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5.111 Principles of Chemical Science
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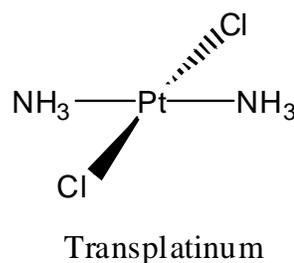
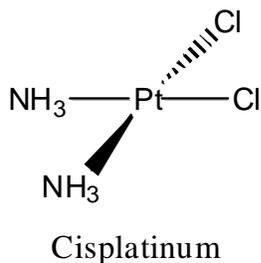
Solutions to selected biology-related questions from problem sets for lectures 27-36

Transition Metals

A.

Cisplatin [$\text{Pt}(\text{NH}_3)_2\text{Cl}_2$] is a potent anticancer drug. **(a)** Draw the structure of this square planar molecule and the structure of its isomer *transplatin*. **(b)** What are the angles for a square planar molecule? **(c)** What is the CN? **(d)** Draw the crystal field energy-level diagram for *cisplatin*, labeling the *d*-orbitals. **(e)** Predict whether *cisplatin* is diamagnetic or paramagnetic? Explain your answer.

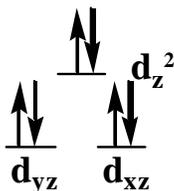
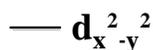
a)



b) 90°

c) Cisplatin has four ligands. CN (coordination number) = 4

d) Pt is in group 10. The d count for cisplatin therefore is $10 - 2 = 8$. d^8



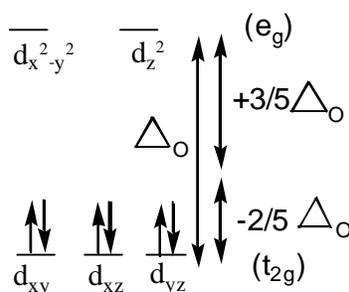
(Square planar
crystal field)

e) Cisplatin is diamagnetic. It has no unpaired electrons.

B.

Octahedral platinum(IV) complexes are used in protein crystallography to help determine three-dimensional protein structures. If the octahedral crystal field splitting energy (Δ_o) is large for these complexes, (a) predict whether they are diamagnetic or paramagnetic, and (b) write the expected d^n electron configuration.

The d-count for Pt^{4+} complexes is 10 (group number) $- 4 = d^6$. To figure out whether the complexes are diamagnetic or paramagnetic, fill the 6 d electrons into a strong (low spin) octahedral field diagram.



(Octahedral crystal field)

- (a) Diamagnetic. There are no unpaired electrons.
 (b) $(t_{2g})^6$

Rate laws and enzyme kinetics

C.

The element technetium has never been found in nature. It can be obtained readily as a product of uranium fission in nuclear power plants, however, and is produced in quantities of many kilograms per year. MIT Chemistry Professor Alan Davison pioneered the use of Technetium in the diagnosis of heart disease. Calculate the total activity (in disintegrations per second) caused by the decay of 0.5 microgram of ^{99m}Tc (an excited nuclear state of ^{99}Tc), which has a half-life of 6.0 hours.

To calculate the activity of a sample of 1.0 mg of ^{99m}Tc , we can use the following equation: $A=kN$. We need to first determine the decay constant, k and the number of nuclei.

To calculate the number of nuclei:

$$\begin{aligned} \# \text{ of nuclei} &= (0.5 \times 10^{-6} \text{ g}) \left(\frac{\text{mol}}{99.00 \text{ g}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}} \right) \\ &= 3.0414 \times 10^{15} \end{aligned}$$

To calculate the decay constant:

$$\begin{aligned}
t_{\frac{1}{2}} &= 6.0 \text{ hrs} \left(\frac{60 \text{ min}}{\text{hr}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) \\
&= 2.16 \times 10^4 \text{ s} \\
k &= \frac{\ln 2}{t_{\frac{1}{2}}} \\
&= \frac{0.6931}{2.16 \times 10^4 \text{ s}} \\
&= 3.2088 \times 10^{-5} \text{ s}^{-1}
\end{aligned}$$

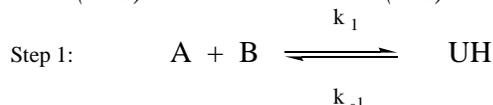
We can now substitute those values into the equation $A = kN$;

$$\begin{aligned}
A &= kN \\
&= (3.2088 \times 10^{-5} \text{ s}^{-1})(3.0414 \times 10^{15} \text{ nuclei}) \\
&= 9.759 \times 10^{10} \\
&= 1 \times 10^{11} \text{ disintegrations per second}
\end{aligned}$$

A sample of $0.5 \mu\text{g}$ of $^{99\text{m}}\text{Tc}$ has the activity of 1×10^{11} disintegrations s^{-1}

D.

Consider the formation of a DNA double helix from strands A and B to form an unstable helix (UH) and a stable helix (SH).



(a) What is the molecularity of each step?

Step 1 is bimolecular and step 2 is unimolecular.

(b) Write the rate law for the formation of the stable helix (SH) using the steady-state approximation. Be sure to eliminate intermediates from the rate expression.

We can make no assumptions as to the speed of each of the steps. First, let's write the expression for step 2; rate = $k_2[\text{UH}]$. Since UH is an intermediate, we need to find a way to remove it.

$$\text{Rate of formation of UH} = k_1[\text{A}][\text{B}]$$

$$\text{Rate of removal of UH} = k_{-1}[\text{UH}] + k_2[\text{UH}]$$

Using the Steady-State Approximation:

$$\text{Rate of formation of UH} = \text{Rate of removal of UH}$$

$$k_1[\text{A}][\text{B}] = k_{-1}[\text{UH}] + k_2[\text{UH}]$$

$$k_1[\text{A}][\text{B}] = [\text{UH}](k_{-1} + k_2)$$

$$[\text{UH}] = \frac{k_1[\text{A}][\text{B}]}{(k_{-1} + k_2)}$$

We can now substitute into the above rate law and get the overall rate expression:

$$\text{rate} = k_2 \left(\frac{k_1[A][B]}{(k_{-1} + k_2)} \right)$$