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- Briefly explain why $\mathrm{H}_{2} \mathrm{Se}$ is a stronger Brønsted-Lowry acid than $\mathrm{H}_{2} \mathrm{O}$ and a weaker

Marks acid than $\mathrm{H}_{2} \mathrm{Te}$.

In general, when comparing binary acids within the same group, the strength of the bond $\mathrm{E}-\mathrm{H}$ between the element $(\mathrm{E}$ ) and hydrogen determines the acidity:

$$
\mathrm{H}_{2} \mathrm{E}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{EH}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$

As the atomic size of $\mathbf{E}$ becomes larger, the $\mathrm{E}-\mathrm{H}$ becomes longer and weaker. Thus $\mathrm{H}_{3} \mathrm{O}^{+}$is more readily formed in aqueous solution and acidity increases.

- Compounds of $d$-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of $\mathrm{V}^{3+}$.

Paramagnetism is associated with the presence of unpaired electron spins. As vanadium is in group $5, \mathbf{V}^{3+}$ has two electrons in its 3d orbitals. These electrons occupy separate orbitals with the same spin to reduce the repulsion between them:

$\mathbf{V}^{3+}$ thus has two unpaired electrons and is paramagnetic.

- Complete the following table. $\left(e n=\right.$ ethylenediamine $\left.=\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)$

| Formula | $\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ | $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}$ | cis- $\left[\mathrm{CrCl}_{2}(\mathrm{en})_{2}\right] \mathrm{Cl}$ |
| :---: | :---: | :---: | :---: |
| Oxidation state of transition metal ion | III or +3 | II or +2 | III or +3 |
| Coordination number of transition metal ion | $\begin{gathered} 6 \\ \left(6 \times \underline{\mathbf{C}} \mathbf{N}^{-}\right) \end{gathered}$ | $\begin{gathered} 6 \\ \left(4 \times \mathrm{NH}_{3}+2 \times \mathrm{H}_{2} \underline{\mathrm{O}}\right) \end{gathered}$ | $\begin{gathered} 6 \\ \left(2 \times \mathrm{Cl}^{-}+2 \times\right. \\ \left.\mathbf{N H}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathbf{N H}_{2}\right) \end{gathered}$ |
| Number of $d$-electrons in the transition metal ion | 5 | 9 | 3 |
| Species formed upon dissolving in water | $\begin{gathered} 3 \mathrm{~K}^{+} \\ {\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}} \end{gathered}$ | $\begin{gathered} {\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}} \\ 2 \mathrm{NO}_{3}^{-} \end{gathered}$ | $\underset{\mathrm{Cl}^{-}}{\operatorname{cis}-\left[\mathrm{CrCl}_{2}(\mathrm{en})_{2}\right]^{+}}$ |

- Solution A consists of a 0.20 M aqueous solution of formic acid, HCOOH , at $25^{\circ} \mathrm{C}$.

Calculate the pH of Solution A. The $\mathrm{p} K_{\mathrm{a}}$ of HCOOH is 3.75 .

The reaction table is:

|  | $\mathbf{H C O O H}(\mathrm{aq})$ | $\mathbf{H}_{2} \mathrm{O}(\mathbf{l})$ | $\rightleftharpoons$ | $\mathbf{H C O O}^{-}(\mathrm{aq})$ | $\mathbf{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| start | 0.20 | large |  | 0 | 0 |
| change | $-\mathbf{x}$ | $-\mathbf{x}$ |  | $+\mathbf{x}$ | $+\mathbf{x}$ |
| equilibrium | $0.20-\mathbf{x}$ | large |  | $\mathbf{x}$ | $\mathbf{x}$ |

As $p K_{a}=-\log _{10}\left(\mathrm{~K}_{\mathrm{a}}\right)=3.75, \mathrm{~K}_{\mathrm{a}}=10^{-3.75}$ and:

$$
K_{a}=\frac{\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]}{[\mathrm{HCOOH}(\mathrm{aq})]}=\frac{(\mathrm{x})(\mathrm{x})}{(0.20-\mathrm{x})}=\frac{\mathrm{x}^{2}}{(0.20-\mathrm{x})}=10^{-3.75}
$$

As $K_{a}$ is very small, $x$ is tiny and $0.20-x \sim x$. Hence,

$$
K_{a} \sim \frac{x^{2}}{(0.20)}=10^{-3.75} \text { or } x^{2}=(0.20) \times\left(10^{-3.75}\right) \text { so } x=\left[H_{3} \mathrm{O}^{+}(\mathrm{aq})\right]=6.0 \times 10^{-4} \mathrm{M}
$$

As $\mathbf{p H}=-\log _{10}\left(\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathbf{a q})\right]:\right.$

$$
\mathrm{pH}=-\log _{10}\left(6.0 \times 10^{-4}\right)=2.22
$$

Answer: $\mathbf{2 . 2 2}$

At $25^{\circ} \mathrm{C}, 1.00 \mathrm{~L}$ of Solution B consists of 13.6 g of sodium formate, $\mathrm{NaHCO}_{2}$, dissolved in water. Calculate the pH of Solution B.

The molar mass of $\mathrm{NaHCO}_{2}$ is
$(22.99(\mathbf{N a}))+(1.008(\mathrm{H}))+(12.01(\mathrm{C}))+(2 \times 16.00(\mathrm{O}))=68.008$
The solution thus contains $\frac{\text { mass }}{\text { molar mass }}=\frac{\mathbf{1 3 . 6}}{\mathbf{6 8 . 0 0 8}}=\mathbf{0 . 2 0 0} \mathrm{mol}$
As this is dissolved in 1.00 L , the concentration is 0.200 M . The reaction table is now:

|  | $\mathbf{H C O O}^{-}(\mathbf{a q})$ | $\mathbf{H}_{2} \mathbf{O}(\mathbf{l})$ | $\rightleftharpoons$ | $\mathbf{H C O O H}_{(a q)}$ | $\mathbf{O H}^{-}(\mathbf{a q})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| start | 0.200 | large |  | $\mathbf{0}$ | $\mathbf{0}$ |
| change | $-\mathbf{y}$ | $-\mathbf{y}$ |  | $+\mathbf{y}$ | $+\mathbf{y}$ |
| equilibrium | $0.200-\mathbf{y}$ | large |  | $\mathbf{y}$ | $\mathbf{y}$ |

As $p K_{\mathrm{a}}+\mathrm{pK}_{\mathrm{b}}=14.00, \mathrm{pK}_{\mathrm{b}}=14.00-3.75=10.25, \mathrm{~K}_{\mathrm{b}}=10^{-10.25}$ and:

$$
K_{b}=\frac{[\mathrm{HCOOH}(\mathrm{aq})]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]}{\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]}=\frac{(\mathrm{y})(\mathrm{y})}{(0.200-\mathrm{y})}=\frac{\mathrm{y}^{2}}{(0.200-\mathrm{y})}=10^{-10.25}
$$

Again $K_{b}$ is very small, $y$ is tiny and $0.200-y \sim y$. Hence, $y^{2}=(0.200) \times\left(10^{-10.25}\right)$ so $\mathbf{y}=\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=3.35 \times 10^{-6} \mathrm{M}$ and $\mathrm{pOH}=-\log _{10}\left(\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=5.47\right.$

As $\mathbf{p H}+\mathbf{p O H}=14.00, \mathbf{p H}=14.00-5.47=8.52$

Answer: $\mathbf{8 . 5 2}$
Solution B $(1.00 \mathrm{~L})$ is poured into Solution A $(1.00 \mathrm{~L})$ and allowed to equilibrate at $25^{\circ} \mathrm{C}$ to give Solution C. Calculate the pH of Solution C.

After mixing solution A $(1.00 \mathrm{~L})$ and solution $B(1.00 \mathrm{~L})$, the total volume is $\mathbf{2 . 0 0}$ $L$. This halves the concentration of the both the acid and the base.

$$
[\text { acid }]=\frac{0.20}{2}=0.10 \mathrm{M} \text { and }[\text { base }]=\frac{0.200}{2}=0.100 \mathrm{M}
$$

Solution $C$ contains a weak acid $(\mathrm{HCOOH})$ and its conjugate base $\left(\mathrm{HCOO}^{-}\right)$. It is a buffer and the $\mathbf{p H}$ can be calculated using the Henderson-Hasselbalch equation can be used:

$$
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log _{10}\left(\frac{[\text { base }]}{[\text { acid }]}\right)=3.75+\log _{10}\left(\frac{0.100}{0.10}\right)=3.75
$$

Answer: $\mathbf{3 . 7 5}$

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00 , which component in the mixture would you need to increase in concentration?
[ HCOOH ] would be increased (the acid)

- Define what is meant by an "allotrope". Give an example of a pair of allotropes involving (i) phosphorus and (ii) oxygen.

Allotropes are different structural forms of the same element. Examples include:
(i) white phosphorus and red phosphorus,
(ii) $\mathrm{O}_{2}$ and $\mathrm{O}_{3}$.

- The $K_{\text {sp }}$ of $\mathrm{Al}(\mathrm{OH})_{3}$ is $1.0 \times 10^{-33} \mathrm{M}^{4}$. What is the solubility of $\mathrm{Al}(\mathrm{OH})_{3}$ in $\mathrm{g} \mathrm{L}^{-1}$ ?

The solubility equilibrium is:

$$
\mathrm{Al}(\mathrm{OH})_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{Al}^{3+}(\mathrm{aq})+3 \mathrm{OH}^{-}(\mathrm{aq})
$$

If the molar solubility $=S$ then $\left[\mathrm{Al}^{3+}(\mathrm{aq})\right]=\mathrm{S}$ and $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=3 \mathrm{~S}$. Hence:

$$
K_{\text {sp }}=\left[\mathrm{Al}^{3+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=(\mathrm{S})(3 \mathrm{~S})^{3}=27 \mathrm{~S}^{4}=1.0 \times 10^{-33}
$$

Hence, $S=\sqrt[4]{\frac{1.0 \times 10^{-33}}{27}}=2.5 \times 10^{-9} \mathrm{M}$
The formula mass of $\mathrm{Al}(\mathrm{OH})_{3}$ is $(\mathbf{2 6 . 9 8}(\mathrm{Al}))+\mathbf{3 \times ( 1 6 . 0 0 ( O )}+\mathbf{1 . 0 0 8 ( H ) )}=\mathbf{7 8 . 0 0 4}$
As mass $=$ number of moles $\times$ formula mass, the solubility in $\mathrm{g}^{-1}$ is:
solubility $=\left(2.5 \times 10^{-9}\right) \times(\mathbf{7 8 . 0 0 4})=1.9 \times 10^{-7} \mathrm{~g} \mathrm{~L}^{-1}$
Answer: $\mathbf{1 . 9 \times 1 0 ^ { - 7 } \mathbf { g ~ L } ^ { - 1 }}$
What is the solubility of $\mathrm{Al}(\mathrm{OH})_{3}$ in $\mathrm{L}^{-1}$ at pH 4.00 ?

As $\mathrm{pH}+\mathrm{pOH}=14.00, \mathrm{pOH}=14.00-4.00=10.00$.
As $\mathbf{p O H}=-\log _{10}\left(\left[\mathrm{OH}^{-}(\mathrm{aq})\right],\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=10^{-10.00} \mathrm{M}\right.$.
From above, $K_{\text {sp }}=\left[\mathrm{Al}^{3+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$. If the molar solubility is S then:

$$
K_{\text {sp }}=(S) \times\left(10^{-10.00}\right)^{3}=1.0 \times 10^{-33} \text { and so } S=1.0 \times 10^{-3} \mathrm{M}
$$

Converting the molar solubility into $g L^{-1}$ gives:

$$
\text { solubility }=\left(1.0 \times 10^{-3}\right) \times(78.004)=0.078 \mathrm{~g} \mathrm{~L}^{-1}
$$

- The following data were obtained for the reaction between gaseous nitric oxide and chlorine at $-10^{\circ} \mathrm{C}$.

$$
2 \mathrm{NO}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NOCl}(\mathrm{~g})
$$

| Experiment <br> Number | Initial [NO] <br> $\left(\mathrm{mol} \mathrm{L}^{-1}\right)$ | Initial [Cl $\left.\mathrm{Cl}_{2}\right]$ <br> $\left(\mathrm{mol} \mathrm{L}^{-1}\right)$ | Initial Reaction Rate <br> $\left(\mathrm{mol} \mathrm{L}^{-1} \mathrm{~min}^{-1}\right)$ |
| :---: | :---: | :---: | :---: |
| 1 | 0.10 | 0.10 | 0.18 |
| 2 | 0.10 | 0.20 | 0.36 |
| 3 | 0.20 | 0.20 | 1.44 |

Deduce the rate law for this reaction and calculate the value of the rate constant.

## RATE LAW

Between experiments (1) and (2), [ NO ] is constant and $\left[\mathrm{Cl}_{2}\right.$ ] is doubled. This doubles the rate:

$$
\text { rate } \alpha\left[\mathrm{Cl}_{2}\right]
$$

Between experiments (2) and (3), [ $\mathrm{Cl}_{2}$ ] is constant and [ NO ] is doubled. The rate increases by a factor of 4:
rate $\alpha[\mathrm{NO}]^{2}$

## Overall,

$$
\text { rate } \alpha\left[\mathrm{Cl}_{2}\right][\mathrm{NO}]^{2}=\mathrm{k}\left[\mathrm{Cl}_{2}\right][\mathrm{NO}]^{2}
$$

RATE CONSTANT
Using any of the three experiments,

$$
\mathrm{k}=\frac{\text { rate }}{\left[\mathrm{Cl}_{2}\right][\mathrm{NO}]^{2}}
$$

For experiment 1:

$$
k=\frac{0.18}{(0.10)(0.10)^{2}}=180
$$

For experiment 2:

$$
k=\frac{0.36}{(0.20)(0.10)^{2}}=180
$$

For experiment 3:

$$
k=\frac{1.44}{(0.20)(0.20)^{2}}=180
$$

The units of $k$ are given by:

$$
\text { units of } \begin{aligned}
k & =\frac{\text { units of rate }}{(\text { concentration units })^{3}} \\
& =\frac{\left(\text { mol L}^{-1} \min ^{-1}\right)}{\left(\mathrm{mol} \mathrm{~L}^{-1}\right)^{3}} \\
& =\operatorname{mol}^{-2} \mathrm{~L}^{2} \mathrm{~min}^{-1}
\end{aligned}
$$

$$
\text { Answer: } \mathbf{1 8 0} \mathbf{~ m o l}^{-2} \mathbf{L}^{2} \mathbf{~ m i n}^{-1}
$$

- Draw the structure of the major organic product formed in the following reactions.




( $2 \times$ Markovnikov addition with H adding to less substituted $C$ each time)



- Suggest reagents you could use to achieve the following transformations.






| A: $\mathrm{NaOH} / \mathrm{H}_{2} \mathrm{O}$ / heat | B: $\mathrm{H}_{2} /$ Pd catalyst |
| :--- | :--- |
| C: Mg / dry ether | D: $1 . \mathrm{CO}_{2} 2 . \mathrm{H}^{\oplus} / \mathrm{H}_{2} \mathrm{O}$ |

- Add curly arrows to complete the following mechanism.

$\mathrm{Br}^{\ominus}$

Classify this reaction as $\mathrm{S}_{\mathrm{N}} 1$ or $\mathrm{S}_{\mathrm{N}} 2$ and explain what the three parts of this descriptor signify.

The reaction is an $\mathrm{S}_{\mathbf{N}} 1$ reaction:
$\mathrm{S}=$ substitution ( $\mathrm{Br}^{-}$is substituted for CN )
$\mathrm{N}=$ nucleophilic ( $\mathrm{CN}^{-}$is negatively charged and attacks the positively charged carbon)
1 = unimolecular (the first step, involving breaking a C-Br bond, is rate determining and involves only one molecule).

- Devise a synthesis of the product $\mathbf{Y}$, starting from compound $\mathbf{X}$. Note that more than one step may be required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

- The amino acids serine and valine are shown below.

serine

valine

List the substituents attached to the stereogenic centre of valine in order of decreasing priority.
highest priority
lowest priority

| $-\mathrm{NH}_{2}$ | -COOH | $-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$ | -H |
| :--- | :--- | :--- | :--- |

Assign the absolute configuration of the stereoisomer of valine shown above.
(S)
(anticlockwise)

Draw a dipeptide formed by the condensation of serine with valine.


What are the two key elements of protein secondary structure?

The secondary structure describes the orientation of segments of the peptide chain and is defined by the $\mathbf{H}$-bonding between amino acid residues. The most common secondary structures are:

- $\alpha$-helices, right handed coils stabilized by H-bonds between amide $\mathbf{N}$ $H$ and $C=O$ groups four residues apart and
- $\quad \beta$-pleated sheets, extended structures stabilized by $\mathbf{H}$-bonds between amide $\mathrm{N}-\mathrm{H}$ and $\mathrm{C}=\mathrm{O}$ groups on different chains
- A saturated solution of iodine in water contains $0.330 \mathrm{~g} \mathrm{I}_{2}$ per litre, but more than this amount can dissolve in a potassium iodide solution because of the following equilibrium.

$$
\mathrm{I}^{-}(\mathrm{aq})+\mathrm{I}_{2}(\mathrm{aq}) \quad \rightleftharpoons \mathrm{I}_{3}^{-}(\mathrm{aq})
$$

A 0.100 M KI solution dissolves 12.5 g of $\mathrm{I}_{2}$ per litre, most of which is converted to $\mathrm{I}_{3}{ }^{-}(\mathrm{aq})$. Assuming that the concentration of $\mathrm{I}_{2}(\mathrm{aq})$ in all saturated solutions is the same, calculate the equilibrium constant for the above reaction.

As 0.330 g of $\mathbf{I}_{\mathbf{2}}$ dissolves in a litre of water, the concentration of $\mathbf{I}_{\mathbf{2}}$ in the saturated solution of iodine in water is therefore:

$$
\left[\mathrm{I}_{2}(\mathrm{aq})\right]=\frac{0.330}{253.8}=0.0013 \mathrm{M}
$$

12.5 g of $\mathrm{I}_{2}$ dissolves in a litre of KI solution, corresponding to $\frac{12.5}{253.8}=0.0493 \mathrm{M}$.

For the equilibrium, the reaction table is therefore:

|  | $\mathbf{I}^{-}(\mathrm{aq})$ | $\mathbf{I}_{\mathbf{2}}(\mathrm{aq})$ | $\rightleftharpoons$ | $\mathbf{I}_{3}{ }^{-}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: |
| [initial] | $\mathbf{0 . 1 0 0}$ | $\mathbf{0 . 0 4 9 3}$ |  | 0 |
| change | -x | -x |  | $+\mathbf{x}$ |
| [equilibrium] | $0.100-\mathrm{x}$ | $0.0493-\mathrm{x}$ |  | $\mathbf{x}$ |

Assuming that $\left[I_{2}(a q)\right]$ is the same as in the saturated solution (as stated in the question), $0.0493-x=0.0013$ so $x=0.048$ giving:
$\left[\mathrm{I}^{-}(\mathrm{aq})\right]=0.100-0.048=0.052 \mathrm{M},\left[\mathrm{I}_{2}(\mathrm{aq})\right]=0.0013 \mathrm{M}$ and $\left[\mathrm{I}_{3}{ }^{-}(\mathrm{aq})\right]=0.048$
M.

The equilibrium constant is therefore:

$$
K_{c}=\frac{\left[I_{3}^{-}(\mathrm{aq})\right]}{\left[\mathrm{I}^{-}(\mathrm{aq})\right]\left[\mathrm{I}_{2}(\mathrm{aq})\right]}=\frac{(0.048)}{(0.052)(0.0013)}=710
$$

