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## 2013-N-11:

- Redox Reactions and Introduction to Electrochemistry

2013-N-12:

- Introduction to Colloids and Surface Chemistry

2013-N-13:

- Chemical Kinetics
- Explain the following terms or concepts.

Marks
3
Third law of thermodynamics
A perfect pure crystal at absolute zero ( 0 K ) has zero entropy. It is not possible to reduce the temperature of any system to absolutel in a finite number of finite operations.

Osmotic pressure
The pressure that needs to be applied to prevent water from flowing across a semipermeable membrane due to osmosis.

Lewis base
A species that can form a bond by donating a lone pair of electrons, e.g. $\mathbf{H}_{\mathbf{2}} \mathrm{O}$.

- The specific heat capacity of water at $0^{\circ} \mathrm{C}$ is undefined. Explain why this is so.

At $0{ }^{\circ} \mathrm{C}$, any heat transferred into or out of the system is either causing the ice to melt or the water to freeze - there is no change in the temperature. Specific heat capacity is defined as $c=q / m \Delta T$. As there is no change in temperature, $\Delta T=0$ and $c$ is undefined.

- Consider the following reaction:

$$
2 \mathrm{~N}_{2} \mathrm{O}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 4 \mathrm{NO}_{2}(\mathrm{~g})
$$

Calculate $\Delta G^{\circ}$ for this reaction given the following data.

$$
\begin{array}{ll}
4 \mathrm{NO}(\mathrm{~g}) \rightarrow 2 \mathrm{~N}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) & \Delta G^{\circ}=-139.56 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) & \Delta G^{\circ}=-69.70 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{array}
$$

Using $\Delta_{\mathrm{r}} G^{\circ}=\sum \Delta_{\mathrm{f}} G^{\circ}$ (products) $-\sum \Delta_{\mathrm{f}} G^{\circ}$ (reactants), the free energy changes in the 3 reactions are, respectively:

$$
\begin{aligned}
& \Delta_{\mathrm{r}} G^{\circ}(1)=4 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{NO}_{2}(\mathrm{~g})\right)-2 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{N}_{2} \mathrm{O}(\mathrm{~g})\right) \\
& \Delta_{\mathrm{r}} G^{\circ}(2)=2 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{N}_{2} \mathrm{O}(\mathrm{~g})\right)-4 \Delta_{\mathrm{f}} G^{\circ}(\mathrm{NO}(\mathrm{~g}))=-139.56 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
& \Delta_{\mathrm{r}} G^{\circ}(3)=2 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{NO}_{2}(\mathrm{~g})\right)-2 \Delta_{\mathrm{f}} G^{\circ}(\mathrm{NO}(\mathrm{~g}))=-69.70 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Mathematically, the combination $2 \Delta_{\mathrm{r}} G^{\circ}(3)-\Delta_{\mathrm{r}} G^{\circ}(2)$ leads to $\Delta_{\mathrm{r}} G^{\circ}(1)$ :

$$
\begin{aligned}
& 2 \Delta_{\mathrm{r}} G^{\circ}(3)= 4 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{NO}_{2}(\mathrm{~g})\right)-4 \Delta_{\mathrm{f}} G^{\circ}(\mathrm{NO}(\mathrm{~g})) \\
& \Delta_{\mathrm{r}} G^{\circ}(2)= 2 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{N}_{2} \mathrm{O}(\mathrm{~g})\right)-4 \Delta_{\mathrm{f}} G^{\circ}(\mathrm{NO}(\mathrm{~g})) \\
& 2 \Delta_{\mathrm{r}} G^{\circ}(\mathbf{3})-\Delta_{\mathrm{r}} G^{\circ}(2)=4 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{NO}_{2}(\mathrm{~g})\right)-2 \Delta_{\mathrm{f}} G^{\circ}\left(\mathrm{N}_{2} \mathrm{O}(\mathrm{~g})\right)=\Delta_{\mathrm{f}} G^{\circ}(\mathbf{1})
\end{aligned}
$$

$$
\begin{aligned}
\Delta_{\mathrm{f}} G^{\circ}(1) & =2 \Delta_{\mathrm{r}} G^{\circ}(3)-\Delta_{\mathrm{r}} G^{\circ}(2)=[(2 \times-69.70)-(-139.56)] \mathrm{kJ} \mathrm{~mol}^{-1} \\
& =0.16 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Answer: $0.16 \mathrm{~kJ} \mathrm{~mol}^{-1}$

- Calculate the molar solubility of silver sulfide, $\mathrm{Ag}_{2} \mathrm{~S}$, given that $K_{\mathrm{sp}}$ is $8 \times 10^{-51}$ at $25^{\circ} \mathrm{C}$.

The dissolution reaction and solubility product are:

$$
\mathrm{Ag}_{2} \mathbf{S}(\mathrm{~s}) \rightleftharpoons 2 \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{S}^{2-}(\mathrm{aq}) \quad K_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}(\mathrm{aq})\right]^{2}\left[\mathbf{S}^{2-}(\mathrm{aq})\right]
$$

If $x$ mol of $\mathrm{Ag}_{2} \mathrm{~S}$ dissolve in one litre, then $\left[\mathrm{Ag}^{+}(\mathrm{aq})\right]=2 x \mathrm{M}$ and $\left[\mathrm{S}^{2-}(\mathrm{aq})\right]=x \mathrm{M}$. Hence:

$$
K_{\text {sp }}=(2 x)^{2}(x)=4 x^{3}=8 \times 10^{-51} \quad \text { so } x=1 \times 10^{-17}
$$

- Calcium carbide, $\mathrm{CaC}_{2}$, reacts with water to produce a gas and a solution containing $\mathrm{OH}^{-}$ions. A sample of $\mathrm{CaC}_{2}$ was treated with excess water and the resulting gas was collected in an evacuated 5.00 L glass bulb. At the completion of the reaction, the pressure inside the bulb was $1.00 \times 10^{5} \mathrm{~Pa}$ at a temperature of $26.8^{\circ} \mathrm{C}$. Calculate the amount (in mol) of the gas produced.
5.00 L corresponds to $5.00 \times 10^{-3} \mathrm{~m}^{3}$ and $26.8^{\circ} \mathrm{C}$ corresponds to $(26.8+273.0) \mathrm{K}$ $=299.8 \mathrm{~K}$. Using the ideal gas law:

$$
\begin{aligned}
P V & =n R T \\
n & =P V / R T \\
& =\left(1.00 \times 10^{5} \mathrm{~Pa}\right)\left(5.00 \times 10^{-3} \mathrm{~m}^{3}\right) /\left(\left(8.314 \mathrm{~Pa} \mathrm{~m}^{3} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)(299.8 \mathrm{~K})\right) \\
& =0.201 \mathrm{~mol}
\end{aligned}
$$

Answer: $\mathbf{0 . 2 0 1 ~ m o l}$
Given that the mass of the gas collected was 5.21 g , show that the molar mass of the gas is $25.9 \mathrm{~g} \mathrm{~mol}^{-1}$.

As the number of moles = mass / molar mass:

$$
\text { molar mass }=\text { mass } / \text { number of moles }=5.21 \mathrm{~g} / 0.201 \mathrm{~mol}=25.9 \mathrm{~g} \mathrm{~mol}^{-1}
$$

Suggest a molecular formula for the gas and write a balanced equation for the reaction that occurred.

As the gas was produced from $\mathrm{CaC}_{2}$ which contains $\mathrm{C}_{2}{ }^{2-}$, a likely formula is $\mathrm{C}_{2} \mathrm{H}_{2}$ :

$$
\text { molar mass }=(2 \times 12.01(\mathrm{C})+2 \times 1.008(\mathrm{H})) \mathrm{g} \mathrm{~mol}^{-1}=26.0 \mathrm{~g} \mathrm{~mol}^{-1}
$$

This is formed by addition of $\mathrm{H}_{2} \mathrm{O}$ :

$$
\mathrm{CaC}_{2}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Ca}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})
$$

- Methane, $\mathrm{CH}_{4}$, reacts with hydrogen sulfide, $\mathrm{H}_{2} \mathrm{~S}$, according the following equilibrium:

$$
\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g}) \rightleftharpoons \mathrm{CS}_{2}(\mathrm{~g})+4 \mathrm{H}_{2}(\mathrm{~g})
$$

In an experiment $1.00 \mathrm{~mol}^{2} \mathrm{CH}_{4}, 2.00 \mathrm{~mol}$ of $\mathrm{H}_{2} \mathrm{~S}, 1.00 \mathrm{~mol}$ of $\mathrm{CS}_{2}$ and 2.00 mol of $\mathrm{H}_{2}$ are mixed in a 250 mL vessel at $960^{\circ} \mathrm{C}$. At this temperature, $K_{\mathrm{c}}=0.034$ (based on a standard state of $1 \mathrm{~mol} \mathrm{~L}^{-1}$ ).
Calculate the reaction quotient, $Q$, and hence predict in which direction the reaction will proceed to reach equilibrium? Explain your answer.

Using concentration $=$ number of moles / volume, the concentrations when the gases are mixed are:

$$
\begin{aligned}
& {\left[\mathrm{CH}_{4}(\mathrm{~g})\right]=1.00 \mathrm{~mol} / 0.250 \mathrm{~L}=4.00 \mathrm{~mol} \mathrm{~L}^{-1}} \\
& {\left[\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})\right]=2.00 \mathrm{~mol} / 0.250 \mathrm{~L}=8.00 \mathrm{~mol} \mathrm{~L}^{-1}} \\
& {\left[\mathrm{CS}_{2}(\mathrm{~g})\right]=1.00 \mathrm{~mol} / 0.250 \mathrm{~L}=4.00 \mathrm{~mol} \mathrm{~L}^{-1}} \\
& {\left[\mathrm{H}_{2}(\mathrm{~g})\right]=\mathbf{2 . 0 0} \mathrm{mol} / 0.250 \mathrm{~L}=8.00 \mathrm{~mol} \mathrm{~L}^{-1}}
\end{aligned}
$$

From the chemical equation, the reaction quotient is:

$$
Q=\frac{\left[\mathrm{CS}_{2}(\mathrm{~g})\right]\left[\mathrm{H}_{2}(\mathrm{~g})\right]^{4}}{\left[\mathrm{CH}_{4}(\mathrm{~g})\right]\left[\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})\right]^{2}}=\frac{(4.00)(8.00)^{4}}{(4.00)(8.00)^{2}}=64.0
$$

As $Q>K_{\mathrm{c}}$, therefore the reaction will shift to the left until $Q=K_{\mathrm{c}}$

Show that the system is at equilibrium when $\left[\mathrm{CH}_{4}(\mathrm{~g})\right]=5.56 \mathrm{M}$.

A reaction table can be constructed to calculate the equilibrium concentrations:

|  | $\mathbf{C H}_{4}(\mathbf{g})+$ | $2 \mathbf{H}_{2} \mathbf{S}(\mathrm{~g})$ | $\rightleftharpoons$ | $\mathbf{C S}_{2}(\mathrm{~g})+$ | $4 \mathbf{H}_{2}(\mathrm{~g})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Initial | 4.00 | 8.00 |  | 4.00 | $\mathbf{8 . 0 0}$ |
| Change | $+x$ | $+2 x$ |  | $-x$ | $-4 x$ |
| Equilibrium | $4.00+x$ | $8.00+2 x$ |  | $4.00-x$ | $8.00-4 x$ |

If $\left[\mathrm{CH}_{4}(\mathrm{~g})\right]_{\text {equilibrium }}=5.56 \mathrm{M}$ then $4.00+x=5.56 \mathrm{M}$ and $x=1.56 \mathrm{M}$. Hence:
$\left[\mathrm{CH}_{4}(\mathrm{~g})\right]_{\text {equilibrium }}=(4.00+x) \mathrm{M}=5.56 \mathrm{M}$
$\left[\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})\right]_{\text {equilibrium }}=(\mathbf{8 . 0 0}+\mathbf{2 x}) \mathrm{M}=11.12 \mathrm{M}$
$\left[C_{2}(\mathrm{~g})\right]_{\text {equilibrium }}=(4.00-x) \mathrm{M}=2.44 \mathrm{M}$
$\left[\mathrm{H}_{2}(\mathrm{~g})\right]_{\text {equilibrium }}=(8.00-4 x) \mathrm{M}=1.76 \mathrm{M}$.
With these concentrations:

$$
K_{\mathrm{c}}=\frac{\left[\mathrm{CS}_{2}(\mathrm{~g})\right]\left[\mathrm{H}_{2}(\mathrm{~g})\right]^{4}}{\left[\mathrm{CH}_{4}(\mathrm{~g})\right]\left[\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})\right]^{2}}=\frac{(2.44)(1.76)^{4}}{(5.56)(11.12)^{2}}=0.034
$$

- Isooctane, an important constituent of petrol, has a boiling point of $99.3{ }^{\circ} \mathrm{C}$ and a standard enthalpy of vaporisation of $37.7 \mathrm{~kJ} \mathrm{~mol}^{-1}$. What is $\Delta S^{\circ}\left(\mathrm{in} \mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}\right)$ for the vaporisation of isooctane?

At the boiling point, $\Delta_{\text {vap }} G^{\circ}=\Delta_{\text {vap }} H^{\circ}-T \Delta_{\text {vap }} S^{\circ}=0$. Hence:

$$
\Delta_{\text {vap }} S^{\circ}=\Delta_{\text {vap }} H^{\circ} / T=\left(37.7 \times 10^{3} \mathrm{~J} \mathrm{~mol}^{-1}\right) /(99.3+273) \mathrm{K}=+101 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}
$$

Answer: $+101 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$

- An aqueous solution with a volume of 10.0 mL contains 0.025 g of a purified protein of unknown molecular weight. The osmotic pressure of the solution was measured in an osmometer to be 0.0036 atm at $20.0^{\circ} \mathrm{C}$. Assuming ideal behaviour and no dissociation of the protein, estimate its molar mass in $\mathrm{g} \mathrm{mol}^{-1}$.

A pressure of $\mathbf{0 . 0 0 3 6} \mathbf{a t m}$ corresponds to $\left(\mathbf{0 . 0 0 3 6} \times 101.3 \times \mathbf{1 0}^{\mathbf{3}}\right) \mathbf{P a}=\mathbf{3 6 0} \mathbf{P a}$. The osmotic pressure, $\Pi$, is related to the concentration of the solute through

$$
\Pi=c R T
$$

## Hence:

$$
\begin{aligned}
c & =\Pi / R T=360 \mathrm{~Pa} /\left(\left(8.314 \mathrm{~Pa} \mathrm{~m}^{3} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)((20.0+273) \mathrm{K})\right) \\
& =0.15 \mathrm{~mol} \mathrm{~m}^{-3}=0.15 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

The number of moles in $10.0 \mathbf{~ m L}$ is therefore:

$$
\begin{aligned}
\text { number of moles } & =\text { concentration } \times \text { volume } \\
& =\left(0.15 \times 10^{-3} \mathbf{~ m o l ~ L}\right.
\end{aligned}
$$

As this is the number of moles in 0.025 g , the molar mass is:
molar mass $=$ mass $/$ number of moles

$$
=0.025 \mathrm{~g} / 1.5 \times 10^{-6} \mathrm{~mol}=17000 \mathrm{~g} \mathrm{~mol}^{-1}
$$

Answer: $\mathbf{1 7 0 0 0} \mathbf{g ~ m o l}^{-1}$

- Ammonia is synthesised according to the following reaction.

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \quad \rightleftharpoons \quad 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

At $500{ }^{\circ} \mathrm{C}$ this reaction has a $K_{\mathrm{c}}$ of $6.0 \times 10^{-2} . \Delta H^{\circ}$ for this reaction is $-92 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Calculate the value of $K_{\mathrm{c}}$ at $200^{\circ} \mathrm{C}$.

The equilibrium constant varies with temperature according to the van't Hoff equation:

$$
\ln \frac{K_{2}}{K_{1}}=\frac{-\Delta H^{\circ}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)
$$

## Hence:

$$
\ln \frac{K_{2}}{6.0 \times 10^{-2}}=\frac{+92 \times 10^{3}}{8.314}\left(\frac{1}{(200+273)}-\frac{1}{(500+273)}\right)
$$

$K_{2}=530$

## Answer: 530

- Good wine will turn to vinegar if it is left exposed to air because the alcohol is oxidised to acetic acid. The equation for the reaction is

$$
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{l})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{l})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

Calculate $\Delta S^{\circ}$ for this reaction in $\mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$.
Data:

|  | $\Delta S^{\circ}\left(\mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}\right)$ |
| :---: | :---: |
| $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{l})$ | 161 |
| $\mathrm{O}_{2}(\mathrm{~g})$ | 205.0 |
| $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{l})$ | 160 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | 69.96 |

Using $\Delta_{r} S^{\circ}=\sum S^{\circ}($ products $)-\sum S^{\circ}($ reactants $)$ :

$$
\Delta_{\mathrm{r}} S^{\circ}=((160+69.96)-(161+205.0)) \mathrm{J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}=-136 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}
$$

$$
\text { Answer: - } \mathbf{1 3 6} \mathbf{~ J ~ K}^{-1} \mathbf{~ m o l}^{-1}
$$

- One of the most important reactions in living cells is the splitting of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and free phosphate $\left(\mathrm{P}_{\mathrm{i}}\right)$ :

$$
\mathrm{ATP} \rightleftharpoons \mathrm{ADP}+\mathrm{P}_{\mathrm{i}}
$$

Based on a standard state of 1 M , the value of $\Delta G^{\circ}$ for this reaction at $37^{\circ} \mathrm{C}$ is $-33 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Calculate the value of the equilibrium constant for the reaction at this temperature.

The equilibrium constant is related to the free energy change by $\Delta G^{\circ}=-R T \ln K_{\mathrm{p}}$ :

$$
\begin{aligned}
& \Delta G^{\circ}=-\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)((37+273) \mathrm{K}) \ln K_{\mathrm{p}}=-33 \times 10^{3} \mathrm{~J} \mathrm{~mol}^{-1} \\
& K_{\mathrm{p}}=3.6 \times 10^{5}
\end{aligned}
$$

Answer: $\mathbf{3 . 6} \times \mathbf{1 0}^{\mathbf{5}}$
The following concentrations are typical in a living cell.

| ATP: 5 mM | ADP: 0.1 mM | $\mathrm{P}_{\mathrm{i}}: 5 \mathrm{mM}$ |
| :---: | :---: | :---: |

Under these conditions, calculate the energy per mole that is available from the splitting of ATP.

With these concentrations, the reaction quotient, $Q$, is:

$$
Q=\frac{[\mathrm{ADP}]\left[\mathrm{P}_{\mathrm{i}}\right]}{[\mathrm{ATP}]}=\frac{\left(0.1 \times \mathbf{1 0}^{-\mathbf{3}}\right)\left(5 \times 10^{-\mathbf{3}}\right)}{\left(5 \times 10^{-\mathbf{3}}\right)}=1 \times 10^{-4}
$$

The energy available has the reaction proceeds to equilibrium is then:

$$
\begin{aligned}
\Delta G & =\Delta G^{\circ}+R T \ln Q \\
& =\left(-33 \times 10^{3}\right)+\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)((37+273) \mathrm{K}) \ln \left(1 \times 10^{-4}\right)=-57 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

## 57 kJ is available for every mole of ATP that is split.

Answer: $\mathbf{5 7} \mathbf{~ k J}$

- Balance the following nuclear reactions and name the decay process occurring.

| Equation | Name of decay process |
| :---: | :---: |
| ${ }_{8}^{15} \mathrm{O} \rightarrow{ }_{7}^{15} \mathrm{~N}+{ }_{1}^{0} \boldsymbol{e}$ | positron emission |
| ${ }_{92}^{238} \mathrm{U} \rightarrow{ }_{90}^{234} \mathrm{Th}+{ }_{2}^{4} \mathrm{He}$ | $\alpha$ decay |
| ${ }_{19}^{40} \mathrm{~K}+{ }_{-1}^{\mathbf{0}} \boldsymbol{e} \quad \rightarrow{ }_{18}^{40} \mathrm{Ar}$ | electron capture |

- What amount of NaOH (in mol) needs to be added to 250 mL of 0.10 M acetic acid to give a solution with a pH of 5.00 ? The $\mathrm{p} K_{\mathrm{a}}$ of acetic acid is 4.76.

If the concentration of $\mathrm{OH}^{-}$which is added is $\boldsymbol{x} \mathrm{M}$ then this will react with acetic acid to produce its conjugate base, acetate, so that:

$$
\begin{aligned}
& {[\text { acid }]=(0.10-x) M \text { and }} \\
& {[\text { base }]=x M}
\end{aligned}
$$

The Henderson-Hasselbalch equation can be used to work out the ratio of these needed for a $\mathbf{p H}$ of 5.00:

$$
\begin{aligned}
& \mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{[\text { base }]}{[\text { acid }]} \\
& 5.00=4.76+\log \frac{x}{0.10-x}
\end{aligned}
$$

## Hence:

$$
\frac{x}{0.10-x}=10^{0.24} \quad \text { so } x=0.0634
$$

To achieve $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=0.0634 \mathrm{~mol} \mathrm{~L}^{-1}$ in 250 mL , the number of moles of NaOH that must be added is:

$$
\begin{aligned}
\text { number of moles } & =\text { concentration } \times \text { volume } \\
& =0.0634 \mathrm{~mol} \mathrm{~L}^{-1} \times 0.250 \mathrm{~L}=0.016 \mathrm{~mol}
\end{aligned}
$$

Answer: $\mathbf{0 . 0 1 6 ~ m o l}$

- Complete the following table.


Identify one paramagnetic and one diamagnetic species from the above table.

| Paramagnetic: $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{CoCl}_{4}\right]$ and $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{OH}_{2}\right)\right] \mathrm{Cl}_{3}$ | Diamagnetic: $\mathbf{K}_{2}\left[\mathbf{P t C l}_{4}\right]$ and $\mathbf{N a}\left[\mathbf{M n O}_{4}\right]$ |
| :---: | :---: |

- What is the electrochemical potential of the following cell at $25^{\circ} \mathrm{C}$ ?

As this is a concentration cell, $E^{0}=0 \mathrm{~V}$. The cell notation corresponds to the 0.100 M solution being the cathode, where reduction occurs, and the 0.010 M solution being the anode, where oxidation occurs. The two half cells are:

$$
\begin{array}{ll}
\text { Anode: } & \mathrm{Fe}(\mathbf{s}) \rightarrow \mathrm{Fe}^{2+}(\mathbf{a q}, \mathbf{0 . 0 1 0} \mathbf{M})+2 \mathrm{e}^{-} \\
\text {Cathode: } & \mathrm{Fe}^{2+}(\mathrm{aq}, \mathbf{0 . 1 0 0} \mathbf{M})+2 \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathbf{s}) \\
\text { Overall: } & \mathrm{Fe}^{2+}(\mathbf{a q}, \mathbf{0 . 1 0 0} \mathbf{M}) \rightarrow \mathrm{Fe}^{2+}(\mathbf{a q}, \mathbf{0 . 0 1 0} \mathbf{M})
\end{array}
$$

The potential is given by the Nernst equation for this two electron reaction:

$$
\begin{aligned}
E & =E^{\circ}-\frac{R T}{n F} \ln Q \\
& =(0 \mathrm{~V})-\frac{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298 \mathrm{~K})}{2 \times 96485 \mathrm{~mol}^{-1}} \ln \frac{(0.010)}{(0.100)}=+0.0296 \mathrm{~V}
\end{aligned}
$$

Answer: +0.0296 V

- Calculate the mass of aluminium which can be produced with the same quantity of electricity that is used to produce 1.00 kg of copper metal.

As the molar mass of $\mathbf{C u}$ is $63.55 \mathrm{~g} \mathrm{~mol}^{-1}, 1.00 \mathrm{~kg}$ corresponds to:

$$
\begin{aligned}
\text { number of moles } & =\text { mass } / \text { molar mass } \\
& =1.00 \times 10^{3} \mathrm{~g} / 63.55 \mathrm{~g} \mathrm{~mol}^{-1}=15.7 \mathrm{~mol} .
\end{aligned}
$$

Reduction of $\mathrm{Cu}^{2+}$ requires 2 mol of electrons. Hence, the number of electrons requires to produce 15.7 mol is:

$$
\text { number of moles of electrons }=2 \times 15.7 \mathrm{~mol}=31.5 \mathrm{~mol}
$$

Reduction of a mole of $\mathrm{Al}^{3+}$ requires 3 mol of electrons. Hence, the number of moles of aluminium produced by 31.5 mol of electrons is:

$$
\text { number of moles of aluminium }=31.5 / 3 \mathrm{~mol}=10.5 \mathrm{~mol}
$$

As the molar mass of aluminium is $26.98 \mathrm{~g} \mathrm{~mol}^{-1}$, this corresponds to:

$$
\text { mass }=\text { number of moles } \times \text { molar mass }=10.5 \mathrm{~mol} \times 26.98 \mathrm{~g} \mathrm{~mol}^{-1}=283 \mathrm{~g} .
$$

- Explain why $\mathrm{Na}(\mathrm{s})$ cannot be obtained by the electrolysis of aqueous NaCl solutions.

From the table of standard reduction potentials:

$$
\begin{array}{ll}
2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{OH}^{-}(\mathrm{aq}) & E^{\circ}=-\mathbf{0 . 8 3} \mathrm{V} \\
\mathrm{Na}^{+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Na}(\mathrm{~s}) & E^{\circ}=-\mathbf{2 . 7 1 ~ V}
\end{array}
$$

Water has a much greater reduction potential than $\mathrm{Na}^{+}$and hence is preferentially reduced, even when the overpotential of water is considered.

- Give a brief definition or explanation of the following concepts in colloid science.


## double layer

The layers of ions on a colloidal particle. The inner (Stern) layer consists of ions that are electrostatically attracted to the charged particle. The outer (diffuse) layer consists of counter ions.
counter ion
An ion of opposite charge to another chemical species.
isoelectric point
The pH value at which an amino acid or peptide has zero net charge.
zeta potential
The zeta potential is a measure of repulsion between adjacent, similarly charged particles in a colloid (i.e. the stability of a colloid). Colloids with high zeta potentials are electrically stabilized, whilst those with low potentials tend to coagulate.
flocculation
The process in which colloidal particles clump together to form larger particles causing separation of the colloid.
electrokinetic mobility
The movement of colloidal particles in response to the application of an electric field.

- The following reaction is run from 4 different starting positions.

$$
\mathrm{H}_{2} \mathrm{SeO}_{3}+6 \mathrm{I}^{-}+4 \mathrm{H}^{+} \rightarrow \mathrm{Se}+2 \mathrm{I}_{3}^{-}+3 \mathrm{H}_{2} \mathrm{O}
$$

| Experiment | Initial $\left[\mathrm{H}_{2} \mathrm{SeO}_{3}\right]$ <br> $\left(\mathrm{mol} \mathrm{L}^{-1}\right)$ | Initial [I $\left.\mathrm{I}^{-}\right]$ <br> $\left(\mathrm{mol} \mathrm{L}^{-1}\right)$ | Initial $\left[\mathrm{H}^{+}\right]$ <br> $\left(\mathrm{mol} \mathrm{L}^{-1}\right)$ | Initial rate of <br> increase of $\left[\mathrm{I}_{3}{ }^{-1}\right.$ <br> $\left(\mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.100 | 0.100 | 0.100 | 1.000 |
| 2 | 0.100 | 0.075 | 0.100 | 0.422 |
| 3 | 0.075 | 0.100 | 0.100 | 0.750 |
| 4 | 0.100 | 0.075 | 0.075 | 0.237 |

Determine the rate law for the reaction.

The rate law is of the form:

$$
\text { rate }=\boldsymbol{k}\left[\mathbf{H}_{2} \mathrm{SeO}_{3}\right]^{x}\left[I^{-}\right]^{y}\left[\mathbf{H}^{+}\right]^{z}
$$

Between experiments (1) and (3), $\left[\left[^{-}\right]\right.$and $\left[\mathrm{H}^{+}\right]$are both constant. The change in rate is due to the change in $\left[\mathrm{H}_{2} \mathrm{SeO}_{3}\right]$ :

$$
\frac{\text { rate }(3)}{\operatorname{rate}(1)}=\frac{k(0.075)^{x}(0.100)^{y}(0.100)^{z}}{k(0.100)^{x}(0.100)^{y}(0.100)^{z}}=\frac{(0.075)^{x}}{(0.100)^{x}}=\frac{0.750}{1.000} \text { so } x=1
$$

Between experiments (1) and (2), $\left[\mathrm{H}_{2} \mathrm{SeO}_{3}\right]$ and $\left[\mathrm{H}^{+}\right]$are both constant. The change in rate is due to the change in [ $\left.\mathrm{I}^{[ }\right]$:

$$
\frac{\operatorname{rate}(2)}{\operatorname{rate}(1)}=\frac{k(0.100)^{x}(0.075)^{y}(0.100)^{z}}{k(0.100)^{x}(0.100)^{y}(0.100)^{z}}=\frac{(0.075)^{y}}{(0.100)^{y}}=\frac{0.422}{1.000} \text { so } y=3
$$

Between experiments (2) and (4), $\left[\mathrm{H}_{2} \mathrm{SeO}_{3}\right]$ and $[\mathrm{I}]$ are both constant. The change in rate is due to the change in $\left[\mathrm{H}^{\dagger}\right]$ :

$$
\frac{\text { rate }(4)}{\text { rate }(2)}=\frac{k(0.100)^{*}(0.075)^{y}(0.075)^{z}}{k(0.100)^{*}(0.075)^{¥}(0.100)^{z}}=\frac{(0.075)^{z}}{(0.100)^{z}}=\frac{0.237}{0.422} \text { so } z=2
$$

## Overall:

$$
\text { rate }=k\left[\mathbf{H}_{2} \mathrm{SeO}_{3}\right]\left[\mathrm{I}^{-}\right]^{3}\left[\mathbf{H}^{+}\right]^{2}
$$

What is the value of the rate constant?

Using, for example, experiment (1), the initial rate of increase of $\left[I_{3}{ }^{-}\right]=1.000 \mathrm{~mol}$ $L^{-1} s^{-1}$. As $2 I_{3}{ }^{-}$are produced in the reaction:
rate of reaction $=1 / 2 \times$ rate of increase of $I_{3}=0.5000 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$

$$
\begin{aligned}
\text { rate } & =k\left[\mathrm{H}_{2} \mathrm{SeO}_{3}\right]\left[\mathrm{I}^{-}\right]^{3}\left[\mathrm{H}^{+}\right]^{2} \\
& =k\left(0.100 \mathrm{~mol} \mathrm{~L}^{-1}\right)\left(0.100 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{3}\left(0.100 \mathrm{~mol}^{-1}\right)^{2}=0.5000 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$

## Hence:

$$
k=\left(0.5000 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}\right) /\left(1.00 \times 10^{-6} \mathrm{~mol}^{6} \mathrm{~L}^{-6}\right)=5.00 \times 10^{5} \mathrm{~L}^{5} \mathrm{~mol}^{-5} \mathrm{~s}^{-1}
$$

Answer: $\mathbf{5 . 0 0} \times \mathbf{1 0}^{\mathbf{5}} \mathrm{L}^{\mathbf{5}} \mathbf{~ m o l}^{-5} \mathrm{~s}^{\mathbf{- 1}}$

