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- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Shape of Atomic Orbitals and Quantum Numbers
- Filling Energy Levels in Atoms Larger than Hydrogen
- Band Theory - MO in Solids

2014-N-3:

- Periodic Table and the Periodic Trends
- Wave Theory of Electrons and Resulting Atomic Energy Levels

2014-N-4:

- Nuclear and Radiation Chemistry

2014-N-5:

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- Atomic Electronic Spectroscopy

2014-N-7:

- Lewis Structures
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- Types of Intermolecular Forces


## 2014-N-8:

- Bonding - MO theory $\left(\mathrm{H}_{2}\right)$
- Bonding - MO theory (larger molecules)

2014-N-9:

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- Chemical Equilibrium
- First and Second Law of Thermodynamics

2014-N-11:

- Gas Laws
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- Equilibrium and Thermochemistry in Industrial Processes

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- Electrolytic Cells

2014-N-16:

- Electrochemistry
- Consider the $4 p$ orbital shown below. Note that, for clarity, the nucleus of the atom is not shown.


How many spherical and planar nodes does this orbital have?
Number of spherical nodes: 2
Number of planar nodes: 1
Complete the following table to give a set of quantum numbers that describes an electron in a $4 p$ orbital.

| Quantum number | $n$ | $\boldsymbol{l}$ | $\boldsymbol{m}_{\boldsymbol{l}}$ | $\boldsymbol{m}_{\boldsymbol{s}}$ |
| :--- | :---: | :---: | :---: | :---: |
| Value | 4 | $\mathbf{1}$ | $\mathbf{- 1 , 0} \mathbf{0 r}+\mathbf{1}$ | $1 / 2$ or $-1 / 2$ |

- What factors determine the lattice energy of an ionic crystal?
- The size of the cations and anions: the smaller the ions are, the higher the lattice energy.
- The charges on the cations and anions: the higher the charges on the ions, the higher the lattice energy.
- The crystal structure: broadly, the higher the number of anions around each cation (and vice versa), the higher the lattice energy.
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
- Electron affinity is the enthalpy change for the reaction $A(g)+e \rightarrow A^{-}(g)$.

Give the electron configurations of the following atoms and singly-charged anions. Use [ Ne ] to represent core electrons.

| Atom | Electron configuration | Ion | Electron configuration |
| :---: | :---: | :---: | :---: |
| Si | $[\mathrm{Ne}](3 s)^{2}(3 p)^{2}$ | $\mathrm{Si}^{-}$ | $[\mathrm{Ne}](3 s)^{2}(3 p)^{3}$ |
| P | $[\mathrm{Ne}](3 s)^{2}(3 p)^{3}$ | $\mathrm{P}^{-}$ | $[\mathrm{Ne}](3 s)^{2}(3 p)^{4}$ |
| S | $[\mathrm{Ne}](3 s)^{2}(3 p)^{4}$ | $\mathrm{~S}^{-}$ | $[\mathrm{Ne}](3 s)^{2}(3 p)^{5}$ |

Explain why the value for the electron affinity of phosphorus is anomalous.
The general trend across a row is for the electron affinity to increase, as the number of protons in the nucleus increases.
However, in order to form $\mathrm{P}^{-}$, the extra electron must pair up with an existing electron in one of the $p$-orbitals. The extra repulsion involved leads to the electron affinity being lower for $\mathbf{P}$ than for Si despite the higher nuclear charge.

What trend would you expect for the electron affinities for $\mathrm{Si}^{-}, \mathrm{P}^{-}$and $\mathrm{S}^{-}$? Explain your answer.

The electron affinities of these anions will be much lower than those of the parent atoms, as adding an electron to an already negatively charged species is much less favourable.

The nuclear charge increase along the series so the electron affinities will increases: $\mathrm{Si}^{-}<\mathrm{P}^{-}<\mathrm{S}^{-}$. The electron affinity of $\mathrm{Si}^{-}$will also be further decreased because addition of an electron requires pairing again. However, this will not affect the order as $\mathrm{Si}^{-}$is already has the lowest electron affinity.

- The isotope ${ }_{27}^{60} \mathrm{Co}$ undergoes radioactive decay to produce a stable isotope of nickel.

Give the balanced equation for this decay process.

$$
{ }_{27}^{60} \mathrm{Co} \rightarrow{ }_{28}^{60} \mathrm{Ni}+{ }_{-1}^{0} e
$$

The half-life of ${ }^{60} \mathrm{Co}$ is 5 years. Calculate the value of the decay constant, $\lambda$, (in s ${ }^{-1}$ ).

The decay constant, $\lambda$, is given by:

$$
\lambda=\ln 2 / t_{1 / 2}=\ln 2 /(5 \times 365.25 \times 24 \times 60 \times 60 \mathrm{~s})=4 \times 10^{-9} \mathrm{~s}^{-1}
$$

Answer: $\mathbf{4 \times 1 0 ^ { - 9 }} \mathbf{s}^{-1}$
What is the molar activity of ${ }^{60} \mathrm{Co}\left(\right.$ in $\left.\mathrm{Bq} \mathrm{mol}{ }^{-1}\right)$ ?

The molar activity, $A$, is given by $A=\lambda N_{\mathrm{A}}$ where $N_{\mathrm{A}}$ is Avogadro's number. Hence:

$$
\begin{aligned}
A & =\left(4 \times 10^{-9} \mathrm{~s}^{-1}\right) \times\left(6.022 \times 10^{23} \text { particles } \mathrm{mol}^{-1}\right) \\
& =3 \times 10^{15} \text { particles s }^{-1} \mathrm{~mol}^{-1}=3 \times 10^{15} \mathrm{~Bq} \mathrm{~mol}^{-1}
\end{aligned}
$$

Answer: $\mathbf{3} \times \mathbf{1 0}^{\mathbf{1 5}} \mathbf{B q} \mathbf{~ m o l}^{-1}$
Complete the graph below.


Estimate from the graph the fraction of
${ }^{60}$ Co remaining after 12 years. $\square$

- The diagram on the left of page 15 depicts the three lowest energy levels of the hydrogen atom. Consider an excited hydrogen atom with an electron in the $3 s$ orbital.
(A) Indicate all possible jumps this electron can make as the atom returns to the ground state. One possible jump (a) is shown for you as an example.
(B) Calculate the energy associated with each of these jumps and mark it on the diagram on the right on page 15. Label the transitions. Again, jump (a) is shown as an example.

Working
The energy of a level is given by $E_{n}=-Z^{2} E_{\mathrm{R}}(1 / n)^{2}$ where $Z=1$ for hydrogen. The energies of the $n=1,2$ and 3 levels are therefore:

$$
\begin{aligned}
& E_{n=1}=-(1)^{2} \times\left(\mathbf{2 . 1 8} \times \mathbf{1 0}^{-18} \mathrm{~J}\right) \times(\mathbf{1} / 1)^{2}=-\mathbf{2 . 1 8} \times \mathbf{1 0}^{-18} \mathrm{~J} \\
& E_{n=2}=-(\mathbf{1})^{2} \times\left(\mathbf{2 . 1 8} \times 10^{-18} \mathrm{~J}\right) \times(\mathbf{1} 2)^{2}=-5.45 \times \mathbf{1 0}^{-19} \mathrm{~J} \\
& E_{n=3}=-(\mathbf{1})^{2} \times\left(\mathbf{2 . 1 8} \times \mathbf{1 0}^{-18} \mathrm{~J}\right) \times(\mathbf{1} / 3)^{2}=-\mathbf{2 . 4 2} \times \mathbf{1 0}^{-19} \mathrm{~J}
\end{aligned}
$$

Alongside (a), two jumps are possible:
(b) $\begin{aligned} n=3 \rightarrow 2: \Delta E & =E_{n=2}-E_{n=3}=\left(-5.45 \times 10^{-19} \mathrm{~J}\right)-\left(-2.42 \times 10^{-19} \mathrm{~J}\right) \\ & =3.06 \times 10^{-19} \mathrm{~J}=30.6 \times 10^{-20} \mathrm{~J}\end{aligned}$ $=3.06 \times 10^{-19} \mathrm{~J}=30.6 \times 10^{-20} \mathrm{~J}$
(c) $n=2 \rightarrow 1: \Delta E=E_{n=1}-E_{n=2}=\left(-2.18 \times 10^{-18} \mathrm{~J}\right)-\left(-5.45 \times 10^{-19} \mathrm{~J}\right)$ $=1.64 \times 10^{-19} \mathrm{~J}=164 \times 10^{-20} \mathrm{~J}$

List all of the transitions that are in the visible region and identify the colour associated with each. For reference, the relationship between colours and wavelengths is shown below.

| UV | violet | blue | green | yellow | orange | red | IR |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :---: |
| 400 | 450 | 490 | 560 | 590 | 630 | 700 nm |  |

The energy is related to the wavelength of the light through Planck's relationship, $\Delta E=h c / \lambda$. For the three transitions:
(a) $\Delta E \sim 194 \times 10^{-20} \mathrm{~J}$ (estimated from graph):

$$
\begin{aligned}
\lambda & =h c / \Delta E=\left(6.626 \times 10^{-34} \times 2.998 \times 10^{8}\right) /\left(194 \times 10^{-20}\right) \mathrm{m} \\
& =1.02 \times 10^{-7} \mathrm{~m}=102 \mathrm{~nm}
\end{aligned}
$$

(b) $\Delta E \sim 30.6 \times 10^{-20} \mathrm{~J}$ :

$$
\begin{aligned}
\lambda & =h c / \Delta E=\left(6.626 \times 10^{-34} \times 2.998 \times 10^{8}\right) /\left(30.6 \times 10^{-20}\right) \mathrm{m} \\
& =1.21 \times 10^{-7} \mathrm{~m}=121 \mathrm{~nm}
\end{aligned}
$$

(b) $\Delta E \sim 164 \times 10^{-20} \mathrm{~J}$ :
$\lambda=h c / \Delta E=\left(6.626 \times 10^{-34} \times 2.998 \times 10^{8}\right) /\left(164 \times 10^{-20}\right) \mathrm{m}$ $=6.56 \times 10^{-7} \mathrm{~m}=656 \mathrm{~nm}$

Transitions (a) and (b) are at shorter wavelength than the visible region. They occur in the UV. Transition (c) occurs in the visible and is in the orange / red region.

ANSWER CONTINUES ON THE NEXT PAGE

If the corresponding transitions were obtained from $\mathrm{He}^{+}$instead of H , would they occur at longer or shorter wavelengths? Give a reason for your answer.
$Z=\mathbf{2}$ for He . The energies of the levels and their separation will be greater for $\mathrm{He}^{+}$than for $\mathbf{H}$. Higher energy corresponds to shorter wavelength.


- Draw the Lewis structure of the following species. The central atom is underlined. Give resonance structures where applicable and indicate whether the species has a dipole moment?

| Species | Lewis structure | Dipole moment |
| :---: | :---: | :---: |
| $\underline{S F}_{4}$ |  | $\underline{\text { Yes / No }}$ |
| $\mathrm{NO}_{2}{ }^{-}$ |  | $\underline{Y e s / N o}$ |

- Complete the table concerning two of the isomers of $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{2}$. Identify the geometry around each atom marked with an asterisk and the list the major intermolecular forces present in the liquid.

| Isomer | A | B |
| :---: | :---: | :---: |
| Chemical structure |  |  |
| Geometry | bent | tetrahedral |
| Major intermolecular forces in liquid | H-bonding, dipole-dipole and dispersion | dipole-dipole and disperson |

The boiling point of isomer A is $141^{\circ} \mathrm{C}$ and that of isomer B is $60^{\circ} \mathrm{C}$. Explain why the boiling point of A is higher than B ?

The molecules are very similar in size so dispersion forces will be of similar magnitude in each.
The strong hydrogen bonding possible for $\mathbf{A}$ is the major reason for its higher boiling point.

- The molecular orbital energy level diagrams for $F_{2}$ and $B_{2}$ are shown below. Fill in the valence electrons for each species in its ground state. Hence calculate the bond order for $\mathrm{F}_{2}$ and $\mathrm{B}_{2}$ and indicate whether these molecules are paramagnetic or diamagnetic.

- Lead shot was traditionally made by dropping molten lead into a tank of water. A piece of lead, initially at $327^{\circ} \mathrm{C}$ is dropped into 200.0 mL of water raising its temperature from 25 to $35^{\circ} \mathrm{C}$. What was the weight of the lead?
Data: Specific heat capacity of Pb is $0.126 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}$
Specific heat capacity of $\mathrm{H}_{2} \mathrm{O}(1)$ is $4.184 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}$
The density of water is $1.0 \mathrm{~g} \mathrm{~mL}^{-1}$
200.0 mL of water corresponds to 200.0 g . When this quantity warms from $25^{\circ} \mathrm{C}$ to $35^{\circ} \mathrm{C}$, the heat change is:

$$
q_{\text {water }}=m C \Delta T=(200.0 \mathrm{~g}) \times\left(4.184 \mathrm{~J} \mathrm{~g}^{-1} \mathrm{~K}^{-1}\right) \times((35-25) \mathrm{K})=8400 \mathrm{~J}
$$

The mass of lead is $\boldsymbol{x} \mathrm{g}$, the heat change when it cools from $35^{\circ} \mathrm{C}$ to $327^{\circ} \mathrm{C}$ is:

$$
q_{\text {lead }}=m C \Delta T=(x) \times\left(0.126 \mathrm{~J} \mathrm{~g}^{-1} \mathrm{~K}^{-1}\right) \times((35-327) \mathrm{K})=-36.7 x \mathrm{~J}
$$

The heat gained by the water is lost by the lead so these two quantities must be equal in magnitude:

$$
\begin{aligned}
& q_{\text {water }}=-q_{\text {lead }} \\
& 8400 \mathrm{~J}=\mathbf{3 6 . 7 x} \mathrm{J} \\
& \boldsymbol{x}=\mathbf{2 3 0} \mathrm{g}
\end{aligned}
$$

Answer: $\mathbf{2 3 0} \mathrm{g}$
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Use the following equilibria:

$$
K_{1}=9.5 \times 10^{-13}
$$

$$
\begin{aligned}
& 2 \mathrm{CH}_{4}(\mathrm{~g}) \rightleftharpoons \mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \\
& \mathrm{CH}_{4}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
\end{aligned}
$$

$$
K_{2}=2.8 \times 10^{-21}
$$

to calculate the equilibrium constant, $K_{3}$, for the following reaction.

$$
2 \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

Show all working.

The equilibrium constant expressions for the three reactions are:

$$
K_{1}=\frac{\left[\mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})\right]\left[\mathrm{H}_{2}(\mathrm{~g})\right]}{\left[\mathrm{CH}_{4}(\mathrm{~g})\right]^{2}} \quad K_{2}=\frac{\left[\mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})\right]\left[\mathrm{H}_{2}(\mathrm{~g})\right]}{\left[\mathrm{CH}_{4}(\mathrm{~g})\right]\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right]} \quad K_{3}=\frac{\left[\mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})\right]\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right]^{2}}{\left[\mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})\right]^{2}\left[\mathrm{H}_{2}(\mathrm{~g})\right]}
$$

Hence, $K_{3}=K_{1} / K_{2}{ }^{2}$ :

$$
\begin{aligned}
K_{1} / K_{2}{ }^{2}= & \frac{\left[\mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})\right]\left[\mathrm{H}_{2}(\mathrm{~g})\right]}{\left[\mathrm{CH}_{4}(\mathrm{~g})\right]^{2}} / \frac{\left[\mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})\right]^{2}\left[\mathrm{H}_{2}(\mathrm{~g})\right]^{2}}{\left[\mathrm{CH}_{4}(\mathrm{~g})\right]^{2}\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right]^{2}}=\frac{\left[\mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})\right]\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right]^{2}}{\left[\mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})\right]^{2}\left[\mathrm{H}_{2}(\mathrm{~g})\right]} \\
& =\left(\mathbf{9 . 5} \times \mathbf{1 0}^{-13}\right) /\left(\mathbf{2 . 8} \times \mathbf{1 0}^{-21}\right)^{2} \\
& =\mathbf{1 . 2} \times \mathbf{1 0}^{\mathbf{2 9}}
\end{aligned}
$$

Answer: $\mathbf{1 . 2} \times \mathbf{1 0}^{\mathbf{2 9}}$

- The Second Law states that all observable processes must involve a net increase in entropy. When liquid water freezes into ice at $0{ }^{\circ} \mathrm{C}$, the entropy of the water decreases. Since the freezing of water is certainly observable, the processes must still satisfy the Second Law. Provide a brief explanation of how this is so.

The Second Law requires that there is a net increase in the entropy of universe:

$$
\Delta_{\text {universe }} S=\Delta_{\text {system }} S+\Delta_{\text {surroundings }} S>0
$$

When water freezes, $\Delta_{\text {system }} S<0$. However, freezing is an exothermic process: heat is given out to the surroundings. The heat gain in the surroundings is equal and opposite to the heat lost in the system: $q_{\text {surr }}=-\Delta_{\text {freezing }} H$. This increases the entropy in the surroundings:

$$
\Delta_{\text {surroundings }} S=-\Delta_{\text {freezing }} H / T
$$

## Overall:

$$
\Delta_{\text {universe }} S=\Delta_{\text {system }} S-\Delta_{\text {freezing }} H / T
$$

As long as the second term is larger than the first, $\Delta_{\text {universe }} S>0$. This is true at low temperatures.

- Ethanol, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{l})$, is increasingly being used as a fuel. Give the balanced chemical equation for the combustion of ethanol in oxygen to produce carbon dioxide and water.

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

Use the standard enthalpies of formation given below to calculate the molar heat of combustion of gaseous ethanol. Show all working.

| Compound | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{g})$ | $\mathrm{CO}_{2}(\mathrm{~g})$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ |
| :--- | :---: | :---: | :---: |
| $\Delta_{\mathrm{f}} H^{\circ} / \mathrm{kJ} \mathrm{mol}^{-1}$ | -235.3 | -393.5 | -285.8 |

Using $\Delta_{\mathrm{rxn}} H^{\circ}=\Sigma m \Delta_{\mathrm{f}} H^{\circ}$ (products) $-\Sigma n \Delta_{\mathrm{f}} H^{\circ}$ (reactants), the enthalpy of this reaction is:

$$
\begin{aligned}
\Delta H^{\circ}= & \left(2 \Delta _ { \mathrm { f } } H ^ { \circ } \left(\mathrm{CO}_{2}(\mathrm{~g})+3 \Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)-\left(\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{l})\right)+3 \Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{O}_{2}(\mathrm{~g})\right)\right.\right.\right. \\
& =[(2 \times-393.5+3 \times-285.8)-(-235.3+0)] \mathrm{kJ} \mathrm{~mol}^{-1}=-1409.1 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

where $\Delta_{f} H^{\circ}\left(O_{2}(g)\right)$ is zero for an element in its standard state.
Answer: - $\mathbf{1 4 0 9 . 1} \mathbf{~ k J ~ m o l}^{-1}$
Calculate the volume change when 150 g of liquid ethanol is burnt in an engine at $1500^{\circ} \mathrm{C}$ and 2.0 atm pressure. Assume all gases behave as ideal gases. Show all working.

The molar mass of ethanol is:

$$
\begin{aligned}
\text { molar mass } & =(2 \times 12.01(\mathrm{C})+6 \times 1.008(\mathrm{H})+16.00(\mathrm{O})) \mathrm{g} \mathrm{~mol}^{-1} \\
& =46.07 \mathrm{~g} \mathrm{~mol}^{-1}
\end{aligned}
$$

The number of moles in 150 g is therefore:
number of moles $=$ mass $/$ molar mass $=150 \mathrm{~g} / 46.07 \mathrm{~g} \mathrm{~mol}^{-1}=3.3 \mathrm{~mol}$
From the chemical equation when $1 \mathbf{m o l}$ of ethanol burns, there is a net increase of 2 mol of gas ( $\mathbf{3} \mathbf{~ m o l}$ of $\mathrm{O}_{2}(\mathrm{~g})$ is lost and 2 mol of $\mathrm{CO}_{2}(\mathrm{~g})$ and 3 mol of $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ is made). When 3.3 mol of ethanol burns, there is a net increase of $6.6 \mathbf{~ m o l}$ of gas.
With $P=2.0 \mathrm{~atm}$ and $T=1500{ }^{\circ} \mathrm{C}$, the volume increase will be:

$$
\begin{aligned}
\Delta V & =\Delta n R T / P \\
& =(6.6 \mathrm{~mol}) \times\left(0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times((1500+273) \mathrm{K}) / 2.0 \mathrm{~atm} \\
& =470 \mathrm{~L}
\end{aligned}
$$

Answer: $\mathbf{4 7 0}$ L
Why can the volume occupied by the liquid ethanol be ignored in this calculation?

The volume occupied by 150 g of ethanol is very small compared to the volume occupied by the gases.

- The standard Gibbs free energy of the following reaction is $+69.73 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

$$
\mathrm{COCl}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})
$$

What is the expression for the equilibrium constant, $K_{\mathrm{p}}$, for this reaction?

$$
K_{\mathrm{p}}=\frac{P_{\mathrm{Co} P_{\mathrm{Cl}_{2}}} P_{\mathrm{COCl}_{2}}}{\text { and }}
$$

Calculate the value of the equilibrium constant at 298 K .

Using $\Delta G^{0}=-R T \ln K_{\mathrm{p}}$ :

$$
\begin{aligned}
& +69.73 \times 10^{3} \mathrm{~J}=-\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times(298 \mathrm{~K}) \times \ln K_{\mathrm{p}} \\
& \ln K_{\mathrm{p}}=-28.14 \\
& K_{\mathrm{p}}=5.98 \times 10^{-13}
\end{aligned}
$$

$$
K_{\mathrm{p}}=5.98 \times 10^{-13}
$$

In which direction will this reaction proceed if a mixture of gases is made with: $P_{\mathrm{COCl}_{2}}=1.00 \mathrm{~atm} ; P_{\mathrm{Cl}_{2}}=0.01 \mathrm{~atm} ; P_{\mathrm{CO}}=0.50 \mathrm{~atm}$ ? Show working.


$$
Q_{\mathrm{p}}=\frac{(0.50)(0.01)}{(1.00)^{2}}=0.005
$$

As $Q_{\mathrm{p}}>K_{\mathrm{p}}$, the reaction will proceed towards reactants: $P_{\mathrm{COCl}_{2}}$ will increase $P_{\mathrm{CO}}$ and $P_{\mathrm{Cl}_{2}}$ will decrease.

- The diagram below represents the equilibrium constant $K_{\mathrm{p}}$ associated with the formation of the four oxides indicated.


Using the equilibrium constant data above, describe the reaction that proceeds under the following conditions. If you think no reaction will occur, write 'no reaction'.

```
CO and Sn are combined at \(400^{\circ} \mathrm{C}\)
The \(\mathrm{C} / \mathrm{CO}\) line is below the \(\mathrm{Sn} / \mathrm{SnO}\) line: \(\mathrm{Sn}(\mathrm{s})+\mathrm{CO}(\mathrm{g}) \rightarrow \mathrm{SnO}(\mathrm{s})+\mathrm{C}(\mathrm{s})\)
```

Al and SnO are combined at $400^{\circ} \mathrm{C}$
The $\mathrm{Sn} / \mathrm{SnO}$ line is below the $\mathrm{Al} / \mathrm{Al}_{2} \mathrm{O}_{3}$ line: $\mathbf{2 \mathrm { Al } ( \mathrm { s } ) + \mathbf { 3 S n O } ( \mathrm { s } ) \rightarrow \mathrm { Al } _ { 2 } \mathrm { O } _ { \mathbf { 3 } } ( \mathrm { s } ) + \mathbf { 3 S n } ( \mathrm { s } )}$

C and ZnO are mixed at $900^{\circ} \mathrm{C}$
The $\mathrm{Zn} / \mathrm{ZnO}$ line is below the $\mathrm{C} / \mathrm{CO}$ line: $\mathrm{C}(\mathrm{s})+\mathrm{ZnO}(\mathrm{s}) \rightarrow \mathrm{CO}(\mathrm{g})+\mathrm{Zn}(\mathrm{s})$

Which oxide has the largest (most negative) enthalpy of formation?
$K_{\mathrm{P}}$ is largest for the formation of $\mathrm{Al}_{2} \mathrm{O}_{3}$. It has the most negative $\boldsymbol{\Delta}_{\mathrm{f}} \boldsymbol{G}^{\mathbf{0}}$.
$\Delta_{i} S^{0}$ is negative for all of the metal oxide as the number of moles of gas is reduced. As $\Delta_{\mathrm{f}} G^{0}=\Delta_{\mathrm{f}} H^{0}-T \Delta_{f} S^{0}$ and $-T \Delta_{f} S^{0}$ is positive, then $\Delta_{f} H^{0}$ must be most negative for $\mathrm{Al}_{2} \mathrm{O}_{3}$.

- An electrochemical cell consisting of a $\mathrm{Ni}^{2+} / \mathrm{Ni}$ half-cell with unknown $\left[\mathrm{Ni}^{2+}\right]$ and a $\mathrm{Cu}^{2+} / \mathrm{Cu}$ half-cell with $\left[\mathrm{Cu}^{2+}\right]=2.5 \mathrm{M}$ has a cell voltage of 0.64 V at 298 K . What is the initial concentration of $\mathrm{Ni}^{2+}$ in the $\mathrm{Ni}^{2+} / \mathrm{Ni}$ half-cell?

From the reduction potential table,

$$
\begin{aligned}
& E_{\text {cell }}\left(\mathrm{Ni}^{2+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Ni}(\mathrm{~s})\right)=-0.24 \mathrm{~V} \\
& E_{\text {cell }}^{0}\left(\mathrm{Cu}^{2+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq})\right)=+0.34 \mathrm{~V}
\end{aligned}
$$

The $\mathrm{Ni}^{2+} / \mathbf{N i}$ half cell has the more negative reduction potential so it is the half cell that is turned around to act as the oxidation half cell:

$$
E_{\text {cell }}{ }^{0}\left(\mathrm{Ni}(\mathrm{~s}) \rightarrow \mathrm{Ni}^{2+}(\mathrm{aq})+\mathrm{e}^{-}\right)=+0.24 \mathrm{~V}
$$

In combination with the $\mathrm{Cu}^{2+} / \mathrm{Cu}$ reduction half cell, this gives an overall reaction and cell potential of:

$$
\mathrm{Ni}(\mathrm{~s})+\mathrm{Cu}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Ni}^{2+}(\mathrm{aq})+\mathrm{Cu}(\mathrm{~s}) \quad E^{0}=((+0.24)+(0.34)) \mathrm{V}=0.58 \mathrm{~V}
$$

For this reaction with $\left[\mathrm{Cu}^{2+}(\mathrm{aq})\right]=2.5 \mathrm{M}$ :

$$
Q=\frac{\left[\mathrm{Ni}^{2+}(\mathrm{aq})\right]}{\left[\mathrm{Cu}^{2+}(\mathrm{aq})\right]}=\frac{\left[\mathrm{Ni}^{2+}(\mathrm{aq})\right]}{(2.5)}
$$

For the $2 \mathrm{e}^{-}$reaction, the Nernst equation gives the cell potential as:

$$
\begin{aligned}
E_{\text {cell }} & =E^{\circ}-\frac{R T}{n F} \ln Q \\
& =(0.58 \mathrm{~V})-\frac{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298 \mathrm{~K})}{\left(2 \times 96485 \mathrm{C} \mathrm{~mol}^{-1}\right)} \ln \frac{\left[\mathrm{Ni}^{2+}(\mathrm{aq})\right]}{(2.5)}=0.64 \mathrm{~V}
\end{aligned}
$$

Solving this gives, $\left[\mathrm{Ni}^{2+}(\mathrm{aq})\right]=\mathbf{0 . 0 2 3} \mathrm{M}$.

## Answer: $\mathbf{0 . 0 2 3} \mathbf{~ M}$

Calculate the equilibrium constant for the reaction at $25^{\circ} \mathrm{C}$.
Using $E^{0}=\frac{R T}{n F} \ln K$ :

$$
0.58 \mathrm{~V}=\frac{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298 \mathrm{~K})}{\left(2 \times 96485 \mathrm{C} \mathrm{~mol}^{-1}\right)} \ln K
$$

$$
K=4.2 \times 10^{19}
$$

Calculate the standard Gibbs free energy change for the reaction at $25^{\circ} \mathrm{C}$.
Using $\Delta G^{0}=-n F E^{0}$ :

$$
\Delta G^{0}=-2 \times\left(96485 \mathrm{C} \mathrm{~mol}^{-1}\right) \times(0.58 \mathrm{~V})=-110 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

- Chlorine is produced by the electrolysis of an aqueous sodium chloride solution using inert electrodes. What products are formed at the anode and cathode? Explain your answer.

There are two possible oxidation reactions at the anode:

$$
\begin{array}{ll}
2 \mathrm{Cl}^{-}(\mathrm{aq}) \rightarrow \mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{e}^{-} & E^{0}=-1.36 \mathrm{~V} \\
2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{e}^{-} & E^{0}=-1.23 \mathrm{~V}
\end{array}
$$

Although oxidation of water appears easier, based on its less negative potential, oxidation of chloride occurs due to the overpotential associated with oxidising water.

There are two possible reduction reactions at the cathode:

$$
\begin{array}{ll}
\mathrm{Na}^{+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Na}(\mathrm{~s}) & E^{0}=-2.71 \mathrm{~V} \\
\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{OH}^{-}(\mathrm{aq}) & E^{0}=-\mathbf{0 . 8 3} \mathrm{V}
\end{array}
$$

The reduction of $\mathrm{Na}^{+}(\mathrm{aq})$ has a much more negative reduction potential and so reduction of water occurs, despite the overpotential.

Answer: anode: $\mathbf{C l}_{\mathbf{2}}(\mathbf{g})$;
cathode: $\mathrm{H}_{\mathbf{2}}(\mathrm{g})+\mathrm{OH}^{-}(\mathrm{aq})$
Write a balanced equation for the overall reaction of the electrolytic cell.

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

Assuming a $\left[\mathrm{Cl}^{-}\right]$of 1.0 M and no overpotential, what would be the minimum voltage required to drive the overall cell reaction at pH 14 ? Assume gases are at 1 atm .

At $\mathbf{p H}=14,\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=1.0 \mathrm{M}$. This corresponds to standard conditions for the reduction for $\mathrm{H}_{2} \mathrm{O} \cdot\left[\mathrm{Cl}^{-}(\mathrm{aq})\right]=1.0 \mathrm{M}$ also corresponds to standard conditions for the oxidation of $\mathrm{Cl}^{-}(\mathrm{aq})$.

$$
E_{\text {cell }}^{0}=E_{\text {red }}{ }^{0}+E_{\mathrm{ox}}^{0}=(-0.83 \mathrm{~V})+(-1.36) \mathrm{V}=-2.19 \mathrm{~V}
$$

A potential of $>2.19 \mathrm{~V}$ is required.
Answer: > 2.19 V

Considering the cell potentials suggest a reason ruthenium oxide electrodes are employed in this reaction rather than carbon electrodes.
$\mathrm{RuO}_{2}$ acts as a catalyst for the reaction.

- What is the voltage of a concentration cell constructed from two beakers containing $2.5 \mathrm{M} \mathrm{CuSO}_{4}$ and $0.025 \mathrm{M} \mathrm{CuSO}_{4}$ at 298 K ?

The concentration of $\mathrm{Cu}^{2+}(\mathrm{aq})$ in the 2.5 M beaker will decrease: this is the reduction half cell:

$$
\mathrm{Cu}^{2+}(2.5 \mathrm{M}, \mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}(\mathrm{~s})
$$

The concentration of $\mathrm{Cu}^{2+}(\mathrm{aq})$ in the 0.025 M beaker will increase: this is the oxidation half cell:

$$
\mathrm{Cu}(\mathrm{~s})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}^{2+}(0.025 \mathrm{M}, \mathrm{aq})
$$

## Overall:

$$
\begin{aligned}
& \mathrm{Cu}^{2+}(2.5 \mathrm{M})+\mathrm{Cu}(\mathrm{~s}) \rightarrow \mathrm{Cu}^{2+}(0.025 \mathrm{M}, \mathrm{aq})+\mathrm{Cu}(\mathrm{~s}) \\
& \qquad Q=\frac{\left[\mathrm{Cu}^{2+}(0.025 \mathrm{M}, \mathrm{aq})\right]}{\left[\mathrm{Cu}^{2+}(2.5 \mathrm{M}, \mathrm{aq})\right]}=\frac{0.025}{2.5}
\end{aligned}
$$

The standard cell potential, $E^{0}=0.00 \mathrm{~V}$. For the $2 \mathrm{e}^{-}$reaction, the Nernst equation gives the cell potential as:

$$
\begin{aligned}
E_{\text {cell }} & =E^{\circ}-\frac{R T}{n F} \ln Q \\
& =(0.00 \mathrm{~V})-\frac{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298 \mathrm{~K})}{\left(2 \times 96485 \mathrm{C} \mathrm{~mol}^{-1}\right)} \ln \frac{0.025}{2.5}=+0.059 \mathrm{~V}
\end{aligned}
$$

Answer: +0.059 V
Explain the changes necessary for the cell to reach equilibrium.

Current will flow with the reduction and oxidation reactions above occurring until the concentrations are equal. At this point, $Q=1$ and $E=0$.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

