 \text{ M}} \right) \]

\[ = 1.103 \text{ V} + 4.13 \times 10^{-2} \text{ V} = 1.144 \text{ V}. \]

(b) The first step is to calculate the new concentrations of \( \text{Zn}^{2+} \) and \( \text{Cu}^{2+} \). We do this by calculating the change in the number of moles of \( \text{Zn}^{2+} \) and \( \text{Cu}^{2+} \) that result from passing a current of 10.0 A for 10 hours.

The total charge, \( Q \) (Coulombs), passed = Current \( I \) (A) \( \times \) Time \( t \) (s)

\[ \therefore Q = 10.0 \text{ (A)} \times 10.0 \text{ hr} \times 3600 \text{ s hr}^{-1} = 3.60 \times 10^5 \text{ C} \]

Thus, the number of moles of charge passed = \( (3.60 \times 10^5 \text{ C})/96,485 \text{ C mol}^{-1} \)

\[ = 3.73 \text{ moles}. \]

Since 2 moles of electrons are involved in the net reaction shown in part (a), the number of moles of \( \text{Cu}^{2+} \) consumed = \( (3.73/2) = 1.865 \text{ moles} \) = the number of moles of \( \text{Zn}^{2+} \) produced.

Initially, in a 1.00 L solution we had 2.50 moles of \( \text{Cu}^{2+} \) and 0.10 moles of \( \text{Zn}^{2+} \).

After 10 hours, \([\text{Cu}^{2+}] = (2.50 - 1.865) = 0.635 \text{ M}; [\text{Zn}^{2+}] = (0.10 + 1.865) = 1.965 \text{ M}\]

Thus, after 10 hours, \( Q = (1.965/0.635) = 3.09, \) and

\[ \Delta E = 1.103 \text{ V} - \left( \frac{8.314 \text{ J mol}^{-1} \text{K}^{-1}}{2 \left( 96,485 \text{ C mol}^{-1} \right)} \right) \ln (3.09) \]

\[ = 1.103 \text{ V} - 1.45 \times 10^{-2} \text{ V} = 1.09 \text{ V} \]

(c) \( \text{Cu(s)} \) is produced at the cathode. Charge passed produced 1.865 mole \( \text{Cu} \) at the cathode.

Mass of \( \text{Cu} \) produced at the cathode = \( 1.865 \text{ mol} \times 63.456 \text{ g mol}^{-1} = 118 \text{ g} \)

So, after 10 hours, cathode weighs (200 + 118) = 318 g.

(d) Here we need to calculate the time required to consume 200 g of \( \text{Zn} \). The mass of the \( \text{Zn} \) anode is equivalent to \( 200 \text{ g}/(65.39 \text{ g mol}^{-1}) \) moles of \( \text{Zn} \) -- i.e. 3.06 mol \( \text{Zn} \). Since 2 moles of electronic charge are required to consume 1 mole of \( \text{Zn} \), passage of 6.12 Faradays of charge will consume the \( \text{Zn} \) anode.
Time, $t$, required to consume the anode = \( \frac{\text{Charge, } Q, \text{ (C)}}{\text{Current, } I, \text{ (A)}} \)

= \( \frac{(6.12 \text{ Faradays})(96,485 \text{ C/Faraday})}{10.0 \text{ C/s}} \) = \( 5.9 \times 10^4 \text{ s} = 16.4 \text{ hrs} \)

**Question 10**

(a) \( K_{sp}(PbCl_2) = [Pb^{2+}] [Cl^-]^2; \quad K_{sp}(AgCl) = [Ag^+] [Cl^-] \).

(b) If \([Pb^{2+}] = 0.01 \text{ M}\), then from \( K_{sp}(PbCl_2) \), minimum chloride concentration required for PbCl_2 precipitation is given by

\[
[Cl^-] = \left( \frac{1.6 \times 10^{-6}}{0.01} \right)^{1/2} = 1.3 \times 10^{-2} \text{ M}. 
\]

Similarly, minimum chloride concentration required for AgCl precipitation is given by

\[
[Cl^-] = \left( \frac{1.8 \times 10^{-10}}{0.01} \right) = 1.8 \times 10^{-8} \text{ M}. 
\]

Thus, we expect AgCl to precipitate long before PbCl_2, and we need \([Cl^-] \geq 1.8 \times 10^{-8} \text{ M}\).

(c) From part(b), PbCl_2 will start to precipitate when \([Cl^-] = 1.3 \times 10^{-2} \text{ M}\). When \([Cl^-]\) reaches this level, \([Ag^+] = \left( \frac{1.8 \times 10^{-10}}{1.3 \times 10^{-2}} \right) = 1.4 \times 10^{-8} \text{ M}\).

(d) Since everything has come to equilibrium, each solid will have precipitated according to its \( K_{sp} \) value. Hg_2Cl_2 with a \( K_{sp} \approx 10^{-18} \) is very, very insoluble. Thus, we expect that some Hg_2Cl_2(s) will appear; this will use up some of the free Cl\(^-\) in solution and, as a result, some of the more soluble salts (AgCl and PbCl_2) will dissolve slightly. Thus, the number of grams of AgCl(s) would be expected to decrease.