CM1401* (Practice Questions)

NUS Chemical Sciences Society Editorial Team

Disclaimer: This set of practice questions is designed to complement your personal practice and revision only. It is NOT meant to simulate any part of the actual test/exam.

Physical Chemistry

1. The absolute potential of a redox reaction can be given as:

$$E_{abs} = E + E_{abs}(H^+/H)$$

where $E_{abs}(H^+/H)$ is the absolute potential of the H⁺/H couple and E is the redox potential against the standard hydrogen electrode. The following data are provided:

At 298K, $\Delta G_{aq}^{\circ}(H^{+}) = -1104.5 \text{ kJ mol}^{-1}$ $\Delta G_{f}^{\circ}(H) = +203.246 \text{ kJ mol}^{-1}$ $\Delta S^{\circ}(IE, H) = +16.968 \text{ J mol}^{-1} \text{ K}^{-1}$ $E^{\circ}(Fe^{2+}/Fe^{3+}) = +0.770 \text{ V}$

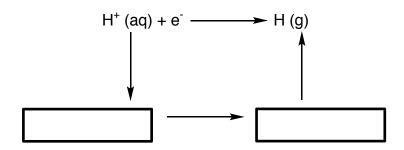
(a) Use the Bohr model to calculate the ionisation energy of H, $\Delta H(IE, H)$, in kJ mol⁻¹.

(b) Hence, find $\Delta G(IE, H)$.

(c) By considering the following Hess' Cycle or otherwise, determine ΔG for the reaction: $H^+(aq) + \, e^- \to H(g)$

Hence determine the potential for this reaction, $E_{abs}(H^+/H)$.

Hess' Cycle



(d) Use all the information above to calculate the **absolute** potential of a Fe³⁺/Fe²⁺ cell where [Fe²⁺] = 2 M, [Fe³⁺] = 0.5 M. If you are unable to produce a value from part (c), use $E_{abs}(H^+/H) = 4.22$ V. (Hint: the given cell is NOT at standard conditions!)

(15 marks)

- 2. CH₃COCH₃ reacts with I₂ under acidic condition to form CH₃COCH₂I. The reaction can be studied by monitoring the concentration of I₂ using UV-vis spectroscopy. I₂ absorbs radiation at 540 nm.
- (a) If the absorption at 540 nm is due to electronic transition between the HOMO and LUMO in I_2 , what is the energy gap between the two orbitals?

A student, Laurel, was tasked to analyse reaction mixtures **A** to **C**. She failed to label the printout of her results. The results were reported in arbitrary units.

Table 1 – Solutions that Laurel prepared.

Colutions	Volumes (mL)			
Solutions	1 M HCI	4 M CH ₃ COCH ₃	40 μM l ₂	DI H₂O
Α	1	1	1	2
В	1	1	2	1
С	2	1	1	1

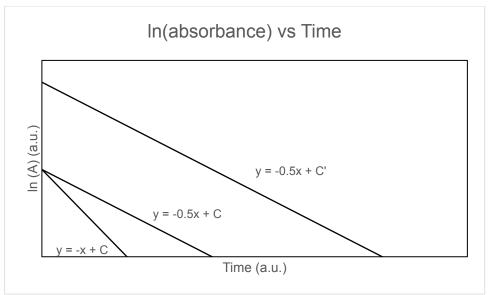


Figure 1 – Laurel's results printout.

Each graph corresponds to changes in In(Absorbance) for a particular solution over time. Label each graph with the solution it represents (**A**, **B** or **C**)

(c) Write down the relationship between C and C' in the equations of the graphs.

(d) What is the order of reaction with respect to I_2 ?

(e) The mechanism for the reaction is shown. Based on your answer to (d), identify which step (1, 2 or 3) is the slow step.

$$\stackrel{\circ}{ \longrightarrow} \stackrel{H}{ \longrightarrow} \stackrel{H}{ \longrightarrow} \stackrel{\oplus}{ \longrightarrow} \stackrel{H}{ \longrightarrow} \stackrel{\oplus}{ \longrightarrow} \stackrel{1}{ \longrightarrow} \stackrel{H}{ \longrightarrow} \stackrel{\oplus}{ \longrightarrow} \stackrel{1}{ \longrightarrow}$$

(15 marks)

3(a) Calculate the pH of a 0.26 M solution of HF (pK_a = 3.14).

(b) Clement is a life science student investigating a pH-dependent drug delivery system. He requires a buffer solution of pH 5.2 to test out his experimental procedure. Unfortunately, Clement has 100 mL of 0.100 M hydrochloric acid, solid sodium ethanoate and a lack of Chemistry knowledge. Given pK_a of ethanoic acid = 4.75, explain to Clement what mass of sodium ethanoate ($M_r = 82.0$) should be dissolved in his hydrochloric acid solution to form the required buffer.

(10 marks)

Organic Chemistry

1. The details of three ${}^{1}H$ NMR spectra (1-3) were obtained from compounds **A**, **B** and **C**, not necessarily in that order. Determine which spectrum belongs to which molecule and briefly explain your reasoning.

Spectrum 1

Chemical Shift (ppm)	Integral	Multiplicity			
3.669	3 H	singlet			
2.557	1 H	septet			
1.170	6 H	doublet			

Spectrum 2

Chemical Shift (ppm)	Integral	Multiplicity
3.8	1 H	singlet
2.249	3 H	singlet
1.394	6 H	singlet

Spectrum 3

Chemical Shift (ppm)	Integral	Multiplicity			
3.715	2 H	multiplet			
2.7	1 H	singlet			
2.69	1 H	sextet			
2.206	3 H	singlet			
1.134	3 H	doublet			

(9 marks)

2(i) The carbon atoms adjacent to the C=O bond in carbonyl compounds are known as the alpha-carbon atoms. Hydrogens bonded to this carbon are acidic and can be removed by a strong base such as ethoxide to give a stable carbanion.

$$\begin{array}{c}
O \\
H \\
H
\end{array}$$

$$\begin{array}{c}
H \\
H
\end{array}$$

$$\begin{array}{c}
K_1 \\
H
\end{array}$$

$$\begin{array}{c}
O \\
H
\end{array}$$

$$\begin{array}{c}
H \\
H
\end{array}$$

The pK_a of ethanol is 15.7. Calculate the value of K_1 .

(ii) Carbanions such as the one above can act as nucleophiles. Draw the stepwise mechanism for the following reaction:

(9 marks)

3. Propose a reasonable synthesis for compound ${\bf E}$ from compound ${\bf D}$. You may use any inorganic reagent and any organic reagents ${\bf F}$ to ${\bf I}$.

(8 marks)

4. Consider the following reaction scheme:

Br
$$\xrightarrow{\text{tBuOK}}$$
 \leftarrow K $\xrightarrow{\text{1. O}_3}$ \leftarrow L $\xrightarrow{\text{1 equiv. CH}_3\text{MgBr}}$ \leftarrow M \leftarrow CO₂H

- (i) Give the IUPAC name for compound **J**.
- (ii) Predict the products K, L and M.

(12 marks)

5. For compound N, mark all the chiral centres with an asterisk (*) and assign absolute configurations (R or S) to each chiral centre.

(12 marks)