

Answer all questions in the booklets provided. A periodic table is attached.

[12] Question 1

The following data have been obtained at 25°C for the anation by Y^- of $[Ti(H_2O)_6]^{3+}$ (k_{an}) and aquation of $[Ti(H_2O)_5Y]^{n+}$ (k_{aq}).

Y^{n-}	$k_{an} (M^{-1} s^{-1})$	$k_{aq} (s^{-1})$
H ₂ O	8.6×10^3	8.6×10^3
NCS ⁻	8.0×10^4	9.1×10^3
CH ₃ CO ₂ H	9.7×10^2	5.7×10^3
CH ₃ CO ₂ ⁻	1.8×10^6	7.5×10^3
ClCH ₂ CO ₂ H	6.7×10^2	4.8×10^3
ClCH ₂ CO ₂ ⁻	2.1×10^5	9.5×10^3

- What can you say about the *intimate* mechanism from the data of these two reactions? Explain your answer thoroughly. (3 marks)
- If you were told that the $\Delta H^\ddagger = +10 (\pm 2) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -2 (\pm 3) \text{ J mol}^{-1} \text{ K}^{-1}$ for the anation process when $Y = \text{NCS}^-$, would this help in supporting your conclusion in a)? Why or why not? (3 marks)
- If you were told that $\Delta V^\ddagger = -5.8 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ for the anation process when $Y = \text{NCS}^-$, would this help in supporting your conclusion in a)? Why or why not? (2 marks)
- If you were told that a plot of $\ln k_{an}$ versus $\ln K_{\text{reaction}}$ had a slope of close to 0.5 would this support your conclusion in a)? Why or why not? (2 marks)
- Can you draw *any* conclusions about the *stoichiometric* mechanism? Explain. (2 marks)

[11] Question 2

- While substitution in square-planar complexes usually occurs via an *associative* process (negative values of ΔS^\ddagger and ΔV^\ddagger) the *rate determining step* for substitution may or may not be dependent on the nature of the entering ligand. Explain how this is possible with the aid of a reaction-profile diagram(s). (4 marks)
- The reaction of *cis*-[PtMe₂(Me₂S=O)(PPh₃)] with pyridine (py) leads to *cis*-[PtMe₂(py)(PPh₃)] and the rate of reaction shows no dependence on the concentration of pyridine. At 298 K, the value of ΔS^\ddagger is $+24 \text{ J K}^{-1} \text{ mol}^{-1}$. Briefly explain these observations. (3 marks)
- Briefly explain the difference between the *trans effect* and the *trans influence* (4 marks).

[14] Question 3

Draw the structure and give the valence electron count for the metal of the following species. (Show your work). (3 marks each)

- $(\eta^3\text{-C}_3\text{H}_5)_2\text{Rh}(\mu\text{-CO})_2\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2$ (contains Rh-Rh bond)
- $\text{Ni}(\eta^5\text{-Cp})_2$ $\text{Cp}^- = \text{cyclopentadienyl anion } (\text{C}_5\text{H}_5^-)$
- $[(\eta^5\text{-Cp})\text{Co}(\text{CH}_3)(\text{PMe}_3)_2]^+$
- $[\text{IrCl}_2(\text{PPh}_3)_2(\text{CO})_2]^+$
- Which of the above complexes would be most reactive? Why? (2 marks)

[13] Question 4

- The outer-sphere reduction of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ by $[\text{Rh}(\text{CN})_6]^{5-}$ in benzene is relatively slow (i.e. high ΔG^\ddagger). Which of the three free-energy of activation terms: $\Delta G^\ddagger_{\text{OS}}$; $\Delta G^\ddagger_{\text{IS}}$; or $\Delta G^\ddagger_{\text{ES}}$, do you think would contribute the *most* to the overall activation energy, $\Delta G^\ddagger_{\text{total}}$? Why? Explain the relative sizes of the other two energy terms. (6 marks)
- Would you expect the reaction to speed up or slow down even further if performed in water? Explain. (3 marks)
- Define the Marcus equation. i.e. What does it predict? How does it predict it? Why is this useful? (4 marks)