

**Topics in the June 2006 Exam Paper for CHEM1903**

Click on the links for resources on each topic.

2006-J-2:

- [Bonding in H<sub>2</sub> - MO theory](#)
- [Bonding in O<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>O](#)
- [Band Theory - MO in Solids](#)

2006-J-3:

- [Nuclear and Radiation Chemistry](#)
- [Wave Theory of Electrons and Resulting Atomic Energy Levels](#)

2006-J-4:

- [Ionic Bonding](#)

2006-J-5:

- [Bonding in O<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>O](#)

2006-J-6:

- [Lewis Structures](#)
- [VSEPR](#)
- [Wave Theory of Electrons and Resulting Atomic Energy Levels](#)

2006-J-7:

- [Thermochemistry](#)
- [First and Second Law of Thermodynamics](#)
- [Nitrogen in the Atmosphere](#)

2006-J-8:

- [Thermochemistry](#)

2006-J-9:

- [Equilibrium and Thermochemistry in Industrial Processes](#)

2006-J-10:

- [Electrochemistry](#)

2006-J-11:

- [Electrolytic Cells](#)

2006-J-12:

- [First and Second Law of Thermodynamics](#)

- In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.

(a) Pauli exclusion principle

**The principle that states that no two electrons in an atom or molecule can have the same set of quantum numbers. It limits the number of electrons that can occupy an orbital to two.**

(b) electronegativity

**The ability of an atom to attract electron density towards itself in a covalent bond. Fluorine is the most electronegative element.**

(c) ionic bond

**The low energy state found in ionic solids associated with the Coulombic attraction of unlike charged ions.**

(d) paramagnetic

**A property of an atom, ion, molecule or solid resulting from the presence of at least one unpaired electron spin. Paramagnets are attracted towards a magnetic field.**

(e) n-type semiconductor

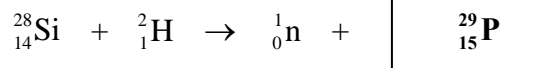
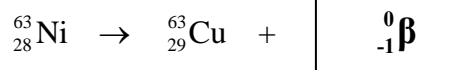
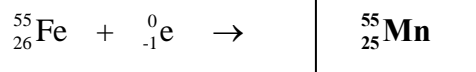
**A semiconductor has electrical conductivity in between that of a metal and that of an insulator. A n-type semiconductor is obtained by adding a type of atoms to a semiconductor in order to increase the number of negative charge carrier. For example, doping a group 14 element such as Si with a group 15 element such as As leads to extra electrons in the conductance band which are free to move and carry the charge.**

(e)  $\sigma$  bond

**A bond produced by the occupation of a  $\sigma$ -bonding molecular orbital. This orbital is made by overlap of atomic orbitals, such as end-on/end-on overlap of p-orbitals or of s-orbitals, to produce a molecular orbital with no nodes along the internuclear axis. The electron density is along the internuclear axis.**

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- Balance the following nuclear reactions by identifying the missing nuclide.



- Identify the decay mechanism for the following three unstable nuclides given that the only stable isotopes of Pr and Eu are  ${}_{59}^{141}\text{Pr}$ ,  ${}_{63}^{151}\text{Eu}$  and  ${}_{63}^{153}\text{Eu}$ . There are no stable isotopes of Rn.

Isotope	Nuclear Decay Mechanism
${}_{59}^{142}\text{Pr}$	<b>Stable nucleus has fewer neutrons: <u><math>\beta^-</math> decay</u></b>
${}_{63}^{150}\text{Eu}$	<b>Stable nucleus has more neutrons: <u><math>\beta^+</math> decay or <math>e^-</math> capture</u></b>
${}_{86}^{222}\text{Rn}$	<b><math>\alpha</math> decay</b>

- Identify two specific features of atomic structure that can only be explained by reference to the wave-like nature of electrons. Give reasons.

**Electrons occupy certain stable “orbits” that correspond to the standing waves obtained by solving the Schrödinger Equation. Each solution (orbital) corresponds to a different allowed energy level. As a consequence of this;**

- electrons do not spiral in towards the nucleus despite the electrostatic attraction between them**
- the light emitted by excited atoms is a series of discrete spectral lines corresponding to the energy differences between the allowed energy states.**

**Marks**  
**3**

**3**

**2**

- The ionic solids NaCl, LiF, KF and LiCl, all have the same crystal structure. Assuming only electrostatic interactions are involved, use the information below to organise these four ionic solids in order of increasing energy of the crystal lattice.

**Marks**  
**2**

ion	radius ( $10^{-12}$ m)	ion	radius ( $10^{-12}$ m)
Li <sup>+</sup>	76	F <sup>-</sup>	133
Na <sup>+</sup>	102	Cl <sup>-</sup>	181
K <sup>+</sup>	138		

### Working

**The electrostatic attraction between the cations and anions in an ionic solid depends on:**

- The ionic charges: higher cation and anion charges lead to higher lattice energies. In these systems, the cations are all +1 and the anions all -1.**
- The lattice structure: higher coordination numbers lead to higher Madelung constants and higher lattice energies. These systems all adopt the same structure (the rocksalt or NaCl structure).**
- The separation of the cations and anions: higher ionic radii lead to longer separations and lower lattice energies.**

**The cation – anion separation is given by the sum of the ionic radii:**

- NaCl: (102 + 181) = 283 pm, LiF: (76 + 133) = 209 pm, KF: (138 + 133) = 271 pm, LiCl: (76 + 181) = 257 pm.**

**The order of the lattice energies is the same as that of these separations.**

Increasing energy of the crystal lattice →

<b>NaCl</b>	<b>KF</b>	<b>LiCl</b>	<b>LiF</b>
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- Explain why CsCl, NaCl and ZnS have different crystal structures.

**1**

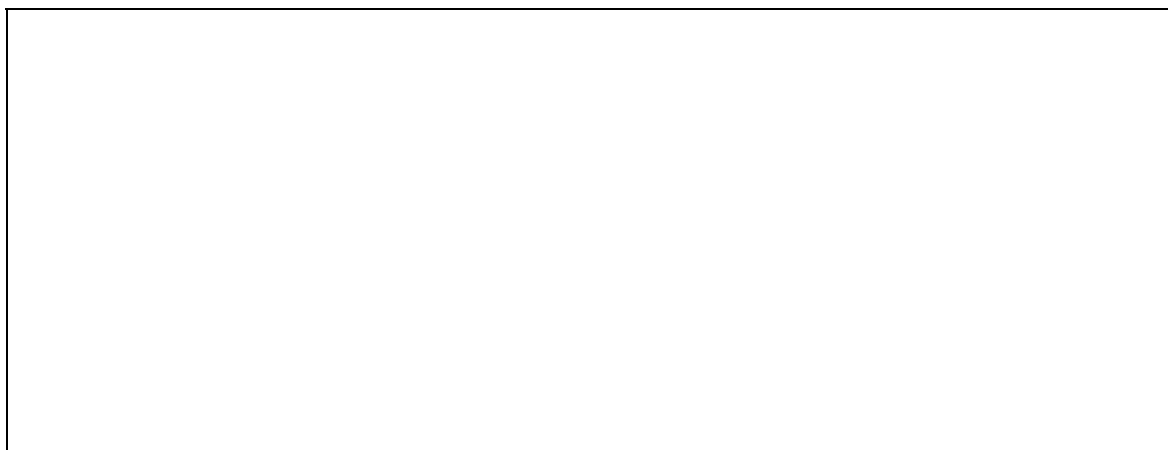
**The lattice energy is higher when the number of cations around the anions and the number of anions around the cations are both maximised. The relative sizes of the ions controls how many can be fitted around each one.**

**Cs<sup>+</sup> is the largest cation and can fit 8 Cl<sup>-</sup> ions around it.**

**Na<sup>+</sup> is smaller and can only fit 6 Cl<sup>-</sup> ions around it.**

**Zn<sup>2+</sup> is even smaller and S<sup>2-</sup> is larger than Cl<sup>-</sup> so that only 6 anions can fit around the cation.**

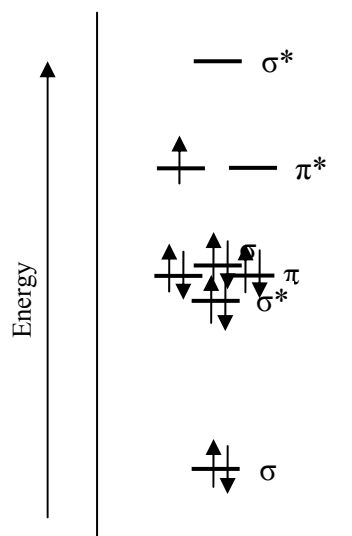
**These ‘radius – ratio’ rules work best in very ionic systems. In those where covalency is also important, orbital overlap can also play a role. For example, ZnS is likely to be significantly more covalent than the alkali metal chlorides. The tetrahedral coordination of Zn<sup>2+</sup> in ZnS may be partly due to covalency.**



**Marks**  
**4**

- The molecular orbital energy level diagram below is for the valence electrons of the  $O_2^+$  ion.

Indicate the ground state electronic configuration of  $O_2^+$  using the arrow notation for electron spins on the provided molecular orbital energy level diagram.



Calculate the bond order of  $O_2^+$ .

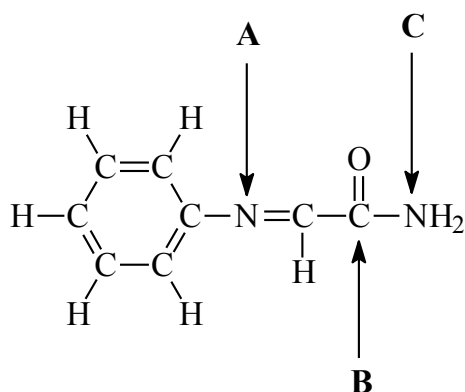
$$\text{Bond order} = \frac{1}{2} (8 - 3) = 2.5$$

Indicate the lowest energy electron excitation in this ion by identifying the initial and final molecular states of the electron undergoing the excitation.

**The gap between the highest occupied  $\sigma$  and the  $\pi^*$  is very similar to that between  $\pi^*$  and  $\sigma^*$ : either  $\sigma \rightarrow \pi^*$  or  $\pi^* \rightarrow \sigma^*$**

- Consider the molecule whose structure is shown below. Complete the table concerning the atoms **A**, **B** and **C** indicated by the arrows.

**Marks**  
**3**



Selected atom	Number of lone pairs about the selected atom	Number of $\sigma$ -bonds associated with the selected atom	Geometry of $\sigma$ -bonds about the selected atom
<b>A</b>	<b>1</b>	<b>2</b>	<b>bent</b>
<b>B</b>	<b>0</b>	<b>3</b>	<b>trigonal planar</b>
<b>C</b>	<b>1</b>	<b>3</b>	<b>trigonal pyramidal</b>

- Calculate the energy (in J) and the wavelength (in nm) of the photon of radiation emitted when the electron in  $\text{Be}^{3+}$  drops from an  $n = 3$  state to an  $n = 2$  state.

**3**

$\text{Be}^{3+}$  has only 1  $e^-$  so the equation  $E_n = \frac{-E_R Z^2}{n^2}$  where  $E_R = 2.18 \times 10^{-18} \text{ J}$  can be used. Be has  $Z = 4$ .

The energy of the  $n = 3$  and  $n = 2$  levels are:

$$E_3 = \frac{-E_R (4)^2}{(3)^2} = -\frac{16}{9} E_R \quad \text{and} \quad E_2 = \frac{-E_R (4)^2}{(2)^2} = -\frac{16}{4} E_R = -4E_R$$

The energy separation is  $\frac{20}{9} E_R = \frac{20}{9} \times (2.18 \times 10^{-18}) = 4.84 \times 10^{-18} \text{ J}$

$$\text{As } E = \frac{hc}{\lambda},$$

$$\lambda = \frac{hc}{E} = \frac{(6.634 \times 10^{-34}) \times (2.998 \times 10^8)}{(4.84 \times 10^{-18})} = 4.11 \times 10^{-8} \text{ m} = 41.1 \text{ nm}$$

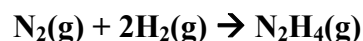
Energy =  $4.84 \times 10^{-18} \text{ J}$

Wavelength = **41.1 nm**

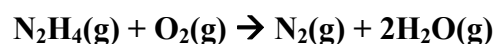


**Marks**  
**4**

- Write the equation whose enthalpy change represents the standard enthalpy of formation of hydrazine,  $\text{N}_2\text{H}_4(\text{g})$ .



Write the equation whose enthalpy change represents the enthalpy of combustion of hydrazine,  $\text{N}_2\text{H}_4(\text{g})$  to produce water vapour.



Given the following data, calculate the standard enthalpy of formation of  $\text{N}_2\text{H}_4(\text{g})$ .

$$\Delta H^\circ_f(\text{H}_2\text{O}(\text{g})) = -242 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{comb}}(\text{N}_2\text{H}_4(\text{g})) = -580 \text{ kJ mol}^{-1}$$

Using  $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - \sum n\Delta_fH^\circ(\text{reactants})$ , the enthalpy change for the combustion reaction is:

$$\Delta_{\text{comb}}H^\circ = [2\Delta_fH^\circ(\text{H}_2\text{O}(\text{g}))] - [\Delta_fH^\circ(\text{N}_2\text{H}_4(\text{l}))]$$

as the remaining compounds are elements in their standard states.

Hence:

$$[2 \times -242] - [\Delta_fH^\circ(\text{N}_2\text{H}_4(\text{l}))] = -580 \text{ kJ mol}^{-1}$$

$$\Delta_fH^\circ(\text{N}_2\text{H}_4(\text{l})) = +96 \text{ kJ mol}^{-1}$$

Answer: **+96 kJ mol<sup>-1</sup>**

**3**

- Estimate the temperature of Mars given its radius of 3400 km and the solar power density at its surface of  $590 \text{ J m}^{-2} \text{ s}^{-1}$ . Assume an average albedo of 16% and zero Greenhouse effect.

With an average albedo of 16%, 84% of the solar energy is not reflected. As the solar power density is  $590 \text{ J m}^{-2} \text{ s}^{-1}$ :

$$E_{\text{in}} = \pi r^2 \times 590 \times 0.84$$

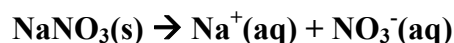
$$E_{\text{out}} = 4\pi r^2 \times (5.67 \times 10^{-8}) \times T^4$$

As  $E_{\text{out}} = E_{\text{in}}$ :

$$T^4 = \frac{590 \times 0.84}{4 \times 5.67 \times 10^{-8}} \text{ or } T = 216 \text{ K.}$$

**Marks**  
**4**

- In an experiment, 1.76 g of sodium nitrate was dissolved in water inside a calorimeter. Give a balanced equation for the reaction that took place.



The temperature of the solution was found to decrease by 1.22 °C. If the heat capacity of the calorimeter was 77.0 J K<sup>-1</sup> and the heat capacity of the solution was 268 J K<sup>-1</sup>, determine the molar heat of reaction.

**The heat change is given by:**

$$q = (c_{\text{calorimeter}} \times \Delta T) + (c_{\text{solution}} \times \Delta T) = (77.0 \times 1.22) + (268 \times 1.22) = 421 \text{ J}$$

**The process is endothermic as the temperature of the solution decreases.**

**The molar mass of NaNO<sub>3</sub> is (22.99 (Na)) + (14.01 (N)) + (3 × 16.00 (O)) = 85**

**The molar heat of reaction is therefore:**

$$q_m = \frac{85}{1.76} \times 421 = 20300 \text{ J mol}^{-1} = 20.3 \text{ kJ mol}^{-1}$$

Answer: **20.3 kJ mol<sup>-1</sup>**

How long would it take a 250 W power supply to reheat the calorimeter to its starting temperature?

**A 250 W power supply delivers 250 J s<sup>-1</sup>. As 410 J was removed from the calorimeter and the water inside it to reduce the temperature by 1.22 °C, the power supply will take:**

$$t = \frac{421}{250} = 1.68 \text{ s}$$

- At 773 K, the following reaction has an equilibrium constant,  $K_p$ , of  $1.52 \times 10^{-5} \text{ atm}^{-2}$ .

**Marks**  
**4**



If 0.0200 mol of ammonia were introduced into an evacuated 1.00 L container at 773 K, what would be the partial pressures of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  at equilibrium?

**The initial pressure of ammonia can be calculated using the ideal gas law:**

$$p_{\text{NH}_3} = \frac{nRT}{V} = \frac{(0.0200) \times (0.08206) \times 773}{1.00} = 1.27$$

**The reaction table is:**

	$\text{N}_2(\text{g})$	$3\text{H}_2(\text{g})$	$\rightleftharpoons$	$2\text{NH}_3(\text{g})$
<b>start</b>	<b>0</b>	<b>0</b>	<hr style="width: 50%; margin: 0 auto;"/>	<b>1.27</b>
<b>change</b>	<b>x</b>	<b>3x</b>		<b>-2x</b>
<b>equilibrium</b>	<b>x</b>	<b>3x</b>		<b>1.27 - 2x</b>

$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})^3 (p_{\text{H}_2})} = \frac{(1.27-2x)^2}{(x)(3x)^3} = \frac{(1.27-2x)^2}{27x^4} = 1.52 \times 10^{-5}$$

As  $K_p$  is small,  $x$  will be *large* and hence no approximation can be made. The equation rearranges to:

$$(1.27-2x)^2 = (1.52 \times 10^{-5}) \times 27x^4$$

so

$$(1.27-2x) = (2.03 \times 10^{-2})x^2 \quad \text{or} \quad (2.03 \times 10^{-2})x^2 + 2x - 1.27 = 0$$

This must be solved with the quadratic equation using  $a = (2.03 \times 10^{-2})$ ,  $b = 2$  and  $c = -1.27$ :

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a} = \frac{-2 + \sqrt{(2)^2 - (4 \times 2.03 \times 10^{-3} \times -1.27)}}{2 \times (2.03 \times 10^{-2})} = 0.631$$

**Only the positive root has a physical relevance for the equilibrium. Hence:**

$$p_{\text{N}_2} = x = 0.631 \text{ atm}, \quad p_{\text{H}_2} = 3x = 1.89 \text{ atm} \quad \text{and} \quad p_{\text{NH}_3} = (1.27-2x) = 8.07 \times 10^{-3} \text{ atm}$$

$$P(\text{N}_2) = 0.631 \text{ atm}$$

$$P(\text{H}_2) = 1.89 \text{ atm}$$

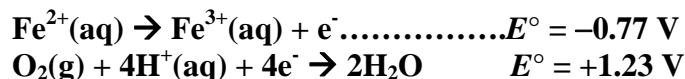
$$P(\text{NH}_3) = 8.07 \times 10^{-3} \text{ atm}$$

**Marks**  
**3**

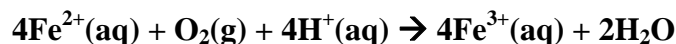
- Refer to the electrochemical potentials on the data sheet.

Show that  $\text{Fe}^{2+}(\text{aq})$  is not stable under 1 atm  $\text{O}_2$  in a 1 M solution of HCl. What happens to  $\text{Fe}^{2+}$ ?

$\text{Fe}^{2+}$  will be oxidised by  $\text{O}_2$  under these conditions. The relevant half cells are:



The overall reaction is:

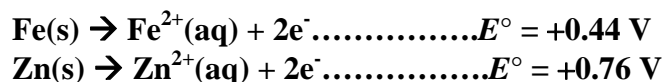


$$E^\circ = -0.77 + 1.23 = +0.46$$

As  $E^\circ > 0$ , the reaction is spontaneous.

Show Fe(s) is stabilised by galvanizing with Zn(s).

The electrode potentials for oxidation of Fe(s) and Zn(s) are:



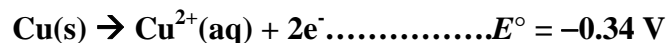
As Zn(s) has a higher oxidation potential, it will be preferentially oxidised and will therefore protect Fe(s).

Show  $\text{Cu}^+(\text{aq})$  is not stable in water. What would happen to  $\text{Cu}^+(\text{aq})$ ?

The electrode potential for reduction of  $\text{Cu}^+(\text{aq})$  is:



The electrode potential for oxidation of Cu(s) is:



The reaction:



therefore has an overall potential of  $E^\circ = (+0.53) + (-0.34) = +0.17 \text{ V}$

This disproportionation reaction has  $E^\circ > 0$  and is spontaneous.

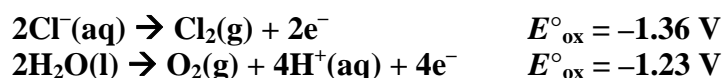
- In the chlor-alkali process  $\text{H}_2(\text{g})$ ,  $\text{OH}^-(\text{aq})$  and  $\text{Cl}_2(\text{g})$  are produced by the electrolysis of a concentrated solution of sodium chloride. Explain how hydrogen gas is produced at the cathode, and why chlorine gas rather than oxygen gas forms at the anode.

At the cathode, water is reduced to  $\text{H}_2$  rather than sodium being reduced to Na metal due to the relative size of the reduction potentials:



Reduction of water has a more favourable (less negative) reduction potentials and is reduced preferentially.

At the anode, the relevant oxidation potentials are:



Oxidation of  $\text{H}_2\text{O}(\text{l})$  has a more favourable oxidation potential so it appears that it should be preferentially oxidised. However, the overpotential for the formation of  $\text{O}_2(\text{g})$  is *much* greater than the overpotential for the formation of  $\text{Cl}_2(\text{g})$ . As a result, it is actually  $\text{Cl}_2(\text{g})$  that is produced rather than  $\text{O}_2(\text{g})$ .

A chlor-alkali plant produces 42.3 tonne of  $\text{Cl}_2$  per day. Calculate the minimum current used. (1 tonne = 1000 kg)

42.3 tonne corresponds to  $42.3 \times 10^3 \text{ kg}$  or  $42.3 \times 10^6 \text{ g}$ . The molar mass of  $\text{Cl}_2$  is  $(2 \times 35.45) = 70.9$ . The number of moles of  $\text{Cl}_2$  produced each day is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{42.3 \times 10^6}{70.9} = 5.97 \times 10^5 \text{ mol.}$$

The half cell reaction for production of  $\text{Cl}_2(\text{g})$  is  $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

Production of 1 mol of  $\text{Cl}_2(\text{g})$  requires 2 mol of electrons so the daily production requires  $2 \times (5.97 \times 10^5) = 1.19 \times 10^6 \text{ mol}$ .

The number of moles of electrons delivered by a current  $I$  is given by:

$$n = \frac{Q}{F} = \frac{It}{F}$$

A day corresponds to  $t = (24 \times 60 \times 60) = 86400$  seconds. The current required to generate  $1.19 \times 10^6 \text{ mol}$  of electrons is therefore:

$$I = \frac{n \times F}{t} = \frac{(1.19 \times 10^6) \times (96485)}{(86400)} = 1.33 \times 10^6 \text{ A}$$

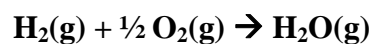
Answer:  $1.33 \times 10^6 \text{ A}$

Calculate the amount of  $\text{H}_2$  produced (in mol) and estimate the daily energy available to the plant through combustion of this hydrogen.  $\Delta H^\circ_f(\text{H}_2\text{O}(\text{g})) = -242 \text{ kJ mol}^{-1}$

**$\text{H}_2(\text{g})$  is produced through the reaction  $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ .**

**The number of moles of  $\text{H}_2(\text{g})$  is the same as that for  $\text{Cl}_2(\text{g}) = 5.97 \times 10^5 \text{ mol}$ .**

**Combustion of  $\text{H}_2$  follows the reaction:**



**Hence,  $\Delta_{\text{comb}}H^\circ(\text{H}_2(\text{g})) = \Delta_fH^\circ(\text{H}_2\text{O}(\text{g})) = -242 \text{ kJ mol}^{-1}$ .**

**Assuming 100% efficiency, combustion of  $5.97 \times 10^5 \text{ mol}$  therefore generates:**

$$\Delta_{\text{comb}}H = (5.97 \times 10^5) \times (-242) = 1.44 \times 10^8 \text{ kJ.}$$

Answer:  $1.44 \times 10^8 \text{ kJ}$

- State the Second Law of Thermodynamics, and explain how the enthalpy of reaction is related to the entropy change of the surroundings.

**The entropy of the universe always increases:  $\Delta_{\text{univ}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S > 0$**

**The surroundings act as a reservoir of heat for the system: heat gained or lost in a reaction is taken or given to the surroundings, respectively.**

**As  $\Delta_{\text{sys}}H = -q_{\text{surr}}$  at constant pressure:**

$$\Delta_{\text{surr}}S = \frac{q_{\text{surr}}}{T} = \frac{-\Delta_{\text{sys}}H}{T}$$

Give an example of a chemical reaction or a chemical process that corresponds to each of the following.

$$\Delta S > 0, \Delta H > 0$$

**As  $\Delta_{\text{surr}}S = \frac{-\Delta_{\text{sys}}H}{T} < 0$ , such processes will only occur if the temperature is sufficiently *high* that  $\Delta_{\text{surr}}S$  is smaller in magnitude than  $\Delta_{\text{sys}}S$ .**

**Examples include:**

- **Melting of ice at 300 K:  $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$**
- **Boiling of water at 400 K:  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$**
- **$\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$**

$$\Delta S > 0, \Delta H < 0$$

**As  $\Delta_{\text{surr}}S = \frac{-\Delta_{\text{sys}}H}{T} > 0$  and  $\Delta_{\text{sys}}S > 0$ , such processes will occur at *all***

**temperatures. Examples include:**

- **Burning of ethane:  $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$**
- **$\text{CaCl}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$**

$$\Delta S < 0, \Delta H < 0$$

**As  $\Delta_{\text{surr}}S = \frac{-\Delta_{\text{sys}}H}{T} > 0$ , such processes will only occur if the temperature is sufficiently *low* that  $\Delta_{\text{surr}}S$  is larger in magnitude than  $\Delta_{\text{sys}}S$ .**

**Examples include:**

- **Freezing of ice at 263 K:  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$**
- **Condensing of steam at 300 K:  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$**