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## 2012-N-2:

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## 2012-N-13:

- Redox Reactions and Introduction to Electrochemistry
- Introduction to Colloids and Surface Chemistry

2012-N-14:

- Complexes

2012-N-15:

- Chemical Kinetics
- Explain the following terms or concepts.
a) Second law of thermodynamics

All processes occur spontaneously in the direction that increases the total entropy of the universe.
b) Vapour pressure

The partial pressure that builds up above the surface of a volatile liquid in a closed container due to evaporation.
c) Isoelectric point

The pH at which a protein or amino acid has no net charge, i.e. it contains equal amounts of positive and negative charges.

- The electron transfer reaction between NADH and oxygen is a spontaneous reaction at $37^{\circ} \mathrm{C}$

$$
\mathrm{NADH}+1 / 2 \mathrm{O}_{2}+\mathrm{H}^{+} \rightarrow \mathrm{NAD}^{+}+\mathrm{H}_{2} \mathrm{O} \quad \Delta G=-220 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

When this reaction is carried out in solution in a test tube via direct mixing of NADH with dissolved oxygen, the reaction releases a significant amount of heat. However, when the reaction occurs in mitochondria during respiration, it produces very little heat. Explain why the heat evolved is much less in mitochondria.

According to the First Law of Thermodynamics, energy can be transferred in the form of heat or work. The amount of energy the reaction releases is constant, so if the heat released in mitochondria is reduced it means more work must be done.
$\Delta G$ is the maximum amount of non- $P V$ work obtainable from a system. The energy released by the oxidation of NADH in mitochondria is used to do non-PV work, viz. the pumping of $\mathrm{H}^{+}$ions across the inner mitochondrial membrane. By storing this energy in the form of an $\mathrm{H}^{+}$gradient, the amount of energy wasted as heat is reduced.

- Copper metal can be obtained by heating copper oxide, CuO , in the presence of

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

$$
\begin{aligned}
& \Delta_{\mathrm{r}} H^{\circ}(1)=\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{CO}_{2}(\mathrm{~g})\right)-\left[\Delta_{\mathrm{f}} H^{\circ}(\mathrm{CuO}(\mathrm{~s}))+\Delta_{\mathrm{f}} H^{\circ}(\mathrm{CO}(\mathrm{~g}))\right] \\
& \Delta_{\mathrm{r}} H^{\circ}(2)=2 \Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{CO}_{2}(\mathrm{~g})\right)-2 \Delta_{\mathrm{f}} H^{\circ}(\mathrm{CO}(\mathrm{~g}))=-566.1 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
& \Delta_{\mathrm{r}} H^{\circ}(3)=2 \Delta_{\mathrm{f}} H^{\circ}(\mathrm{CuO}(\mathrm{~s}))=-\mathbf{3 1 0 . 5} \mathrm{kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Using $\Delta_{f} H^{\circ}=0$ for $\mathrm{Cu}(\mathrm{s})$ and $\mathrm{O}_{2}(\mathrm{~g})$ as these are elements in their standard states.
Rearranging (1) gives:

$$
\begin{aligned}
\Delta_{\mathrm{r}} H^{\circ}(1) & =\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{CO}_{2}(\mathrm{~g})\right)-\Delta_{\mathrm{f}} H^{\circ}(\mathrm{CO}(\mathrm{~g}))-\Delta_{\mathrm{f}} H^{\circ}(\mathrm{CuO}(\mathrm{~s})) \\
& =1 / 2\left(\Delta_{\mathrm{r}} H^{\circ}(2)\right)-1 / 2\left(\Delta_{\mathrm{r}} H^{\circ}(3)\right) \\
& =[1 / 2(-566.1)-1 / 2(-310.5)] \mathrm{kJ} \mathrm{~mol}^{-1}=-127.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

$$
\text { Answer: - } \mathbf{- 1 2 7 . 8} \mathbf{~ k J ~ m o l}{ }^{\mathbf{1}}
$$

- Acetylene burns in air according to the following equation:

$$
\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})+5 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \quad \Delta H^{\circ}=-1255.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

The $\Delta_{\mathrm{f}} H^{\circ}$ of $\mathrm{CO}_{2}(\mathrm{~g})=-393.5 \mathrm{~kJ} \mathrm{~mol}^{-1}, \Delta_{\mathrm{f}} H^{\circ}$ of $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})=-285.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $\Delta_{\text {vap }} H^{\circ}$ of $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})=+44.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$. What is $\Delta_{\mathrm{f}} H^{\circ}$ of $\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})$ ?

Using $\Delta_{\mathrm{r}} H^{\circ}=\sum \Delta_{\mathrm{f}} H^{\circ}$ (products) $-\sum \Delta_{\mathrm{f}} H^{\circ}$ (reactants), the enthalpy of combustion of $\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})$ is:

$$
\begin{aligned}
\Delta_{\text {comb }} H^{\circ}\left(\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})\right)= & {\left[2 \Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{CO}_{2}(\mathrm{~g})\right)+\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right)\right] } \\
& -\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})\right)=-1255.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

The enthalpy of vaporisation for $\mathrm{H}_{\mathbf{2}} \mathrm{O}(\mathrm{g})$ corresponds to $\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ :

$$
\Delta_{\text {vap }} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)=\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right)-\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)=+44.0 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

and so,

$$
\begin{aligned}
\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right) & =\Delta_{\text {vap }} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)+\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right) \\
& =(+44.0+\mathbf{- 2 8 5 . 8}) \mathrm{kJ} \mathrm{~mol}^{-1}=-241.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Substituting the data into the expression for $\Delta_{\text {comb }} H^{\circ}\left(\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})\right)$

$$
\begin{aligned}
& \Delta_{\text {comb }} H^{\circ}\left(\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})\right)= {[(2 \times-393.5+-241.8)} \\
&\left.-\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})\right)\right] \mathrm{kJ} \mathrm{~mol} \\
& \\
& \hline 1
\end{aligned}=-1255.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

So:

$$
\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})=[(2 \times-393.5+-241.8)+1255.8] \mathrm{kJ} \mathrm{~mol}^{-1}=+227.0 \mathrm{~kJ} \mathrm{~mol}^{-1}\right.
$$

- A sample of gas is found to exert a pressure of $7.00 \times 10^{4} \mathrm{~Pa}$ when it is in a 3.00 L
flask at $10.00{ }^{\circ} \mathrm{C}$. Calculate the new volume if the pressure becomes $1.01 \times 10^{5} \mathrm{~Pa}$ and the temperature is unchanged.

Using the ideal gas law, $P V=n R T$, the number of moles present is:

$$
\begin{aligned}
n & =P V / R T=\left(7.00 \times 10^{4} \mathrm{~Pa}\right)\left(3.00 \times 10^{-3} \mathrm{~m}^{3}\right) /\left(8.314 \mathrm{~m}^{3} \mathrm{~Pa} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(283.00 \mathrm{~K}) \\
& =8.925 \times 10^{-2} \mathrm{~mol}
\end{aligned}
$$

At the new pressure, the volume occupied by this amount is:

$$
\begin{aligned}
V & =n R T / P=\left(8.925 \times 10^{-2} \mathrm{~mol}\right)\left(8.314 \mathrm{~m}^{3} \mathrm{~Pa} \mathrm{~K}\right. \\
& \left.=2.08 \times 1 \mathrm{~mol}^{-1}\right)(283.00 \mathrm{~K}) /\left(1.01 \times 10^{3} \mathrm{~Pa}\right) \\
& 2.08 \mathrm{~L}
\end{aligned}
$$

More quickly, $P_{1} V_{1}=P_{2} V_{2}$ can be used:

$$
V_{2}=P_{1} V_{1} / P_{2}=\left(7.00 \times 10^{4} \mathrm{~Pa}\right)(3.00 \mathrm{~L}) /\left(1.01 \times 10^{5} \mathrm{~Pa}\right)=2.08 \mathrm{~L}
$$

Answer: $\mathbf{2 . 0 8} \mathbf{L}$
Calculate the new pressure if the volume becomes 2.00 L and the temperature is unchanged.

From above, $n=8.925 \times 10^{-2} \mathrm{~mol}$. The pressure when $V=2.00 \mathrm{~L}$ and $T=283.00$ $K$ is:

$$
\begin{aligned}
P & =n R T / V \\
& =\left(8.925 \times 10^{-2} \mathrm{~mol}\right)\left(8.314 \mathrm{~m}^{3} \mathrm{~Pa} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(283.00 \mathrm{~K}) /\left(2.00 \times 10^{-3} \mathrm{~m}^{3}\right) \\
& =1.05 \times 10^{5} \mathrm{~Pa}
\end{aligned}
$$

$P_{1} V_{1}=P_{2} V_{2}$ can again be used without calculating $\boldsymbol{n}$ :

$$
P_{2}=P_{1} V_{1} / V_{2}=\left(7.00 \times 10^{4} \mathrm{~Pa}\right) \times(3.00 \mathrm{~L}) /(2.00 \mathrm{~L})=1.05 \times 10^{5} \mathrm{~Pa}
$$

$$
\text { Answer: } \mathbf{1 . 0 5} \times \mathbf{1 0}^{\mathbf{5}} \mathbf{~ P a}
$$

Calculate the new pressure if the temperature is raised to $50.0^{\circ} \mathrm{C}$ and the volume is unchanged, i.e. still 3.00 L .

From above, $n=8.925 \times 10^{-2} \mathrm{~mol}$. The pressure when $V=3.00 \mathrm{~L}$ and $T=323.0 \mathrm{~K}$ is:

$$
\begin{aligned}
P & =n R T / V \\
& =\left(8.925 \times 10^{-2} \mathrm{~mol}\right)\left(8.314 \mathrm{~m}^{3} \mathrm{~Pa} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(323.0 \mathrm{~K}) /\left(3.00 \times 10^{-3} \mathrm{~m}^{3}\right) \\
& =7.99 \times 10^{4} \mathrm{~Pa}
\end{aligned}
$$

The new pressure can be calculated directly using $P_{1} / T_{1}=P_{2} / T_{2}$ :

$$
P_{2}=P_{1} \times T_{2} / T_{1}=\left(7.00 \times 10^{4} \mathrm{~Pa}\right) \times 323.0 / 283.0=7.99 \times 10^{4} \mathrm{~Pa}
$$

Answer: $\mathbf{7 . 9 9 \times 1 0 ^ { 4 }} \mathbf{~ P a}$

- Consider the following reaction.

$$
\mathrm{SO}_{2}(\mathrm{~g})+\mathrm{NO}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{SO}_{3}(\mathrm{~g})+\mathrm{NO}(\mathrm{~g})
$$

An equilibrium mixture in a 1.00 L vessel was found to contain $\left[\mathrm{SO}_{2}(\mathrm{~g})\right]=0.800 \mathrm{M}$, $\left[\mathrm{NO}_{2}(\mathrm{~g})\right]=0.100 \mathrm{M},\left[\mathrm{SO}_{3}(\mathrm{~g})\right]=0.600 \mathrm{M}$ and $[\mathrm{NO}(\mathrm{g})]=0.400 \mathrm{M}$. If the volume and temperature are kept constant, what amount (in mol) of $\mathrm{NO}(\mathrm{g})$ needs to be added to the reaction vessel to give an equilibrium concentration of $\mathrm{NO}_{2}(\mathrm{~g})$ of 0.300 M ?

From the chemical equation,

$$
K_{\mathrm{eq}}=\frac{\left[\mathrm{SO}_{3}(\mathrm{~g})\right][\mathrm{NO}(\mathrm{~g})]}{\left[\mathrm{SO}_{2}(\mathrm{~g})\right]\left[\mathrm{NO}_{2}(\mathrm{~g})\right]}
$$

As the original mixture is at equilibrium:

$$
K_{\mathrm{eq}}=\frac{\left[\mathrm{SO}_{3}(\mathrm{~g})\right][\mathrm{NO}(\mathrm{~g})]}{\left[\mathrm{SO}_{2}(\mathrm{~g})\right]\left[\mathrm{NO}_{2}(\mathrm{~g})\right]}=\frac{(0.600)(0.400)}{(0.800)(0.100)} \quad=3.00
$$

This equilibrium is now disturbed by the addition of $x$ M of $\mathrm{NO}(\mathrm{g})$. To reestablish equilibrium, the reaction will shift to the left by an unknown amount $y$. The reaction table for this is:

|  | $\mathrm{SO}_{2}(\mathrm{~g})$ | $\mathrm{NO}_{2}(\mathrm{~g})$ |  | $\mathrm{SO}_{3}(\mathrm{~g})$ | $\mathrm{NO}(\mathrm{g})$ |
| :---: | :---: | :---: | :--- | :---: | :---: |
| initial | 0.800 | 0.100 | $\rightleftharpoons$ | 0.600 | $0.400+x$ |
| change | $+y$ | $+y$ |  | $-y$ | $-\underline{y}$ |
| equilibrium | $0.800+y$ | $0.100+y$ |  | $0.600-y$ | $0.400+x-y$ |

As $\left[\mathrm{NO}_{2}(\mathrm{~g})\right]=0.300 \mathrm{M}$ at the new equilibrium, $\boldsymbol{y}=(0.300-0.100) \mathrm{M}=0.200 \mathrm{M}$. Hence, the new equilibrium concentrations are:

$$
\begin{aligned}
& {\left[\mathrm{SO}_{2}(\mathrm{~g})\right]=(\mathbf{0 . 8 0 0}+\mathbf{0 . 2 0 0}) \mathrm{M}=\mathbf{1 . 0 0 0} \mathrm{M}} \\
& {\left[\mathrm{NO}_{2}(\mathrm{~g})\right]=\mathbf{0 . 3 0 0} \mathrm{M}} \\
& {\left[\mathrm{SO}_{3}(\mathrm{~g})\right]=(\mathbf{0 . 6 0 0}-\mathbf{0 . 2 0 0}) \mathrm{M}=\mathbf{0 . 4 0 0} \mathbf{M}} \\
& {[\mathrm{NO}(\mathrm{~g})]=(\mathbf{0 . 4 0 0}+\boldsymbol{x}-\mathbf{0 . 2 0 0}) \mathrm{M}=(\mathbf{0 . 2 0 0}+\boldsymbol{x}) \mathbf{M}}
\end{aligned}
$$

As the system is at equilibrium,

$$
K_{\mathrm{eq}}=\frac{\left[\mathrm{SO}_{3}(\mathrm{~g})\right][\mathrm{NO}(\mathrm{~g})]}{\left[\mathrm{SO}_{2}(\mathrm{~g})\right]\left[\mathrm{NO}_{2}(\mathrm{~g})\right]}=\frac{(0.400)(0.200+x)}{(1.000)(0.300)}=3.00
$$

Solving this gives $x=2.05 \mathrm{M}$. As the reaction is carried out in a 1.00 L container, this is also the number of moles required.

- Phenylketonuria is an inherited disorder in which phenylacetic acid, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{COOH}$,

As HPAc is a weak acid, the equilibrium for its dissociation can be studied using an 'ICE' table:

|  | HPAc | $\rightleftharpoons$ | $\mathrm{PAc}^{-}$ | $\mathbf{H}^{+}$ |
| :--- | :--- | :--- | :--- | :--- |
| initial | $\mathbf{0 . 1 2}$ |  | 0 | 0 |
| change | $-\boldsymbol{x}$ |  | $+\boldsymbol{x}$ | $+\boldsymbol{x}$ |
| final | $\mathbf{0 . 1 2 - x}$ |  | $\boldsymbol{x}$ | $\boldsymbol{x}$ |

By definition, $\mathbf{p H}=-\log _{10}\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ so $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=10^{-2.60} \mathrm{M}$. From the reaction
table, $x=\left[\mathbf{H}^{+}(\mathrm{aq})\right]_{\mathrm{eq}}$ so:

$$
\begin{aligned}
& {\left[\mathrm{HPAc}_{\mathrm{eq}}=0.12-x=\left(0.12-10^{-2.60}\right) \mathrm{M}=0.12 \mathrm{M} \text { (to } 2 \text { s.f. }\right)} \\
& {\left[\mathrm{H}^{+}(\mathrm{aq})\right]_{\mathrm{eq}}=x=10^{-2.60} \mathrm{M}} \\
& {\left[\mathrm{PAc}^{-}(\mathrm{aq})\right]_{\mathrm{eq}}=x=10^{-2.60} \mathrm{M}}
\end{aligned}
$$

The equilibrium constant $K_{\mathrm{a}}$ is given by:

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{HPac}^{-}\right]\left[\mathrm{H}^{+}\right]}{[\mathrm{HPAc}]}=\frac{\left(10^{-2.60}\right)\left(10^{-2.60}\right)}{(0.12)}=5.26 \times 10^{-5}
$$

By definition, $\mathrm{p} K_{\mathrm{a}}=-\log _{10} K_{\mathrm{a}}$ so:

$$
\mathrm{p} K_{\mathrm{a}}=-\log _{10}\left(5.26 \times 10^{-5}\right)=4.28
$$

Answer: 4.28

- The concentration of NaCl used in intravenous drips is 150 mM . Explain why this particular concentration is used and what the consequences would be for a patient if pure water were used instead.

150 mM is used because this corresponds to the NaCl concentration in extracellular fluids and thus prevents any change in osmotic conditions in the blood. If water were used, water would flow into the red blood cells causing them to swell up and possibly burst. This may have fatal consequences for the patient.

- A calorimeter, consisting of an insulated coffee cup containing 50.0 g of water at $21.0^{\circ} \mathrm{C}$, has a total heat capacity of $9.4 \mathrm{~J} \mathrm{~K}^{-1}$. When a 30.4 g sample of an alloy at $92.0^{\circ} \mathrm{C}$ is placed into the calorimeter, the final temperature of the system is $31.2^{\circ} \mathrm{C}$. What is the specific heat capacity of the alloy?

The calorimeter is heated from $21.0^{\circ} \mathrm{C}$ to $31.2^{\circ} \mathrm{C}$ corresponding to a temperature increase of:

$$
\Delta T_{\text {calorimeter }}=(31.2-21.0) \mathrm{K}=+10.2 \mathrm{~K}
$$

As the heat capacity of the calorimeter is $9.4 \mathrm{~J} \mathrm{~K}^{-1}$, the heat change of the caloriometer is:

$$
q_{\text {calorimeter }}=C_{\text {calorimeter }} \Delta T_{\text {calorimeter }}=\left(9.4 \mathrm{~J} \mathrm{~K}^{-1}\right)(\mathbf{1 0 . 2} \mathbf{K})=+\mathbf{9 5 . 9} \mathbf{~ J}
$$

As this heat comes from the alloy:

$$
q_{\text {alloy }}=-q_{\text {calorimeter }}=-95.9 \mathrm{~J}
$$

The alloy cools from $92.0^{\circ} \mathrm{C}$ to $31.2^{\circ} \mathrm{C}$ corresponds to a temperature change of:

$$
\Delta T_{\text {alloy }}=(31.2-92.0) \mathrm{K}=-60.8 \mathrm{~K}
$$

Using $q=m C \Delta T$,

$$
C=q / m \Delta T=-95.9 \mathrm{~J} /(30.4 \mathrm{~g} \times-60.8)=0.052 \mathrm{~J} \mathrm{~g}^{-1} \mathrm{~K}^{-1}
$$

$$
\text { Answer: } \mathbf{0 . 0 5 2} \mathbf{J ~ g}^{-1} \mathbf{K}^{-1}
$$

- At $21.0^{\circ} \mathrm{C}$, a solution of 18.26 g of a non-volatile, non-polar compound in 33.25 g of bromoethane, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}$, has a vapour pressure of $4.42 \times 10^{4} \mathrm{~Pa}$. The vapour pressure of pure bromoethane at this temperature is $5.26 \times 10^{4} \mathrm{~Pa}$. What is the molar mass of the compound?

The molar mass of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}$ is:

$$
\begin{aligned}
\text { molar mass } & =(2 \times 12.01(\mathrm{C})+5 \times 1.008(\mathrm{H})+79.90(\mathrm{Br})) \mathrm{g} \mathrm{~mol}^{-1} \\
= & 108.96 \mathrm{~g} \mathrm{~mol}^{-1}
\end{aligned}
$$

The number of moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}$ in 18.26 g is therefore:

$$
n_{\text {solvent }}=\text { mass } / \text { molar mass }=33.25 \mathrm{~g} / 108.96 \mathrm{~g} \mathrm{~mol}^{-1}=0.305 \mathrm{~mol}
$$

From Raoult's law, the vapour pressure of a solution, $P_{\text {solution }}$, is related to the vapour pressure of the pure solvent, $\boldsymbol{P}_{\text {solvent }}^{0}$ and its mole fraction, $X_{\text {solvent }}$ :

$$
P_{\text {solution }}=X_{\text {solvent }} \times P_{\text {solvent }}^{0}
$$

Using $P_{\text {solution }}=4.42 \times 10^{4} \mathrm{~Pa}$ and $P^{0}{ }_{\text {solvent }}=5.26 \times 10^{4} \mathrm{~Pa}$, the mole fraction must be:

$$
X_{\text {solvent }}=P_{\text {solution }} / P_{\text {solvent }}^{0}=\left(4.42 \times 10^{4} / 5.26 \times 10^{4}\right)=0.840
$$

The mole fraction of solvent is given by the number of moles of solvent divided by the total number of moles of solvent and solute:

$$
X_{\text {solvent }}=n_{\text {solvent }} /\left(n_{\text {solvent }}+n_{\text {solute }}\right)=0.840
$$

Using $\boldsymbol{n}_{\text {solvent }}=0.305 \mathrm{~mol}$ from above,

$$
\begin{aligned}
& n_{\text {solvent }} /\left(n_{\text {solvent }}+n_{\text {solute }}\right)=0.305 /\left(0.305+n_{\text {solute }}\right)=0.840 \\
& n_{\text {solute }}=(0.305 / 0.840-0.305) \mathrm{mol}=0.0581 \mathrm{~mol}
\end{aligned}
$$

As this corresponds to a mass of 18.26 g , the molar mass is:
molar mass $=$ mass $/$ number of moles $=18.26 \mathrm{~g} / 0.0581 \mathrm{~mol}=315 \mathrm{~g} \mathrm{~mol}^{-1}$
Answer: $\mathbf{3 1 5} \mathbf{g ~ m o l}^{-1}$

- Buffer 1 is a solution containing $0.08 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ and $0.12 \mathrm{M} \mathrm{NH}_{3}$. Buffer 2 is a solution containing $0.15 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ and $0.05 \mathrm{M} \mathrm{NH}_{3}$. The acid dissociation constant of the ammonium ion is $5.50 \times 10^{-10}$. What are the pH values of each of the buffer solutions?

By definition, $\mathrm{p} K_{\mathrm{a}}=-\log _{10} K_{\mathrm{a}}$ so:

$$
\mathrm{p} K_{\mathrm{a}}=-\log _{10}\left(5.50 \times 10^{-10}\right)=9.26
$$

Using the Henderson-Hasselbalch equation,

$$
\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{[\text { base }]}{[\text { acid }]}=9.290+\log \frac{\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{NH}_{3} \mathrm{Cl}\right]}
$$

## For buffer 1:

$$
\mathrm{pH}=9.26+\log \frac{0.12}{0.08}=9.44
$$

## For buffer 2:

$$
\mathrm{pH}=9.26+\log \frac{0.05}{0.15}=8.78
$$

Buffer $1 \mathrm{pH}=\mathbf{9 . 4 4}$
Buffer $2 \mathrm{pH}=\mathbf{8 . 7 8}$
Which buffer is better able to maintain a steady pH on the addition of small amounts of both a strong acid and strong base? Explain.

Buffer 1 is better able to maintain a steady pH because its pH is closer to the $\mathrm{p} K_{\mathrm{a}}$ of $\mathbf{N H}_{4}{ }^{+}$. This is because it has relatively high concentrations of both $\mathbf{N H}_{4}{ }^{+}$ and $\mathrm{NH}_{3}$ which can react with any added $\mathrm{OH}^{-}$or $\mathrm{H}^{+}$respectively.

- Order the following salts from lowest to highest molar solubility.

| Salt | CuCl | $\mathrm{Cd}\left(\mathrm{IO}_{3}\right)_{2}$ | $\mathrm{BaSO}_{4}$ | $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ |
| :---: | :---: | :---: | :---: | :---: |
| $K_{\text {sp }}$ | $1.9 \times 10^{-7}$ | $2.3 \times 10^{-8}$ | $1.1 \times 10^{-10}$ | $2.6 \times 10^{-12}$ |

(1) For $\mathrm{CuCl}, K_{\text {sp }}$ refers to the dissolution reaction:

$$
\mathrm{CuCl}(\mathrm{~s}) \rightleftharpoons \mathrm{Cu}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \quad K_{\mathrm{sp}}=\left[\mathrm{Cu}^{+}(\mathrm{aq})\right]\left[\mathrm{Cl}^{-}(\mathrm{aq})\right]
$$

If the solubility is $x \mathrm{~mol} \mathrm{~L}^{-1}$ then $\boldsymbol{x ~ m o l ~ o f ~} \mathrm{CuCl}(\mathrm{s})$ dissolves in one litre. From the dissolution equation, this leads to $\left[\mathrm{Cu}^{+}(\mathrm{aq})\right]=x \mathrm{M}$ and $\left[\mathrm{Cl}^{-}(\mathrm{aq})\right]=x \mathrm{M}$. Hence,

$$
K_{\mathrm{sp}}=(x)(x)=x^{2}=1.9 \times 10^{-7} \quad \text { or } x=\left(1.9 \times 10^{-7}\right)^{1 / 2} \quad \mathrm{M}=4.4 \times 10^{-4} \mathrm{M}
$$

(2) For $\mathrm{Cd}\left(\mathrm{IO}_{3}\right)_{2}, K_{\text {sp }}$ refers to the dissolution reaction:

$$
\mathrm{Cd}\left(\mathrm{IO}_{3}\right)_{2}(\mathrm{~s}) \rightleftharpoons \mathrm{Cd}^{2+}(\mathrm{aq})+2 \mathrm{IO}_{3}^{-}(\mathrm{aq}) \quad K_{\mathrm{sp}}=\left[\mathrm{Cd}^{2+}(\mathrm{aq})\right]\left[\mathrm{IO}_{3}^{-}(\mathrm{aq})\right]^{2}
$$

If the solubility is $x \mathrm{~mol} \mathrm{~L}^{-1}$ then $x \mathrm{~mol}$ of $\mathrm{Cd}\left(\mathrm{IO}_{3}\right)_{2}(\mathrm{~s})$ dissolves in one litre. From the dissolution equation, this leads to $\left[\mathrm{Cd}^{2+}(\mathrm{aq})\right]=x \mathrm{M}$ and $\left[\mathrm{IO}_{3}{ }^{-}(\mathrm{aq})\right]=x \mathrm{M}$. Hence,

$$
K_{\text {sp }}=(x)(2 x)^{2}=4 x^{3}=2.3 \times 10^{-8} \quad \text { or } x=\left(2.3 \times 10^{-8} / 4\right)^{1 / 3} \quad \mathrm{M}=1.8 \times 10^{-3} \mathrm{M}
$$

(3) For $\mathrm{BaSO}_{4}, K_{\text {sp }}$ refers to the dissolution reaction:

$$
\mathrm{BaSO}_{4}(\mathrm{~s}) \rightleftharpoons \mathrm{Ba}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq}) \quad K_{\mathrm{sp}}=\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]
$$

If the solubility is $x \mathrm{~mol} \mathrm{~L}^{-1}$ then $x \mathrm{~mol}$ of $\mathrm{BaSO}_{4}(\mathrm{~s})$ dissolves in one litre. From the dissolution equation, this leads to $\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]=x \mathrm{M}$ and $\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]=x \mathrm{M}$. Hence,

$$
K_{\mathrm{sp}}=(x)(x)=x^{2}=1.1 \times 10^{-10} \quad \text { or } x=\left(1.1 \times 10^{-10}\right)^{1 / 2} \quad \mathrm{M}=1.0 \times 10^{-5} \mathrm{M}
$$

(4) For $\mathrm{Ag}_{2} \mathrm{CrO}_{4}, K_{\text {sp }}$ refers to the dissolution reaction:

$$
\mathrm{Ag}_{2} \mathrm{SO}_{4}(\mathrm{~s}) \rightleftharpoons 2 \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{CrO}_{4}{ }^{2-}(\mathrm{aq}) \quad K_{\text {sp }}=\left[\mathrm{Ag}^{+}(\mathrm{aq})\right]^{2}\left[\mathrm{CrO}_{4}{ }^{2-}(\mathrm{aq})\right]
$$

If the solubility is $x \mathrm{~mol} \mathrm{~L}^{-1}$ then $x \mathrm{~mol}$ of $\mathrm{Ag}_{2} \mathrm{CrO}_{4}(\mathrm{~s})$ dissolves in one litre. From the dissolution equation, this leads to $\left[\mathrm{Ag}^{+}(\mathrm{aq})\right]=2 \boldsymbol{x} \mathrm{M}$ and $\left[\mathrm{CrO}_{4}{ }^{2-}(\mathrm{aq})\right]=x \mathrm{M}$. Hence,

$$
K_{\mathrm{sp}}=(2 x)^{2}(x)=4 x^{3}=2.6 \times 10^{-12} \quad \text { or } x=\left(2.6 \times 10^{-12} / 4\right)^{1 / 2} \mathrm{M}=8.7 \times 10^{-5} \mathrm{M}
$$

Overall, solubility increases in the order:

$$
\mathrm{BaSO}_{4}<\mathrm{Ag}_{2} \mathrm{CrO}_{4}<\mathrm{CuCl}<\mathrm{Cd}\left(\mathrm{IO}_{3}\right)_{2}
$$

- Give the equilibrium concentration of $\mathrm{Ni}^{2+}(\mathrm{aq})$ ions in a solution formed by dissolving 0.15 mol of $\mathrm{NiCl}_{2}$ in 0.500 L of 2.00 M KCN solution. The $K_{\text {stab }}$ of $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}=1.7 \times 10^{30}$.

When the $\mathrm{NiCl}_{2}$ is added to 0.500 L , the concentration of $\mathrm{Ni}^{\mathbf{2 +}}(\mathrm{aq})$ :

$$
\begin{aligned}
\text { concentration }=\left[\mathrm{Ni}^{2+}(\mathrm{aq})\right] & =\text { number of moles } / \text { volume } \\
& =0.15 \mathrm{~mol} / 0.500 \mathrm{~L}=0.30 \mathrm{M}
\end{aligned}
$$

As $K_{\text {stab }}$ is so large, essentially all of this will be complexed by the excess $\mathrm{CN}^{-}(\mathrm{aq})$ ions:

$$
\mathrm{Ni}^{2^{+}}(\mathrm{aq})+4 \mathrm{CN}^{-}(\mathrm{aq}) \rightleftharpoons\left[\mathrm{Ni}(\mathrm{CN})_{4}{ }^{2-}(\mathrm{aq})\right]
$$

As essentially all of the $\mathrm{Ni}^{\mathbf{2}^{+}}(\mathrm{aq})$ becomes $\left[\mathrm{Ni}(\mathrm{CN}) 4^{\mathbf{2 -}}(\mathrm{aq})\right]$ :

$$
\begin{aligned}
& {\left[\mathrm{Ni}(\mathrm{CN})_{4}{ }^{2-}(\mathrm{aq})\right]=0.30 \mathrm{M}} \\
& {\left[\mathrm{CN}^{-}(\mathrm{aq})\right]=(2.00-4 \times 0.30) \mathrm{M}=0.80 \mathrm{M}}
\end{aligned}
$$

$K_{\text {stab }}$ is the equilibrium constant for the reaction so:

$$
K_{\text {stab }}=\frac{\left[\mathrm{Ni}(\mathbf{C N})_{4}^{2-}(\mathbf{a q})\right]}{\left[\mathrm{Ni}^{2+}(\mathbf{a q})\right]\left[\mathrm{CN}^{-}(\mathbf{a q})\right]^{4}}
$$

If the tiny amount of uncomplexed $\mathrm{Ni}^{2+}(\mathrm{aq})$ has a concentration of $\boldsymbol{x}$ M then:

$$
K_{\text {stab }}=\frac{(0.30)}{(x)(0.80)^{4}}=1.7 \times 10^{30} \quad \text { so } x=4.3 \times 10^{-31} \mathrm{M}
$$

- What mass of isotope would be initially required if a medical procedure needs 2.0 mg

The activity coefficient, $\lambda$, is related to the half life, $t_{1 / 2}$ through:

$$
\lambda=\ln 2 / t_{1 / 2}=\ln 2 /(6.0 \text { hours })=0.115 \text { hours }^{-1}
$$

The number of nuclei, $N$, decays with time according to:

$$
\ln \left(N_{\mathrm{t}} / N_{0}\right)=\lambda t
$$

As the mass is proportional to the number of nuclei, this can be rewritten as:

$$
\ln \left(m_{0} / m_{t}\right)=\lambda t
$$

If the mass after $\boldsymbol{t}=\mathbf{5 0}$. hours is $\boldsymbol{m}_{\mathrm{t}} \mathbf{=} \mathbf{2 . 0} \mathbf{~ m g}$, then

$$
\ln \left(m_{0} / 2.0\right)=(0.115) \times(50)
$$

so:

$$
m_{0}=650 \mathrm{mg}
$$

## Answer: $\mathbf{6 5 0} \mathbf{~ m g}$

- Comment on the stability of the following nuclides, and the type of radioactive decay (if any) that they undergo.


## ${ }_{10}^{18} \mathrm{Ne}$

For this nuclide, $Z=10$ and $N=(18-10)=8$. With an $N: Z$ ratio of 0.8 , it has too few neutrons. It would undergo positron ( $\boldsymbol{\beta}^{+}$) emission or electron capture to increase this ratio.

## ${ }_{16}^{32} \mathrm{~S}$

For this nuclide, $Z=16$ and $N=(32-16)=16$. With an $N: Z$ ratio of 1.0 , it is probably stable.

As $Z>83$, it is beyond the zone of stability and is unstable. It will indergoes $\alpha$ decay to reduce its mass.

- A galvanic cell consists of a $\mathrm{Cr}^{3+} / \mathrm{Cr}$ half-cell with unknown $\left[\mathrm{Cr}^{3+}\right]$ and a $\mathrm{Ni}^{2+} / \mathrm{Ni}$ halfcell with $\left[\mathrm{Ni}^{2+}\right]=1.20 \mathrm{M}$. The electromotive force of the cell at $25^{\circ} \mathrm{C}$ was measured to be 0.55 V . What is the concentration of $\mathrm{Cr}^{3+}$ in the $\mathrm{Cr}^{3+} / \mathrm{Cr}$ half-cell?

From the standard reduction potentials,

$$
\begin{array}{ll}
\mathrm{Cr}^{3+}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathbf{C r}(\mathbf{s}) & E^{0}=-0.74 \mathrm{~V} \\
\mathrm{Ni}^{2^{+}}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Ni}(\mathrm{~s}) & E^{0}=-0.24 \mathrm{~V}
\end{array}
$$

The most negative is reversed to give an overall reaction and cell potential of

$$
3 \mathrm{Ni}^{2+}(\mathrm{aq})+2 \mathrm{Cr}(\mathrm{~s}) \rightarrow 3 \mathrm{Ni}(\mathrm{~s})+2 \mathrm{Cr}^{3+}(\mathrm{aq}) \quad E^{0}=(+0.74-0.24) \mathrm{V}=0.50 \mathrm{~V}
$$

From the Nernst equation for this $\mathbf{6}$ electron reaction,

$$
\begin{aligned}
E & =E^{\circ}-\frac{R T}{n F} \ln Q=E^{\circ}-\frac{R T}{n F} \ln \frac{\left[\mathrm{Cr}^{3+}(\mathrm{aq})\right]^{2}}{\left[\mathrm{Ni}^{2+}(\mathrm{aq})\right]^{3}} \\
& =(0.50 \mathrm{~V})-\frac{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298 \mathrm{~K})}{6 \times 96485 \mathrm{~mol}^{-1}} \ln \frac{\left[\mathrm{Cr}^{3+}(\mathrm{aq})\right]^{2}}{(1.20)^{3}}
\end{aligned}
$$

Solving this gives,

$$
\left[\mathrm{Cr}^{3+}(\mathrm{aq})\right]=3.8 \times 10^{-3} \mathrm{M}
$$

Answer: $\mathbf{3 . 8} \times \mathbf{1 0}^{-\mathbf{3}} \mathbf{M}$
Calculate the equilibrium constant of the reaction at $25^{\circ} \mathrm{C}$.

The equilibrium constant is related to the standard cell potential through:

$$
E^{0}=\frac{R T}{n F} \ln K
$$

Using $E^{0}=+0.50 \mathrm{~V}$,

$$
0.50 \mathrm{~V}=\frac{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298 \mathrm{~K})}{6 \times 96485 \mathrm{~mol}^{-1}} \ln K
$$

Solving this gives:

$$
K=5.5 \times 10^{50}
$$

Calculate the standard Gibbs free energy of the reaction at $25^{\circ} \mathrm{C}$.

The Gibbs free energy change is related to the standard cell potential through:

$$
\begin{aligned}
\Delta G^{0} & =-n F E^{0} \\
& =-6 \times\left(96485 \mathrm{~mol}^{-1}\right) \times(0.50 \mathrm{~V})=-290 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Answer: - $\mathbf{2 9 0} \mathbf{~ k J ~ m o l}{ }^{-1}$
Express the overall reaction in the shorthand voltaic cell notation.
$\operatorname{Cr}(\mathrm{s})\left|\mathrm{Cr}^{3+}(\mathrm{aq}) \| \mathrm{Ni}^{2+}(\mathrm{aq})\right| \mathbf{N i}(\mathrm{s})$

- A strip of copper and a strip of zinc are embedded in a lemon, and are connected by wires to a voltmeter; a voltage is generated and can be read at the voltmeter. What chemical reactions are occurring that lead to the generation of current?

$$
\begin{aligned}
& \mathrm{Zn}(\mathrm{~s}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \quad \text { at the anode } \\
& \mathbf{2 \mathrm { H } ^ { + } ( \mathrm { aq } ) + 2 \mathrm { e } ^ { - } \rightarrow \mathrm { H } _ { 2 } ( \mathrm { g } ) \quad \text { at the cathode }}
\end{aligned}
$$

Assuming there are no losses in the circuit and the conditions are similar to standard, what voltage can be read at the voltmeter?

The $\mathbf{Z n}^{\mathbf{2 +}} / \mathbf{Z n}$ reduction potential is the more negative so is reversed to give $\boldsymbol{E}^{\mathbf{0}}{ }_{\text {ox }}$ $=+0.76 \mathrm{~V}$. The $\mathrm{H}^{+} / \mathrm{H}_{2}$ reduction potential is $\boldsymbol{E}_{\text {red }}^{0}=0.00 \mathrm{~V}$. Overall

$$
E^{0}=E_{o x}^{0}+E_{\text {red }}^{0}=(+0.76+0.00) \mathrm{V}=+0.76 \mathrm{~V}
$$

- The rate constant of a polymer cross-linking reaction was established as a function of temperature. How can we demonstrate that the kinetics of this reaction follow Arrhenius behaviour? If it does follow Arrhenius behaviour, how can we derive the activation energy for the reaction and the pre-exponential factor $A$ ?

The Arrhenius equation relates the rate constant to the temperature, $k=A \mathrm{e}^{-E a / R T}$ Taking natural logarithms of this gives $\ln \boldsymbol{k}=\ln \boldsymbol{A}-\frac{1}{T}\left(\frac{E_{\mathrm{a}}}{R}\right)$ A plot of $\ln k$ (on $\boldsymbol{y}$-axis) versus $\frac{1}{T}$ (on $\boldsymbol{x}$-axis) will be a straight line if Arrhenius behaviour is followed. If so, it has a gradient of $-\frac{E_{\mathrm{a}}}{R}$ and a $\boldsymbol{y}$-intercept of $\ln A$.

- A 20.0 mL sample of $0.121 \mathrm{M} \mathrm{Fe}^{2+}$ in an acid solution was used to titrate 23.5 mL of a $\mathrm{KMnO}_{4}$ solution of unknown concentration. Write the balanced redox reaction that occurs in solution upon titration, and calculate the molarity of the $\mathrm{KMnO}_{4}$ solution.

From the standard reduction potentials, the two relevant half cells are:

$$
\begin{aligned}
& \mathrm{MnO}_{4}^{-}(\mathrm{aq})+8 \mathrm{H}^{+}(\mathrm{aq})+5 \mathrm{e}^{-} \rightarrow \mathrm{Mn}^{2+}(\mathrm{aq})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
& \mathrm{Fe}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Fe}^{3+}(\mathrm{aq})
\end{aligned}
$$

Giving the overall reaction:

$$
5 \mathrm{Fe}^{2+}(\mathrm{aq})+\mathrm{MnO}_{4}^{-}(\mathrm{aq})+8 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow 5 \mathrm{Fe}^{3+}(\mathrm{aq})+\mathrm{Mn}^{2+}(\mathrm{aq})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

The number of moles of $\mathrm{Fe}^{2+}$ used in the titration is:

$$
\begin{aligned}
& \text { number of moles of } \mathrm{Fe}^{2+}=\text { concentration } \times \text { volume } \\
& \left.=0.121 \mathrm{~mol} \mathrm{~L}^{-1}\right) \times(0.0200 \mathrm{~L})=2.42 \times 10^{-3} \mathbf{~ m o l}
\end{aligned}
$$

From the balanced equation, the number of moles of $\mathrm{MnO}_{4}^{-}(\mathrm{aq})$ is therefore:

$$
\text { number of moles of } \mathrm{MnO}_{4}^{-}=1 / 5 \times 2.42 \times 10^{-3} \mathrm{~mol}=4.84 \times 10^{-4} \mathrm{~mol}
$$

This amount is present in $23.5 \mathbf{m L}$ so its concentration must be:

$$
\begin{aligned}
\text { concentration } & =\text { number of moles } / \text { volume } \\
& =4.82 \times 10^{-4} \mathrm{~mol} / 0.0235 \mathrm{~L}=0.0206 \mathrm{M}
\end{aligned}
$$

Answer: $\mathbf{0 . 0 2 0 6}$ M

- Why do phospholipids self-assemble in solution, what structures do they form, and why are they relevant to cell biology?

Phospholipids contain a hydrophilic head and 2 hydrophobic tails.
They self assemble in bilayers with the hydrophobic tails in the centre and the hydrophilic heads at the interface with the solution.
Lipid bilayers (intercalated with proteins) make up over $50 \%$ of cell membranes in biology, as the bilayer arrangement makes an effective barrier against the free passage of water and ions into and out of cells.

- What is a dative bond and does it differ from a covalent bond? Use examples from
- Draw all stereoisomers of the complex ion of $\left[\mathrm{CoCl}_{2}(\mathrm{en})_{2}\right] \mathrm{Cl}$. Label the non-optically active isomer with its systematic name.
(en $=$ ethylenediamine $=1,2$-ethanediamine $=\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ )

enantiomers coordination chemistry and elsewhere to illustrate your answer.

Dative bonds are similar to covalent bonds, but both electrons in the bond are donated by one atom.

They are typically found in coordination complexes where the lone pair on the ligand forms a bond with the metal ion. See the above $\mathbf{C o}($ IIII) complexes for examples and the $\mathrm{BF}_{3}$-ether adduct below for a different type of example. In general, dative bonds are weaker, longer and less directional than covalent bonds.


- The major pollutants emitted by cars, $\mathrm{NO}(\mathrm{g}), \mathrm{CO}(\mathrm{g}), \mathrm{NO}_{2}(\mathrm{~g})$ and $\mathrm{CO}_{2}(\mathrm{~g})$, can react

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

The following rate data were collected at $215^{\circ} \mathrm{C}$.

| Experiment | $\left[\mathrm{NO}_{2}\right]_{0}(\mathrm{M})$ | $[\mathrm{CO}]_{0}(\mathrm{M})$ | Initial rate <br> $\left(\mathrm{d}\left[\mathrm{NO}_{2}\right] / \mathrm{dt}, \mathrm{M} \mathrm{s}^{-1}\right)$ |
| :---: | :---: | :---: | :---: |
| 1 | 0.263 | 0.826 | $1.44 \times 10^{-5}$ |
| 2 | 0.263 | 0.413 | $1.44 \times 10^{-5}$ |
| 3 | 0.526 | 0.413 | $5.76 \times 10^{-5}$ |

Determine the rate law for the reaction.

Between experiments (1) and (2), $\left[\mathrm{NO}_{2}\right]_{0}$ is kept constant and $[\mathrm{CO}]_{0}$ is halved. There is no effect on the rate. The rate is not dependent on $[\mathrm{CO}]_{0}$. It is zero order with respect to CO.

Between experiments (2) and (3), $[\mathrm{CO}]_{0}$ is kept constant and $[\mathrm{NO}]_{0}$ is doubled. This causes the rate to increase by a factor of $\left(5.76 \times 10^{-5} / 1.44 \times 10^{-5}\right)=4$. The rate depends on the square of $[\mathrm{NO}]$. It is second order with respect to NO .

Overall,

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

Suggest a possible mechanism for the reaction based on the form of the rate law.
Explain your answer.

The rate law is determined by the rate of the slowest step. The concentration of the species in this step are determined only by steps before it.

As the rate does not depend on [CO], it must be involved in steps after the rate determining step.

The rate depends on $\left[\mathrm{NO}_{2}\right]^{2}$ which is consistent with two molecules of $\mathbf{N O}_{2}$ colliding in the rate determining step.

The simplest mechanism which fits these points and is consistent with the overall chemical reaction is:

$$
\begin{array}{lll}
\text { Step 1: } & \mathrm{NO}_{2}+\mathrm{NO}_{2} \rightarrow \mathrm{NO}_{3}+\mathrm{NO} & \text { slow, rate determining step } \\
\text { Step 2: } & \mathrm{NO}_{3}+\mathbf{C O} \rightarrow \mathrm{NO}_{2}+\mathbf{C O}_{2} & \text { fast }
\end{array}
$$

