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2014-J-12:

- First Law of Thermodynamics
- Complete the following table by filling in the compound name or formula as required.
- What is the molarity of the solution formed when 0.50 g of aluminium fluoride is dissolved in 800.0 mL of water?

The molar mass of $\mathrm{AlF}_{3}$ is:

$$
\text { molar mass }=(26.98(\mathrm{Al})+3 \times 19.00(\mathrm{~F})) \mathrm{g} \mathrm{~mol}^{-1}=83.98 \mathrm{~g} \mathrm{~mol}^{-1}
$$

The number of moles in 0.50 g is therefore:

$$
\text { number of moles }=\text { mass } / \text { molar mass }=0.50 \mathrm{~g} / 83.98 \mathrm{~g} \mathrm{~mol}^{-1}=0.0060 \mathrm{~mol}
$$

The concentration of this amount in 800.0 mL is then:

$$
\begin{aligned}
\text { concentration } & =\text { number of moles } / \text { volume } \\
& =0.0060 \mathrm{~mol} / 0.8000 \mathrm{~L}=0.0074 \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

Answer: $\mathbf{0 . 0 0 7 4} \mathbf{~ m o l ~ L ~}{ }^{-1}$ or $\mathbf{0 . 0 0 7 4} \mathbf{~ M}$
What is $\left[\mathrm{F}^{-}\right]$in this solution?

As the formula is $\mathrm{AlF}_{3}$, dissolution results in $\mathbf{3 F}^{-}(\mathrm{aq})$ per formula unit.
$\left[F^{-}(\mathrm{aq})\right]=3 \times 0.0074 \mathrm{~mol} \mathrm{~L}^{-1}=0.022 \mathrm{~mol} \mathrm{~L}^{-1}$
Answer: $\mathbf{0 . 0 2 2} \mathbf{~ m o l ~ L}{ }^{-1}$ or $\mathbf{0 . 0 2 2} \mathbf{M}$
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Explain, using words and diagrams, the type of bonding present in lithium oxide and compare this to the type of bonding in carbon dioxide.

Lithium oxide is an ionic compound formed between a metal $(\mathbf{L i})$ and a nonmetal ( $\mathbf{O}$ ) by the complete transfer of electrons from Li to O to give $\mathrm{Li}^{+}$cations and $\mathrm{O}^{2-}$ anions. These ions are held in place in the crystal lattice by strong electrostatic attractions between the positively and negatively charged ions. This results in a solid compound with high melting point.
Carbon dioxide is a molecular covalent compound. The carbon and oxygen atoms share their electrons forming strong covalent $\mathrm{C}=\mathbf{O}$ double bonds. There is no formal bonding between the individual $\mathrm{O}=\mathrm{C}=\mathbf{O}$ molecules. The molecules are attracted to each other by weak dispersion forces. $\mathrm{CO}_{2}$ is therefore a gas at room temperature.

Carbon and oxygen can also react to form carbon monoxide. Draw the Lewis structure of this molecule.
:C三O:

Explain any difference in the polarity of carbon monoxide and carbon dioxide.

Covalent bonds formed between atoms with different electronegativities are always polarised, hence $\mathbf{C O}$ is a polar molecule. Although the two $\mathrm{C}=\mathbf{O}$ bonds in $\mathrm{CO}_{2}$ are polarised, $\mathrm{CO}_{2}$ is a linear molecule and the two bond dipoles cancel each other out. Hence $\mathrm{CO}_{2}$ does not have a permanent dipole moment.

- Hydrazine $\left(\mathrm{N}_{2} \mathrm{H}_{4}\right)$ reacts with dinitrogen tetraoxide $\left(\mathrm{N}_{2} \mathrm{O}_{4}\right)$ to produce nitrogen and water, all in the gas phase, according to the following unbalanced equation.

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

Balance the above equation.

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

Describe the physical characteristics of a gas and sketch how the atoms of gaseous nitrogen might be represented in a container.

Diatomic molecules of $\mathbf{N}_{\mathbf{2}}$ fill the container, but the individual molecules are far apart. The molecules are travelling in different directions and at different speeds colliding with each other and the walls of the container.

1.00 L of hydrazine was mixed with 1.00 L of dinitrogen tetraoxide at $25^{\circ} \mathrm{C}$ and 1.00 atm pressure. Briefly explain Avogadro's Law and determine the mole ratio of hydrazine to dinitrogen tetraoxide present at room temperature.

Avogadro's law states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

From this, 1.00 L of hydrazine and 1.00 L of dintrogen tetraoxide contain the same number of molecules. Hence the mole ratio of $\mathrm{N}_{2} \mathrm{H}_{4}$ to $\mathrm{N}_{2} \mathrm{O}_{4}$ is 1:1.

Using the ideal gas equation, calculate the number of moles of hydrazine gas under these conditions.

From the ideal gas law, $P V=n R T$. Hence the number of moles is given by:

$$
n=P V / R T
$$

With $P=1.00 \mathrm{~atm}, V=1.00 \mathrm{~L}, R=0.08206 \mathrm{~L}$ atm $\mathrm{K}^{-1} \mathrm{~mol}^{-1}$ and $T=25{ }^{\circ} \mathrm{C}=298$
K:

$$
n=(1.00 \mathrm{~atm} \times 1.00 \mathrm{~L}) /\left(0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \times 298 \mathrm{~K}\right)=0.0409 \mathrm{~mol}
$$

If the pressure remains constant at 1.00 atm , calculate the volume occupied by this mixture of gases after it was heated to $305^{\circ} \mathrm{C}$, before any reaction takes place.

The initial volume, $V_{1}$, and temperature, $T_{1}$, are related by:

$$
V_{1} / T_{1}=n R / P
$$

At the new volume, $V_{2}$, and temperature, $T_{2}$, they are similarly related by:

$$
V_{2} / T_{2}=n R / P
$$

As the number of moles and pressure are constant, these are equal:

$$
V_{1} / T_{1}=V_{2} / T_{2}
$$

At 298 K , the combined gases have a volume of 2.00 L so $V_{1}=2.00 \mathrm{~L}$ and $T_{1}=$ 298 K . When $T_{2}=305{ }^{\circ} \mathrm{C}=578 \mathrm{~K}$ :
$2.00 \mathrm{~L} / 298 \mathrm{~K}=V_{2} / 578 \mathrm{~K}$

$$
V_{2}=3.88 \mathrm{~L}
$$

## Answer: $\mathbf{3 . 8 8} \mathbf{L}$

The molar heat capacity of $\mathrm{N}_{2} \mathrm{H}_{4}$ is $63 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ and that of $\mathrm{N}_{2} \mathrm{O}_{4}$ is $77 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$. Calculate the heat capacity of this mixture.

From 2014-J-4, there are 0.0409 mol of $\mathrm{N}_{2} \mathrm{H}_{4}$ and $\mathrm{N}_{2} \mathrm{O}_{4}$ present in the mixture. Molar heat capacity are the heat capacity for one moles.

The heat capacity of the mixture containing these amounts is therefore:

$$
\begin{aligned}
\text { heat capacity } & =\left(63 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \times 0.0409 \mathrm{~mol}\right)+\left(77 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \times 0.0409 \mathrm{~mol}\right) \\
& =5.73 \mathrm{~J} \mathrm{~K}^{-1}
\end{aligned}
$$

## Answer: $\mathbf{5 . 7 3} \mathbf{~ J ~ K}^{\mathbf{- 1}}$

Calculate the energy required to heat this mixture from $25^{\circ} \mathrm{C}$ to $305^{\circ} \mathrm{C}$.

The temperature rise $=\Delta T=(305-25)=280 . K$. Using $q=C \Delta T$, the heat needed is therefore:

$$
q=C \Delta T=\left(5.73 \mathrm{~J} \mathrm{~K}^{-1}\right) \times(280 . \mathrm{K})=1.60 \mathrm{~kJ}
$$

Answer: $\mathbf{1 . 6 0} \mathbf{J}$ or $\mathbf{1 . 6 0} \times \mathbf{1 0}^{\mathbf{3}} \mathbf{~ k J}$
ANSWER CONTINUES ON THE NEXT PAGE

Calculate the maximum mass of nitrogen gas that could be produced in this reaction.

From 2014-J-5, the balanced equation is:

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

and there are 0.0409 mol of $\mathrm{N}_{2} \mathrm{H}_{4}$ and 0.0409 mol of $\mathrm{N}_{2} \mathrm{O}_{4}$ present. As each $\mathrm{N}_{2} \mathrm{O}_{4}$ requires $2 \mathrm{~N}_{2} \mathrm{H}_{4}$, there is insufficient $\mathrm{N}_{2} \mathrm{H}_{4}$ for all of the $\mathrm{N}_{2} \mathrm{O}_{4}$ to react: $\mathrm{N}_{2} \mathrm{H}_{4}$ is the limiting reagent.

From the balanced equation, $\mathbf{2} \mathbf{~ m o l}$ of $\mathbf{N}_{2} \mathbf{H}_{4}$ produces $\mathbf{3} \mathbf{~ m o l}$ of $\mathbf{N}_{\mathbf{2}}$. Therefore:

$$
\text { number of moles of } \mathrm{N}_{2}=3 / 2 \times 0.0409 \mathrm{~mol}=0.0613 \mathrm{~mol}
$$

As the molar mass of $\mathbf{N}_{2}$ is $2 \times 14.01 \mathrm{~g} \mathrm{~mol}^{-1}=28.02 \mathrm{~g} \mathrm{~mol}^{-1}$. The mass of $\mathbf{N}_{2}$ in 0.0613 mol is therefore:

$$
\begin{aligned}
\text { mass } & =\text { number of moles } \times \text { molar mass } \\
& =0.0613 \mathrm{~mol} \times 28.02 \mathrm{~g} \mathrm{~mol}^{-1}=1.72 \mathrm{~g}
\end{aligned}
$$

- Complete the following table. The central atom is underlined.

| Species | Lewis structure | Molecular geometry |
| :---: | :---: | :---: |
| $\underline{\mathrm{NH}_{3}}$ |  | trigonal pyramidal |
| $\underline{\mathrm{SO}_{3}}$ |  | trigonal planar |
| $\underline{\mathrm{ICl}} 3$ |  | T-shaped |
| $\mathrm{ICl}_{4}{ }^{-}$ |  | square planar |

- Complete the Lewis structure of formic acid below by adding double bond(s) and lone pair(s).


Formic acid can form dimers in which two molecules are paired by mutual hydrogen bonding. Draw a dimer of formic acid, clearly showing the hydrogen bonds between the molecules.


Formic acid may lose $\mathrm{H}^{+}$from the oxygen to give a formate ion, shown in Equation 1.

$$
\mathrm{HCOOH}(\mathrm{aq}) \quad \rightleftharpoons \mathrm{HCOO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \quad \text { Equation } 1
$$

Draw a Lewis structure of the formate ion and use it to illustrate the concept of resonance.


Comment on the carbon-oxygen bond lengths in formic acid and the carbon-oxygen bond lengths in the formate ion.

In formic acid, the $\mathbf{C}=\mathbf{O}$ double bond is shorter than the $\mathbf{C}-\mathbf{O}$ bond. In the formate ion, the two $\mathrm{C}-\mathrm{O}$ bonds are identical because of resonance and hence are the same length.

THIS QUESTION IS CONTINUED ON THE NEXT PAGE.

What is the molecular geometry of the formate ion?

With 3 C-O bonds and no lone pairs on the $\mathbf{C}$ atom, the geometry is trigonal planar.

Write the equilibrium constant expression for Equation 1.

$$
K=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]}{[\mathrm{HCOOH}(\mathrm{aq})]}
$$

At equilibrium at $25^{\circ} \mathrm{C}$, the amount of formate ion formed from a 0.100 M solution of formic acid is $4.2 \%$. Calculate the concentration of $\mathrm{H}^{+}(\mathrm{aq})$ in this solution.

From equation 1, the amount of formate ion is equal to the amount of $\mathbf{H}^{+}$. Hence:

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=0.042 \times 0.100 \mathrm{M}=0.0042 \mathrm{M}
$$

Answer: $\mathbf{0 . 0 0 4 2} \mathbf{M}$
Calculate the value of the equilibrium constant, $K$, for Equation 1 at this temperature.

From above, $\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]=\left[\mathrm{H}^{+}(\mathrm{aq})\right]=0.0042 \mathrm{M}$. The remaining formic acid has is:

$$
[\mathrm{HCOOH}(\mathrm{aq})]=(0.100-0.0042) \mathrm{M}
$$

## Hence:

$$
K=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]}{[\mathrm{HCOOH}(\mathrm{aq})]}=\frac{(0.0042)(0.0042)}{(0.100-0.0042)}=1.8 \times 10^{-4} \mathrm{M}
$$

Answer: $\mathbf{1 . 8} \times \mathbf{1 0}^{-4} \mathbf{M}$
Hence calculate the concentration of formate ion in a 0.500 M solution of formic acid.

The reaction table for this equilibrium is:

|  | $\mathrm{HCOOH}(\mathrm{aq})$ | $\rightleftharpoons$ | $\mathrm{H}^{+}(\mathrm{aq})$ | $\mathrm{HCOO}^{-}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: |
| initial (M) | 0.500 |  | 0 | 0 |
| change (M) | $-x$ |  | $+x$ | $+x$ |
| equilibrium | $0.500-x$ |  | $x$ | $x$ |

The equilibrium constant in terms of $x$ is therefore:

$$
K=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]}{[\mathrm{HCOOH}(\mathrm{aq})]}=\frac{(x)(x)}{(0.500-x)}=\frac{x^{2}}{(0.500-x)}=1.8 \times 10^{-4}
$$

As $K$ is very small, $0.500-x \sim 0.500$. Using this approximation:

$$
\begin{aligned}
& \frac{x^{2}}{(0.500-x)} \sim \frac{x^{2}}{0.500}=1.8 \times 10^{-4} \\
& x^{2}=0.500 \times 1.8 \times 10^{-4} \\
& x=\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]=0.0096 \mathrm{M}
\end{aligned}
$$

- By adding double bonds and lone pairs, complete the structural formula of the molecule caffeine below.

- Briefly discuss the relationship between the electron configuration of an element and its position in the Periodic Table.

Elements in the Periodic Table belong to groups and periods. For main group elements (i.e. those in Groups 1, 2 and 13-18), elements in a group have the same outer shell electron configuration (i.e they have the same number of valence electron). Each period (row) of the Table has a set number of inner electron shells, those holding the non-valence electrons.

Carbon and lead are both in Group 14. One is a non-metal and the other is a metal. Outline one physical and one chemical characteristic of a non-metal and a metal and explain the reason for the trend from one to another in Group 14.

|  | Non-metal | Metal |
| :---: | :---: | :---: |
| Physical <br> characteristic | dull, brittle, non-conductor | malleable, ductile, conductor |
| Chemical <br> characteristic | forms covalent bonds <br> with non-metals | forms ionic bonds <br> with non-metals |

Explanation for trend in Group 14
Going down the group, the elements change from non-metals (C) to semimetals ( $\mathbf{S i}, \mathbf{G e}$ ) to metals ( $\mathbf{S n}, \mathrm{Pb}$ ). As the atoms become bigger, the valence electrons are further from the nucleus and less tightly bound. Bonding therefore tends to involve loss of electrons, typical fo metallic behaviour.

- Rechargeable nickel-cadmium batteries normally operate (discharge) with the following oxidation and reduction half-cell reactions.

$$
\begin{array}{ll}
\mathrm{Cd}(\mathrm{OH})_{2}(\mathrm{~s})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cd}(\mathrm{~s})+2 \mathrm{OH}^{-}(\mathrm{aq}) & E^{\circ}(1)=-0.82 \mathrm{~V} \\
\mathrm{AlF}_{6}^{3-}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathrm{Al}(\mathrm{~s})+6 \mathrm{~F}^{-}(\mathrm{aq}) & E^{\circ}(2)=-2.07 \mathrm{~V}
\end{array}
$$

Write out a balanced overall cell reaction.

The reduction potential is more negative for the second reaction so this is reversed. To balance the electrons, the first reaction is multiplied by 3 and the second reaction is multiplied by 2 .

$$
3 \mathrm{Cd}(\mathrm{OH})_{2}(\mathrm{~s})+2 \mathrm{Al}(\mathrm{~s})+12 \mathrm{~F}^{-}(\mathrm{aq}) \rightarrow 3 \mathrm{Cd}(\mathrm{~s})+6 \mathrm{OH}^{-}(\mathrm{aq})+2 \mathrm{AlF}_{6}{ }^{3-}(\mathrm{aq})
$$

Calculate the overall cell potential under standard conditions.

With the second reaction reversed, $E^{\circ}($ oxidation $)=+2.07 \mathrm{~V}$. Hence:

$$
E^{\circ}=E^{\circ}(\text { reduction })+E^{\circ}(\text { oxidation })=((-0.82)+(+2.07)) \mathrm{V}=1.75 \mathrm{~V}
$$

$$
\text { Answer: + } \mathbf{1 . 2 5 ~ V}
$$

A constant current of 3.15 A is measured during the operation of this cell. What would be the change in mass of the aluminium electrode after 10.0 minutes?

The number of electrons passed by a 3.15 A current in $\mathbf{1 0 . 0}$ minutes is:

$$
\begin{aligned}
\text { number of moles of } \mathrm{e}^{-} & =I t / F=(3.15 \mathrm{~A}) \times(10.0 \times 60.00 \mathrm{~s}) /\left(96485 \mathrm{C} \mathrm{~mol}^{-1}\right) \\
& =0.0196 \mathrm{~mol}
\end{aligned}
$$

Formation of $\mathrm{AlF}_{6}{ }^{3-}$ from $\mathrm{Al}(\mathrm{s})$ requires $3 \mathrm{e}^{-}$per mol so the number of moles formed is:

```
number of moles of }\mathbf{Al(s) lost = 0.0196 / 3 mol = 0.00653 mol
```

Hence the mass of aluminium lost is:

$$
\begin{aligned}
\text { mass of aluminium } & =\text { number of moles } \times \text { molar mass } \\
& =0.00653 \mathrm{~mol} \times 26.98 \mathrm{~g} \mathrm{~mol}^{-1}=0.176 \mathrm{~g}
\end{aligned}
$$

Answer: $\mathbf{0 . 1 7 6} \mathbf{g}$ is lost

Write out the overall cell reaction that would occur spontaneously if half-cell (1) were coupled to a standard hydrogen electrode (SHE).

By definition, the standard hydrogen electron has $E^{0}=0.00 \mathrm{~V}$. As the reduction half cell (1) has a more negative potential, it is reversed and becomes the oxidation half cell:

$$
\mathrm{Cd}(\mathrm{~s})+2 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{Cd}(\mathrm{OH})_{2}(\mathrm{~s})+2 \mathrm{e}^{-}
$$

This is then coupled with the SHE, $2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{~g})$, to give the overall reaction:

$$
\mathrm{Cd}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Cd}(\mathrm{OH})_{2}(\mathrm{~s})+\mathrm{H}_{2}(\mathrm{~g})
$$

What would be the cell potential for this new cell?

The SHE has, by definition, $E^{\circ}$ (reduction) $=0.00 \mathrm{~V}$. As cell (1) is reversed, $E^{\circ}$ (oxidation) $=+0.82 \mathrm{~V}$. Hence:

$$
E^{0}=E^{0}(\text { reduction })+E^{0}(\text { oxidation })=(0.00+0.82) \mathrm{V}=0.82 \mathrm{~V}
$$

- Combustion of 15.0 g of coal provided sufficient heat to increase the temperature of 7.5 kg of water from 286 K to 298 K . Calculate the amount of heat (in kJ) absorbed by the water. The heat capacity of water, $C_{\mathrm{p}}{ }^{\circ}=4.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}$.

The temperature rise of water is:

$$
\Delta T=(298-286) \mathrm{K}=12 \mathrm{~K} .
$$

As the heat capacity $C_{\mathrm{p}}{ }^{\circ}=4.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}$, the heat absorbed by 7.5 kg of water is:

$$
q=m C_{\mathrm{p}}{ }^{\circ} \Delta T=\left(7.5 \times 10^{3} \mathrm{~g}\right) \times\left(4.2 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}\right) \times(12 \mathrm{~K})=380 \mathrm{~kJ}
$$

Answer: $\mathbf{3 8 0} \mathbf{~ k J}$
Assuming that coal is pure carbon, calculate the heat of combustion (in $\mathrm{kJ} \mathrm{mol}^{-1}$ ) of the coal.

The number of moles of carbon in 15.0 g is:
number of moles $=$ mass $/$ molar mass $=15.0 \mathrm{~g} / 12.01 \mathrm{~g} \mathrm{~mol}^{-1}=1.25 \mathrm{~mol}$
As this quantity generates 380 kJ , the amount generated by $\mathbf{1 ~ m o l}$ is:

$$
q=380 \mathrm{~kJ} / 1.25 \mathrm{~mol}=300 \mathrm{~kJ}
$$

As energy is released by the combustion reaction, it is exothermic. Hence:

$$
\Delta_{\text {combustion }} H=-300 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

Answer: $\boldsymbol{\Delta}_{\text {combustion }} \boldsymbol{H}=\mathbf{- 3 0 0} \mathbf{k J ~ m o l}^{-1}$

- The standard enthalpy of formation of $\mathrm{SO}_{2}(\mathrm{~g})$ is the enthalpy change that accompanies which reaction?

$$
\mathrm{S}(\mathrm{~s})+\mathrm{O}_{\mathbf{2}}(\mathrm{g}) \rightarrow \mathrm{SO}_{\mathbf{2}}(\mathrm{g})
$$

Calculate the standard enthalpy of formation of $\mathrm{SO}_{2}(\mathrm{~g})$ given the following data.

$$
\begin{array}{ll}
\mathrm{SO}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{SO}_{3}(\mathrm{~g}) & \Delta H=-99 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\mathrm{~S}(\mathrm{~s})+{ }^{3} / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{SO}_{3}(\mathrm{~g}) & \Delta H=-396 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{array}
$$

Using $\Delta_{\mathrm{rxn}} H=\Sigma m \Delta_{\mathrm{f}} H^{\circ}$ (products) $-\Sigma n \Delta_{\mathrm{f}} H^{\circ}($ reactants $)$, the enthalpy of these two reactions are:
(1) $\Delta_{\mathrm{rxn}} H=\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{SO}_{3}(\mathrm{~g})\right)-\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{SO}_{2}(\mathrm{~g})\right)=-\mathbf{9 9} \mathrm{kJ} \mathrm{mol}^{-1}$
(2) $\Delta_{\mathrm{rxn}} H=\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{SO}_{3}(\mathrm{~g})\right)=-369 \mathrm{~kJ} \mathrm{~mol}^{-1}$
as $\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{O}_{2}(\mathrm{~g})\right)$ and $\Delta_{\mathrm{f}} H^{\circ}(\mathrm{S}(\mathrm{s}))$ are both zero as $\mathrm{O}_{2}(\mathrm{~g})$ and $\mathrm{S}(\mathrm{s})$ are elements in their standard states.

## ANSWER CONTINUES ON THE NEXT PAGE

Substituting (2) into (1) gives:
$\left(-396 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)-\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{SO}_{2}(\mathrm{~g})\right)=-99 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Hence:
$\Delta_{\mathrm{f}} H^{\circ}\left(\mathrm{SO}_{3}(\mathrm{~g})\right)=-297 \mathrm{~kJ} \mathrm{~mol}^{-1}$

- The standard heat of formation of $\mathrm{ClF}_{3}(\mathrm{~g})$ is $-159 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Use the bond enthalpies below to calculate the average $\mathrm{Cl}-\mathrm{F}$ bond enthalpy in $\mathrm{ClF}_{3}(\mathrm{~g})$.

| Bond | Cl-Cl | F-F |
| :---: | :---: | :---: |
| Bond enthalpy $/ \mathrm{kJ} \mathrm{mol}^{-1}$ | 243 | 158 |

The heat of formation of $\mathrm{ClF}_{3}(\mathrm{~g})$ corresponds to the reaction:

$$
1 / 2 \mathrm{Cl}_{2}(\mathrm{~g})+3 / 2 \mathrm{~F}_{2}(\mathrm{~g}) \rightarrow \mathrm{ClF}_{3}(\mathrm{~g})
$$

In terms of bond enthalpies, this corresponds to (i) breaking $\mathbf{1 / 2} \mathbf{~ m o l}$ of $\mathbf{C l}-\mathrm{Cl}$ bonds and $\mathbf{3 / 2} \mathbf{~ m o l}$ of $\mathrm{F}-\mathrm{F}$ bonds and (ii) forming $\mathbf{3 ~ \mathrm { mol }}$ of $\mathrm{Cl}-\mathrm{F}$ bonds:

$$
\begin{aligned}
& \Delta_{\mathrm{f}} H^{0}=(1 / 2 \times 243+3 / 2 \times 158)-3 \times \Delta_{\mathrm{bond}} H(\mathrm{Cl}-\mathrm{F})=-159 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
& \Delta_{\mathrm{bond}} H(\mathrm{Cl}-\mathrm{F})=+173 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Answer: $\mathbf{+ 1 7 3} \mathbf{~ k J ~ m o l}^{-1}$
Explain why this number is different from the average Cl-F bond enthalpy estimated for $\mathrm{ClF}_{5}(\mathrm{~g})$ of $151 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

Bond strength is dependent on the interaction between the bonding electrons and the two nuclei of the atoms involved. The bonds in $\mathrm{CIF}_{3}$ and $\mathrm{CIF}_{5}$ are similar but not identical. For example, the oxidation numbers of Cl are +3 and +5 and it has 2 and 1 lone pair respectively. This leads to the CI-F bonds being a little different in strength.

- Explain the observation that the boiling point of ethanol is much higher than that of dimethyl ether despite these compounds having the same molar mass.

| compound | formula | boiling point $/{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: |
| ethanol | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ | 78.3 |
| dimethyl ether | $\mathrm{CH}_{3} \mathrm{OCH}_{3}$ | -22.0 |

Ethanol can from strong intermolecular hydrogen bonds. Dimethyl ether cannot, it can only form much weaker dispersion forces and dipole-dipole interactions.

