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- Atomic Electronic Spectroscopy


## 2012-N-3:

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- Wave Theory of Electrons and Resulting Atomic Energy Levels


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## 2012-N-10:

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## 2012-N-12:

- First and Second Law of Thermodynamics

2012-N-13:

- Chemical Equilibrium

2012-N-14:

- Electrochemistry
- Nitrogen dioxide, $\mathrm{NO}_{2}$, is formed in the atmosphere from industrial processes and automobile exhaust. It is an indicator of poor quality air and is mostly responsible for the brown haze seen in large cities. This question about $\mathrm{NO}_{2}$ extends over many pages, but each sub-question is essentially independent of the others.
a) $\mathrm{NO}_{2}$ is a pungent red-orange coloured gas. According to the colour wheel for human vision, reproduced below, what colour light does $\mathrm{NO}_{2}$ absorb?

b) An atmospheric chemist, monitoring pollution in Sydney, measured the absorption of light at 425 nm due to $\mathrm{NO}_{2}$. Measured over a distance of $100 \mathrm{~m}, 425 \mathrm{~nm}$ light was attenuated by $5 \%$ (i.e. $95 \%$ transmission). What is the concentration of $\mathrm{NO}_{2}$ in the atmosphere? Give your answer in $\mathrm{mol} \mathrm{L}^{-1}$.
Data: $\varepsilon\left(\mathrm{NO}_{2}, 425 \mathrm{~nm}\right)=300 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$.

As the transmittance is $\mathbf{9 5 \%} ; I / I_{0}=\mathbf{0 . 9 5}$ and so the absorbance, $A$, is:

$$
A=-\log _{10}\left(I / I_{0}\right)=-\log _{10}(0.95)=0.0223
$$

From the Beer-Lambert law, absorbance, $A$, is related to the extinction coefficient for the substance, $\varepsilon$, concentration, $c$, and the path length, $l$ :

$$
A=\varepsilon c l
$$

With $A=0.0223, \varepsilon=300 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ and $l=100 \mathrm{~m}$ or $100 \times 10^{2} \mathrm{~cm}$ :

$$
\begin{aligned}
c=A / \varepsilon l & =0.0223 /\left(\left(300 \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right) \times\left(100 \times 10^{2} \mathrm{~cm}\right)\right) \\
& =7.4 \times 10^{-9} \mathrm{M}=7.4 \times 10^{-9} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

Answer: $7.4 \times \mathbf{1 0}^{-9} \mathbf{~ m o l ~ L}^{-1}$
c) The Australian air quality guidelines stipulate a concentration of less than

Does your answer in part b) exceed Australian air quality guidelines?

> YES / NO

What is the partial pressure of $\mathrm{NO}_{2}$ (in Pa ) that corresponds to the Australian guidelines at $25^{\circ} \mathrm{C}$ and 100 kPa ?

From the ideal gas law:

$$
P V=n R T
$$

or

$$
P=(n / V) \times R T=c \times R T
$$

When $\boldsymbol{c}=\mathbf{5 . 0} \times \mathbf{1 0}^{\mathbf{- 9}} \mathbf{~ m o l ~ L}{ }^{\mathbf{- 1}}$, at $\mathbf{2 5}{ }^{\circ} \mathrm{C}$ (equivalent to 298 K ):

$$
\begin{aligned}
P & =\left(5.0 \times 10^{-9} \mathrm{~mol} \mathrm{~L}^{-1}\right) \times\left(0.08206 \mathrm{~atm} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right) \times(298 \mathrm{~K}) \\
& =1.2 \times 10^{-7} \mathrm{~atm}
\end{aligned}
$$

As $1 \mathbf{a t m}=101.3 \mathrm{kPa}$, this corresponds to:

$$
P=\left(1.2 \times 10^{-7} \times 101.3\right) \mathrm{kPa}=1.2 \times 10^{-5} \mathrm{kPa}=0.012 \mathrm{~Pa}
$$

Answer: $\mathbf{0 . 0 1 2 ~ P a ~}$
d) When $\mathrm{NO}_{2}$ absorbs UVA light in the atmosphere, at wavelengths shorter than 400 nm , it dissociates into $\mathrm{NO}+\mathrm{O}$ :

$$
\mathrm{NO}_{2}+h v \rightarrow \mathrm{NO}+\mathrm{O}
$$

What is the bond dissociation energy (in $\mathrm{kJ} \mathrm{mol}^{-1}$ ) of the $\mathrm{N}-\mathrm{O}$ bond in $\mathrm{NO}_{2}$ ?

The energy per molecule required to break the bond is given by Planck's relationship:

$$
\begin{aligned}
E & =h c / \lambda \\
& =\left(6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}\right) \times\left(2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}\right) /\left(\mathbf{4 0 0} \times 10^{-9} \mathrm{~m}\right)=5.0 \times 10^{-19} \mathrm{~J}
\end{aligned}
$$

The energy required per mole is therefore:

$$
\left.E=5.0 \times 10^{-19} \mathrm{~J}\right) \times\left(6.022 \times 10^{23} \mathrm{~mol}^{-1}\right)=300 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

e) The oxygen atom in the reaction in part d) is formed in its ground electronic state.

What is the ground state electronic configuration for O ?

$$
1 s^{2} 2 s^{2} 2 p^{4}
$$

Draw an atomic orbital energy level diagram for the ground state O atom. Name the orbitals and show all electrons.


Name and sketch the atomic orbitals for the highest occupied atomic orbital and the lowest unoccupied atomic orbital in the ground state O atom. Make sure all nodes are clearly identified in your sketch.

| sketch of highest occupied orbital | sketch of lowest unoccupied orbital |
| :--- | :--- |
| planar node- |  |
| Name: $\mathbf{2 p}$ orbital | Name: $\mathbf{3 s}$ orbital |

f) The NO molecule formed in the reaction in part d) is also formed in its ground electronic state. Complete the molecular orbital diagram for NO by filling in the valence electrons in the occupied orbitals. Sketch the shape of the $\pi$ and $\pi^{*}$ orbitals, clearly showing all nodes. Determine the bond order of NO and whether it is paramagnetic or diamagnetic.
MO orbital energy level diagram for NO $\quad$ Sketch of the $\pi$ MO
g) In the atmosphere, nitrogen oxides exist in many forms, including NO and $\mathrm{NO}_{2}$. Two other forms are $\mathrm{N}_{2} \mathrm{O}$ and $\mathrm{N}_{2} \mathrm{O}_{4}$ (the dimer of $\mathrm{NO}_{2}$ ). Draw Lewis structures for both $\mathrm{N}_{2} \mathrm{O}$ and $\mathrm{N}_{2} \mathrm{O}_{4}$. Examine your structures closely. If you can draw a second, valid, Lewis structure, draw it underneath.

| $\mathrm{N}_{2} \mathrm{O}$ structure $: N \equiv N-\ddot{\mathrm{O}}:$ | $\mathrm{N}_{2} \mathrm{O}_{4}$ structure |
| :---: | :---: |
| Second structure, if appropriate $\therefore \mathrm{N}=\mathrm{N}=\dot{\mathrm{O}} \dot{\square}$ | Second structure, if appropriate |

h) Use VSEPR theory to determine the shape of $\mathrm{N}_{2} \mathrm{O}$ and $\mathrm{N}_{2} \mathrm{O}_{4}$. Sketch the shape below and indicate the approximate bond angle for all angles in the molecule. Be clear in your sketch as to planar and non-planar structures where appropriate. Hence, or otherwise, indicate whether either molecule has a permanent dipole moment.

|  | (2000 |
| :---: | :---: |
| Dipole moment? YES / NO | Dipole moment? YES / NO |

i) $\mathrm{N}_{2} \mathrm{O}$ is sparingly soluble in water. What does this tell you about the strength of any hydrogen bonding that exists? Rationalise your answer in terms of the structures of the $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{N}_{2} \mathrm{O}$ molecules.

As $\mathrm{N}_{2} \mathrm{O}$ is only sparingly soluble in water, it follows that any H -bonds from $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{N}_{2} \mathrm{O}$ must be quite weak.
$\mathrm{N}_{2} \mathrm{O}$ can only act as an H -bond acceptor, not as a donor. As nitrogen and oxygen are of similar electronegativity, the $\mathrm{N}-\mathrm{O}$ bond is not as polarised as the $\mathrm{O}-\mathrm{H}$ bonds in water.

As a consequence, any H -bonds formed between water and $\mathrm{N}_{2} \mathrm{O}$ will be weaker than those between 2 water molecules.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- How does the ratio of the number of neutrons to the number of protons in a stable or long-lived radionuclide change as the atomic number increases?

The proton to neutron ratio slowly increases from 1 (for deuterium) to $\sim \mathbf{1 . 5}$ for bismuth.

For light elements, the ratio is approximately 1 . As the number of protons grows, increasing numbers of neutrons are needed to stabilise the nucleus.

After ${ }^{208} \mathbf{P b}$, all nuclei are unstable.

The generation of energy in a nuclear reactor is largely based on the fission of certain long-lived radionuclides (usually ${ }^{235} \mathrm{U}$ or ${ }^{239} \mathrm{Pu}$ ). The fission products include every element from zinc through to the $f$-block. Explain why most of the radioactive fission products are $\beta$-emitters.

The optimal ratio between the number of neutrons, $n$, and the number of protons, $p$, increases as $Z$ increases.

Simply splitting a large nucleus in two will produce nuclides with similar $n: p$ ratios to the parent, which will now be too high. They will emit negative charge to convert neutrons to protons, bringing about a more satisfactory $n: p$ ratio. i.e. they will be $\beta$ emitters.

Two of the more common isotopes produced in nuclear reactors are ${ }^{131}$ (half-life of 8.02 days) and ${ }^{137} \mathrm{Cs}$ (half-life of 30 years). Both are $\beta$-emitters. If you were exposed to equal concentrations of both isotopes for 1 hour, which isotope, ${ }^{137} \mathrm{Cs}$ or ${ }^{131} \mathrm{I}$, would do more damage? Explain your reasoning.
${ }^{131}$ I would do more damage.
It has the shorter half-life so undergoes more disintegrations and produces more radiation in a given time period.

- Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel that produces no greenhouse gases on combustion. In an experiment, gaseous $\mathrm{NH}_{3}$ is burned with $\mathrm{O}_{2}$ in a container of fixed volume according to the following equation.

$$
4 \mathrm{NH}_{3}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{~N}_{2}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

The initial and final states are at 298 K . After combustion with 14.40 g of $\mathrm{O}_{2}$, some $\mathrm{NH}_{3}$ remains unreacted. Calculate the enthalpy change during the process, given the following data.

$$
\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{NH}_{3}(\mathrm{~g})\right)=-46.11 \mathrm{~kJ} \mathrm{~mol}^{-1} \text { and } \Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)=-285.83 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

$\mathrm{O}_{2}$ is the limiting reagent and so determines the enthalpy change. The molar mass of $\mathrm{O}_{\mathbf{2}}$

$$
\text { molar mass }=(2 \times 16.00) \mathrm{g} \mathrm{~mol}^{-1}=32.00 \mathrm{~g} \mathrm{~mol}^{-1} .
$$

The number of moles in 14.40 g is therefore:

$$
\begin{aligned}
\text { number of moles } & =\text { mass } / \text { molar mass } \\
& =(14.40 \mathrm{~g}) /\left(32.00 \mathrm{~g} \mathrm{~mol}^{-1}\right)=0.4500 \mathrm{~mol}
\end{aligned}
$$

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:

$$
\begin{aligned}
\Delta H^{\circ}= & \left(2 \Delta _ { \mathrm { f } } H ^ { \circ } \left(\mathrm{N}_{2}(\mathrm{~g})+6 \Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)-\left(4 \Delta _ { \mathrm { f } } H ^ { \circ } \left(\mathrm{NH}_{3}(\mathrm{~g})+3 \Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{O}_{2}(\mathrm{~g})\right)\right.\right.\right.\right. \\
& =[(0+6 \times-285.83)-(4 \times-46.11+0)] \mathrm{kJ} \mathrm{~mol}^{-1}=-1530.54 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

where $\Delta_{f} H^{\circ}$ for $\mathrm{N}_{2}(\mathrm{~g})$ and $\mathrm{O}_{2}(\mathrm{~g})$ are zero because they are elements in their standard states.

This quantity is for the reaction as written: it is for the consumption of $\mathbf{3} \mathbf{~ m o l}$ of $\mathrm{O}_{2}$. The enthalpy change per mole of $\mathrm{O}_{2}$ is therefore:

$$
\Delta H^{\circ}=(-1530.54 / 3) \mathrm{kJ} \mathrm{~mol}^{-1}=-510.18 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

The enthalpy change for $0.4500 \mathbf{~ m o l}$ of $\mathrm{O}_{2}$ is therefore:

$$
\Delta H^{\circ}=\left(-510.18 \mathrm{~kJ} \mathrm{~mol}^{-1}\right) \times(0.4500 \mathrm{~mol})=-229.6 \mathrm{~kJ}
$$

- ANFO (ammonium nitrate fuel oil) is a powerful explosive used recently in the Oslo bombing. If the fuel oil is replaced by carbon in the form of graphite, calculate what mass of carbon needs to be added to 1.0 kg of ammonium nitrate so that the products of the detonation are $\mathrm{N}_{2}, \mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$.

The molar mass of $\mathbf{N H}_{4} \mathrm{NO}_{3}$ is:

$$
\begin{aligned}
\text { molar mass } & =(2 \times 14.01(\mathrm{~N}))+(4 \times 1.008(\mathrm{H}))+(3 \times 16.00(\mathrm{O})) \mathrm{g} \mathrm{~mol}^{-1} \\
& =80.052 \mathrm{~g} \mathrm{~mol}^{-1}
\end{aligned}
$$

The number of moles in 1.0 kg is therefore:
number of moles $=$ mass $/$ molar mass

$$
=\left(1.0 \times 10^{3} \mathrm{~g}\right) /\left(80.052 \mathrm{~g} \mathrm{~mol}^{-1}\right)=12.5 \mathrm{~mol}
$$

The balanced equation for the detonation reaction is:

$$
2 \mathrm{NH}_{4} \mathrm{NO}_{3}(\mathrm{~s})+\mathrm{C}(\mathrm{~s}) \rightarrow 2 \mathrm{~N}_{2}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathbf{l})
$$

From the chemical equation, the amount of $\mathbf{C}(\mathbf{s})$ required is therefore:
number of moles $=(\mathbf{1 2 . 4 9 2} / \mathbf{2}) \mathbf{~ m o l}=6.25 \mathrm{~mol}$
As the molar mass of $\mathbf{C}$ is $12.01 \mathrm{~g} \mathrm{~mol}^{-1}$, this corresponds to:

$$
\text { mass }=\text { number of moles } \times \text { molar mass }=(6.25 \mathrm{~mol}) \times\left(12.01 \mathrm{~g} \mathrm{~mol}^{-1}\right)=75 \mathrm{~g}
$$

- How many 2.0 L casks of wine and/or juices can be cooled on a hot Sydney day from $30^{\circ} \mathrm{C}$ to a drinkable $10^{\circ} \mathrm{C}$ with one 10.0 kg bag of ice taken from a freezer at $-30^{\circ} \mathrm{C}$ ? Assume the specific heat of the wine and/or juice is the same as that of water, that the cardboard or plastic containers have negligible heat capacity, and that the density of the wine and juices is $1.0 \mathrm{~g} \mathrm{~mL}^{-1}$.

$$
\Delta_{\mathrm{fus}} H\left(\mathrm{H}_{2} \mathrm{O}\right)=6.0 \mathrm{~kJ} \mathrm{~mol}^{-1} ; \quad C_{\mathrm{p}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{~s})\right)=2.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1} ; \quad C_{\mathrm{p}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)=4.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}
$$

The bag of ice will undergo three process in being raised from -30 ${ }^{\circ} \mathrm{C}$ to $+10^{\circ} \mathrm{C}$ :
(a) The ice will be heated from $-30{ }^{\circ} \mathrm{C}$ to $0^{\circ} \mathrm{C}$ for which $\Delta T=+30 \mathrm{~K}$ :

$$
q_{(\mathrm{a})}=m C_{\mathrm{p}}{ }^{\circ} \Delta T=\left(10.0 \times 10^{3} \mathrm{~g}\right) \times\left(2.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}\right) \times(30 \mathrm{~K})=6.60 \times 10^{2} \mathrm{~kJ}
$$

(b) The ice will melt. As the molar mass of $\mathrm{H}_{2} \mathrm{O}$ is $(16.00+2 \times 1.008) \mathrm{g} \mathrm{mol}^{-1}$ or $18.016 \mathrm{~g} \mathrm{~mol}^{-1}$. The number of moles of ice that will be melted is:

$$
\begin{aligned}
\text { number of moles } & =\text { mass } / \text { molar mass } \\
& =\left(10.0 \times 10^{3} \mathrm{~g}\right) /\left(18.016 \mathrm{~g} \mathrm{~mol}^{-1}\right)=555 \mathrm{~mol}
\end{aligned}
$$

As $\Delta_{\text {fus }} H\left(\mathrm{H}_{2} \mathrm{O}\right)=6.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$, the amount of energy required to melt this amount is:

$$
q_{(b)}=(555 \mathrm{~mol}) \times\left(6.0 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)=3.33 \times 10^{3} \mathrm{~kJ}
$$

(c) The melted ice will be heated from $0{ }^{\circ} \mathrm{C}$ to $+10{ }^{\circ} \mathrm{C}$ for which $\Delta T=+10 \mathrm{~K}$ :

$$
q_{(\mathrm{c})}=m C_{\mathrm{p}}{ }^{\circ} \Delta T=\left(10.0 \times 10^{3} \mathrm{~g}\right) \times\left(4.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}\right) \times(10 \mathrm{~K})=4.20 \times 10^{2} \mathrm{~kJ}
$$

Overall, the heat absorbed by the ice is therefore:

$$
\begin{aligned}
q_{\mathrm{ice}} & =q_{(\mathrm{a})}+q_{(\mathrm{b})}+q_{(\mathrm{c})} \\
& =\left(6.60 \times 10^{2} \mathrm{~kJ}\right)+\left(3.33 \times 10^{3} \mathrm{~kJ}\right)+\left(4.20 \times 10^{2} \mathrm{~kJ}\right)=4.4 \times 10^{3} \mathrm{~kJ}
\end{aligned}
$$

This heat is taken from the wine casks so:

$$
q_{\text {wine }}=-4.41 \times 10^{3} \mathrm{~kJ}
$$

The mass of each cask is $\mathbf{2 . 0} \mathbf{k g}$ and the required temperature change is from $\mathbf{+ 3 0}$ ${ }^{\circ} \mathrm{C}$ to $+10{ }^{\circ} \mathrm{C}$ for which $\Delta T=\mathbf{- 2 0} \mathrm{K}$. If $\boldsymbol{x}$ casks are cooled:

$$
q_{\text {wine }}=m C_{\mathrm{p}}{ }^{\circ} \Delta T=\left(2.0 \times 10^{3} \mathrm{~g}\right) \times x \times\left(4.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}\right) \times(-20 \mathrm{~K})=-4.41 \times 10^{3} \mathrm{~kJ}
$$

## Hence:

$$
x=26.3 \quad \text { i.e. } 26 \text { casks can be cooled. }
$$

What other assumption have you made in your calculation?

It has been assumed that all the heat that melts the ice and then warms the water comes solely from the casks being cooled.

This clearly will not be the case - the system is exposed to the atmosphere so that people can access the drinks.

- The standard Gibbs free energy of formation for ammonia, $\mathrm{NH}_{3}(\mathrm{~g})$, is $-16.4 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Consider the following reaction at 298 K .

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

What is the expression for the equilibrium constant, $K_{\mathrm{p}}$, for this reaction?
$K_{\mathrm{p}}=\frac{p^{2}\left(\mathrm{NH}_{3}\right)}{p\left(\mathbf{N}_{2}\right) p^{3}\left(\mathbf{H}_{2}\right)}$

Calculate the value of the equilibrium constant at 298 K .

The reaction as written produces $\mathbf{2} \mathbf{~ m o l}$ of $\mathrm{NH}_{3}$, hence:

$$
\Delta_{\mathrm{r}} G^{0}=2 \times \Delta_{\mathrm{f}} G^{0}\left(\mathrm{NH}_{3}(\mathrm{~g})\right)=2 \times-16.4 \mathrm{~kJ} \mathrm{~mol}^{-1}=-32.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

As $\Delta G^{0}=-R T \ln K_{\mathrm{p}}$ :
$-32.8 \times 10^{3} \mathrm{~J} \mathrm{~mol}^{-1}=-\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times(298 \mathrm{~K}) \times \ln K_{\mathrm{p}}$
$\ln K_{\mathrm{p}}=13.24$

$$
K_{\mathrm{p}}=5.6 \times 10^{5}
$$

$$
K_{\mathrm{p}}=5.6 \times 10^{5}
$$

In which direction will this reaction proceed if a mixture of gases is made with: $P_{\mathrm{NH}_{3}}=1.00 \mathrm{~atm} ; P_{\mathrm{H}_{2}}=1.00 \mathrm{~atm} ; P_{\mathrm{N}_{2}}=0.50 \mathrm{~atm}$ ?

The reaction quotient with this mixture is:

$$
Q_{\mathrm{p}}=\frac{p^{2}\left(\mathrm{NH}_{3}\right)}{p\left(\mathrm{~N}_{2}\right) p^{3}\left(\mathrm{H}_{2}\right)}=\frac{(1.00)^{2}}{(0.50)(1.00)^{3}}=2.00
$$

As $Q_{\mathrm{p}}<K_{\mathrm{p}}$, the reaction will proceed to products (i.e. to the right).

```
- Consider the process \(\mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{l})\)

Give the sign of \(\Delta H^{\circ}\) at 273 K and explain your choice.
\(\Delta H^{\circ}\) is positive: the ice is melting so the reaction is endothermic. Energy must be put into the system to break the hydrogen bonds.

Give the sign of \(\Delta S^{\circ}\) at 273 K and explain your choice.
\(\Delta S^{\circ}\) is positive: the ice is melting so the system goes from solid ice to liquid water. There is increased spreading out of the energy of the system.

How does \(\Delta G^{\circ}\) change with an increase in temperature? Explain your answer.

Using \(\Delta G^{\circ}=\Delta H^{\circ}-T \Delta S^{\circ}\), increasing the temperature will increase the effect of the entropy term.

As \(\Delta S^{\circ}\) is positive, \(-\boldsymbol{T} \Delta S^{\circ}\) is negative so that \(\Delta G^{\circ}\) will become smaller as the temperature increases. When the temperature exceeds a certain value, this negative term is large enough to overcome the positive \(\Delta H^{\circ}\) term and \(\Delta G^{\circ}\) will become negative. The process is then spontaneous.
This temperature is the melting point: 273 K .
- 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 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 NO(g). To reestablish equilibrium, the reaction will shift to the left by an unknown amount \(y\). The reaction table for this is:
\begin{tabular}{|c|c|c|l|c|c|}
\hline & \(\mathrm{SO}_{2}(\mathrm{~g})\) & \(\mathrm{NO}_{2}(\mathrm{~g})\) & & \(\mathrm{SO}_{3}(\mathrm{~g})\) & \(\mathrm{NO}(\mathrm{g})\) \\
\hline initial & 0.800 & 0.100 & \(\rightleftharpoons\) & 0.600 & \(0.400+x\) \\
\hline change & \(+y\) & \(+y\) & & \(-y\) & \(-\underline{y}\) \\
\hline equilibrium & \(0.800+y\) & \(0.100+y\) & & \(0.600-y\) & \(0.400+x-y\) \\
\hline
\end{tabular}

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

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.
- The \(\mathrm{CrO}_{4}{ }^{2-}\) ion can oxidise the \(\mathrm{I}_{3}{ }^{-}\)ion in acidic solution. The products of the reaction are \(\mathrm{Cr}^{3+}\) and \(\mathrm{I}_{2}\). Show the separate balanced half-equations for the oxidation and reduction as well as the net balanced redox equation.
\begin{tabular}{|c|c|}
\hline Oxidation half-equation & \(2 \mathbf{I}_{3}{ }^{-}(\mathrm{aq}) \rightarrow \mathbf{3 I} \mathbf{I}_{\mathbf{2}}(\mathrm{aq})+2 \mathrm{e}^{-}\) \\
\hline Reduction half-equation & \(\mathrm{CrO}_{4}{ }^{2-}(\mathrm{aq})+8 \mathrm{H}^{+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Cr}^{3+}+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})\) \\
\hline Balanced redox equation & \(2 \mathrm{CrO}_{4}{ }^{\mathbf{2 -}}(\mathrm{aq})+16 \mathrm{H}^{+}+6 \mathrm{I}_{3}{ }^{-}(\mathrm{aq}) \rightarrow 2 \mathrm{Cr}^{3+}+8 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+9 \mathrm{I}_{2}(\mathrm{aq})\) \\
\hline
\end{tabular}

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.```

