

Topics in the June 2007 Exam Paper for CHEM1901

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- [Bonding in O₂, N₂, C₂H₂, C₂H₄ and CH₂O](#)
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2007-J-13:

- 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) diamagnetic

A description of an atom or molecule with no unpaired electron spins and hence no net magnetic moment.

(b) covalent bond

A low energy arrangement of two or more atoms arising from the delocalisation of electrons in molecular orbitals.

(c) nucleogenesis

The generation of heavier nuclei by the fusion of lighter nuclei.

(d) hydrogen bond

The electrostatic attraction between a hydrogen atom bonded to a very electronegative atom (F, O or N) and electron lone pairs on another atom.

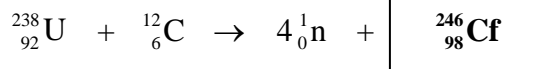
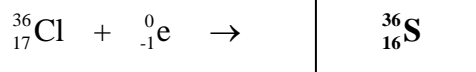
(e) Hund's rule

The requirement that degenerate orbitals are all half-filled with electrons with parallel spins before any of the degenerate orbitals is filled.

(f) electrical conductor

A material in which charged groups can flow in response to an applied electric field or potential. In the case where the material is a solid and the charged "groups" are electrons, this requires a small to zero band gap.

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



Marks
3

- The half life of ${}^{90}\text{Sr}$ is 29 years. Calculate the remaining activity (in Bq) of a sample containing ${}^{90}\text{Sr}$ after 100 years given that the initial activity was 1000 Bq.

2

From $t_{1/2} = \frac{\ln 2}{\lambda}$, $\lambda = \frac{\ln 2}{29} = 0.0239 \text{ yr}^{-1}$.

The activity after 100 years is related to the initial activity by:

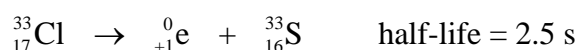
$$\ln\left(\frac{A_0}{A_t}\right) = \lambda t = (0.0239) \times 100 = 2.39 \text{ so } \frac{A_0}{A_t} = e^{2.39}$$

As $A_0 = 1000 \text{ Bq}$, $A_t = \frac{1000}{e^{2.39}} = 92 \text{ Bq}$

Answer: **92 Bq**

- The three unstable isotopes ${}_{17}^{33}\text{Cl}$, ${}_{36}^{77}\text{Kr}$ and ${}_{12}^{27}\text{Mg}$ are unsuitable for use in medical imaging. For each isotope, provide a reason why it is unsuitable. The following data may be of use:

3



${}_{17}^{33}\text{Cl}$ - the half life of 2.5 s is too short to allow for synthesis of host molecules, administration of the nuclide to the patient and measurement of the radiation emitted.

${}_{36}^{77}\text{Kr}$ - krypton is a noble gas and cannot be incorporated into a suitable host molecule for administration to the patient.

${}_{12}^{27}\text{Mg}$ - this nuclide is a β -emitter so little useful radiation would escape the body and local radiation damage would occur.

Marks
5

- The electronic configuration of the molecular oxygen dianion in its ground state is, in order (from left to right) of increasing energy: $\sigma^2 \sigma^{*2} \sigma^2 \sigma^{*2} \sigma^2 \pi^4 \pi^{*4}$

 What is the bond order of O_2^{2-} ?

$$\frac{1}{2}(8 - 6) = 1$$

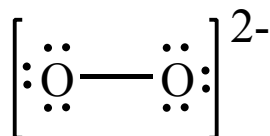
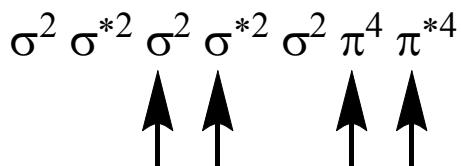
(σ^2 , σ^2 and π^4 are bonding, π^{*4} are antibonding)

 Is O_2^{2-} paramagnetic or diamagnetic? Explain your answer.

All of the spins are paired as every orbital is full. It is therefore diamagnetic.

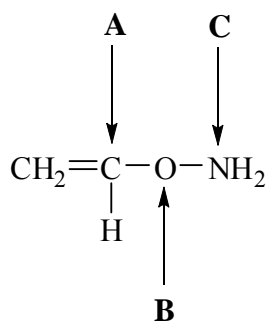
 How many of the valence electrons in O_2^{2-} are in 'lone pairs' according to Lewis theory?

The Lewis structure gives 3 lone pairs on each oxygen atom so 12 electrons are in lone pairs in total.


 On the electron configuration of O_2^{2-} below, indicate by arrows the molecular orbitals that contain the electron 'lone pairs'.


- 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 σ -bonds associated with the selected atom	Geometry of σ -bonds about the selected atom
A	0	3	trigonal planar
B	2	2	bent
C	1	3	trigonal pyramid

- Calculate the energy (in J) and the wavelength (in nm) of the photon of radiation emitted when the electron in Li^{2+} drops from an $n = 4$ state to an $n = 2$ state.

2

As Li^{2+} has 1 electron, its energy levels are described by the equation $E_n = \frac{-E_R Z^2}{n^2}$ where $E_R = 2.18 \times 10^{-18} \text{ J}$ and $Z = 3$.

The energies of the $n = 4$ and $n = 2$ levels are:

$$E_4 = \frac{-E_R(3)^2}{(4)^2} = -\frac{9}{16}E_R \quad \text{and} \quad E_2 = \frac{-E_R(3)^2}{(2)^2} = -\frac{9}{4}E_R = -\frac{36}{16}E_R$$

The energy separation is:

$$\begin{aligned} \Delta E = E_4 - E_2 &= \left[-\frac{9}{16}E_R \right] - \left[-\frac{36}{16}E_R \right] = \frac{27}{16}E_R \\ &= \frac{27}{16} \times (2.18 \times 10^{-18}) = 3.68 \times 10^{-18} \text{ J} \end{aligned}$$

$$\text{Using } E = \frac{hc}{\lambda}, \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}) \times (2.998 \times 10^8)}{(3.68 \times 10^{-18})} = 5.40 \times 10^{-8} \text{ m} = 54.0 \text{ nm}$$

Energy = $3.68 \times 10^{-18} \text{ J}$

Wavelength = **54.0 nm**

Marks
3

- Describe two physical properties of liquid or solid water that distinguishes it from 'normal' liquids or solids.

The solid is less dense than the liquid.

The density of the liquid can decrease on cooling.

The melting and boiling points are significantly higher than would be predicted from extrapolation of the other group 16 dihydrides.

It is capable of dissolving ionic solids to a larger extent than most other liquids.

Identify one property of the water *molecule* that is responsible for at least one of the physical properties you described above. Your answer should include both the molecular property and the physical property associated with it.

The tetrahedral arrangement of H atoms and the lone pairs about the O and the high polarity of the O-H bond lead to a tetrahedral network with strong intermolecular H-bonding. This results in a low density structure with strong intermolecular forces. The high polarity of the molecule also leads to strong ion-dipole interactions with cations and anions.

- Describe one consequence of molecular shape involving *non-polar* molecules.

The shape of molecules can lead to biological specificity, eg in smell and in drug action. The shape of molecules also leads to differences in intermolecular forces such as the different boiling points of straight and branched alkanes and the formation of liquid crystal phases in certain molecules.

- Molecules with multiple resonance structures are said to be "resonance stabilised". Briefly explain the origin of this extra stability in terms of electron waves and molecular orbitals.

The presence of resonance Lewis structures indicates the presence of molecular orbitals that extend over more than a pair of atoms. This greater delocalisation of electrons produces lower energies and hence increased stabilisation of the molecule.

2**2**

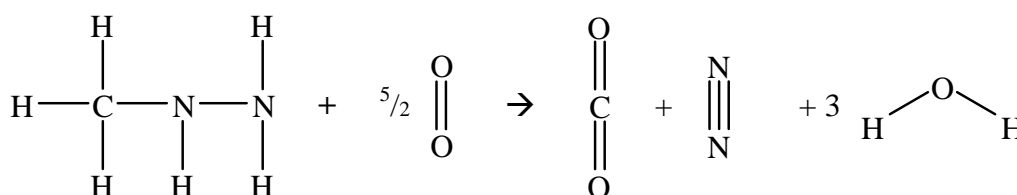
- Write a balanced equation for the combustion of methylhydrazine, $\text{CH}_3\text{NHNH}_2(\text{g})$.

Marks
6



Using bond enthalpies, estimate the enthalpy of combustion of methylhydrazine.

Bond enthalpies:	Bond	$\Delta H / \text{kJ mol}^{-1}$	Bond	$\Delta H / \text{kJ mol}^{-1}$
	C-N	285	O-H	464
	N-N	159	O=O	498
	C-H	416	C=O	806
	N-H	391	N \equiv N	945



$$\begin{aligned} \Delta_{\text{atom}}\text{H}(\text{CH}_3\text{NHNH}_2) &= 3\Delta\text{H}(\text{C-H}) + \Delta\text{H}(\text{C-N}) + 3\Delta\text{H}(\text{N-H}) + \Delta\text{H}(\text{N-N}) \\ &= (3 \times 416) + (285) + (3 \times 391) + (159) = 2865 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta_{\text{atom}}\text{H}(\text{O}_2) = \Delta\text{H}(\text{O=O}) = 498 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{atom}}\text{H}(\text{CO}_2) = 2 \times \Delta\text{H}(\text{C=O}) = (2 \times 806) = 1612 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{atom}}\text{H}(\text{N}_2) = \Delta\text{H}(\text{N}\equiv\text{N}) = 945 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{atom}}\text{H}(\text{H}_2\text{O}) = 2\Delta\text{H}(\text{O-H}) = (2 \times 464) = 928 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta_{\text{comb}}\text{H} &= \Delta_{\text{atom}}\text{H}(\text{reactants}) - \Delta_{\text{atom}}\text{H}(\text{products}) = \\ &= [\Delta_{\text{atom}}\text{H}(\text{CH}_3\text{NHNH}_2) + \frac{5}{2}\Delta_{\text{atom}}\text{H}(\text{O}_2)] \\ &\quad - [\Delta_{\text{atom}}\text{H}(\text{CO}_2) + \Delta_{\text{atom}}\text{H}(\text{N}_2) + 3\Delta_{\text{atom}}\text{H}(\text{H}_2\text{O})] \\ &= [(2865) + (\frac{5}{2} \times 498)] - [(1612) + (945) + (3 \times 928)] = -1231 \text{ kJ mol}^{-1} \end{aligned}$$

Answer: $-1231 \text{ kJ mol}^{-1}$

ANSWERS CONTINUES ON THE NEXT PAGE

Liquid methylhydrazine and liquid oxygen can be used as a rocket fuel. Calculate the calorific value (in kJ g^{-1}) of this fuel.

The molar mass of O_2 is $(2 \times 16.00) = 32.00$. The molar mass of CH_3NHNH_2 is:

$$(12.01 \text{ (C)}) + (6 \times 1.008 \text{ (H)}) + (2 \times 14.01 \text{ (N)}) = 46.078$$

To burn one mole of methylhydrazine requires $5/2$ moles of liquid O_2 to be carried so the combined mass is $(46.078) + (5/2 \times 32.00) = 126.078$.

The calorific value is therefore:

$$\text{calorific value} = \frac{\Delta_{\text{comb}} \text{H}}{\text{molar mass}} = \frac{1231}{126.078} = 9.8 \text{ kJ g}^{-1}$$

Answer: **9.8 kJ g⁻¹**

When methylhydrazine is used as a rocket fuel, the usual oxidant is dinitrogen tetroxide rather than liquid oxygen. Why?

N_2O_4 has a boiling point of 21°C , so there are no problems associated with handling cryogenic liquids. N_2O_4 and methylhydrazine are hypergolic - the reaction occurs spontaneously on contact.

Marks
2

- Estimate the average temperature of Mercury given the solar power density at its surface of $9150 \text{ J m}^{-2} \text{ s}^{-1}$, and assuming an average albedo of 6% and zero Greenhouse effect.

With an albedo of 6%, 94% is *not* reflected. Hence,

$$E_{\text{out}} = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4 \text{ J s}^{-1}$$

$$E_{\text{in}} = \pi r^2 \times 9150 \times 0.94 \text{ J s}^{-1}$$

These balance at a temperature:

$$T = \sqrt[4]{\frac{(\pi r^2) \times (9150) \times (0.94)}{(4\pi r^2) \times (5.67 \times 10^{-8})}} = 441 \text{ K}$$

Answer: **441 K**

3

- The equilibrium constant for the dissolution of silver iodide at 25°C is $1.5 \times 10^{-16} \text{ M}^2$. Calculate the equilibrium concentrations of $\text{Ag}^+(\text{aq})$ and $\text{I}^-(\text{aq})$ if 0.200 mol of $\text{AgI}(\text{s})$ were dispersed in 1.0 L of (a) water, and (b) 0.0050 M aqueous solution of KI.

The solubility equilibrium and constant are:



(a) In water, $[\text{Ag}^+(\text{aq})] = [\text{I}^-(\text{aq})]$. If $[\text{Ag}^+(\text{aq})] = S$:

$$K_{\text{sp}} = S^2 = 1.5 \times 10^{-16} \text{ so } S = [\text{Ag}^+(\text{aq})] = 1.2 \times 10^{-8} \text{ M}$$

(b) In 0.0050 M KI, the $[\text{I}^-(\text{aq})] = 0.0050 \text{ M}$ with only a tiny contribution from AgI because of its low solubility. Hence,

$$K_{\text{sp}} = [\text{Ag}^+(\text{aq})][\text{I}^-(\text{aq})] = [\text{Ag}^+(\text{aq})] \times (0.0050) = 1.5 \times 10^{-16}$$

$$[\text{Ag}^+(\text{aq})] = 3 \times 10^{-14} \text{ M}$$

(a) **$1.2 \times 10^{-8} \text{ M}$**

(b) **$3.0 \times 10^{-14} \text{ M}$**

Marks
4

- A calorimeter containing 300 mL of water at 25 °C was calibrated as follows. A 1000 W heating coil was run for 10 s, after which time the temperature had increased by 7.5 °C. Calculate the heat capacity of the empty calorimeter. The specific heat of water is 4.184 J K⁻¹ g⁻¹.

The heat generated by running a 1000 W coil for 10 s is $(1000 \times 10) = 1 \times 10^4$ J.

The density of water at 25 °C is 0.997 g cm⁻³ so 300 mL has a mass of $(300 \times 0.997) = 299$ g.

As $q = c \times m \times \Delta T$, the heat change of the combined calorimeter and water is:

$$q = (c_{\text{water}} \times m_{\text{water}} \times \Delta T) + (c_{\text{calorimeter}} \times m_{\text{calorimeter}} \times \Delta T)$$

$$= [(4.184 \times 299) + (c_{\text{calorimeter}} \times m_{\text{calorimeter}})] \times 7.5 = 1 \times 10^4$$

Hence,

$$c_{\text{calorimeter}} \times m_{\text{calorimeter}} = 82 \text{ J K}^{-1}$$

Answer: **82 J K⁻¹**

15.0 g of sodium nitrite was dissolved into this calorimeter, and the temperature of the solution was found to decrease by 2.6 °C. Calculate the enthalpy of solution of sodium nitrite.

From above,

$$q = [(c_{\text{water}} \times m_{\text{water}}) + (c_{\text{calorimeter}} \times m_{\text{calorimeter}})] \times \Delta T$$

$$= [(4.184 \times 299) + (82)] \times 2.6 = 3500 \text{ J}$$

The formula mass of NaNO₂ is (22.99 (Na) + 14.01 (N) + 2 × 16.00 (O)) = 69.00.

The number of moles present in 15.0 g is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{15.0}{69.00} = 0.217 \text{ mol}$$

Hence, the enthalpy of solution is:

$$\Delta_{\text{solution}}H = \frac{3500}{0.217} = +16100 \text{ J mol}^{-1} = +16.1 \text{ kJ mol}^{-1}$$

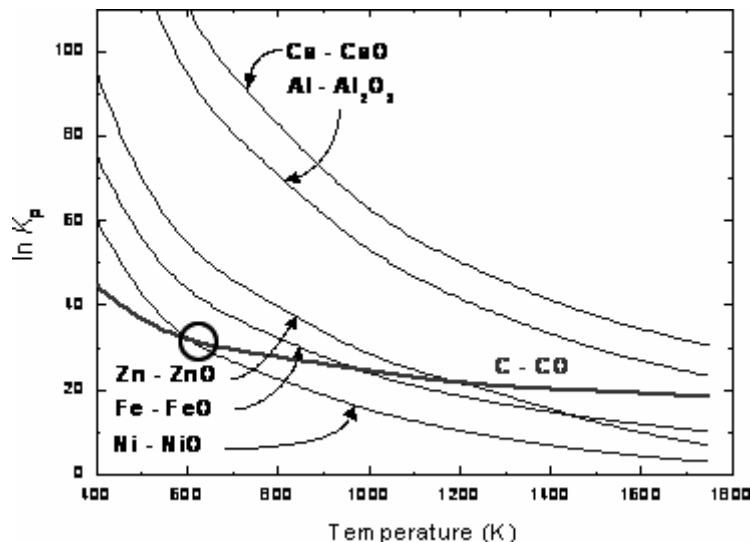
(The reaction leads to a decrease in the temperature of the water and hence it is endothermic.)

Answer: **+16.1 kJ mol⁻¹**

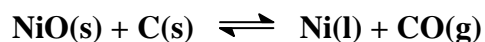
Marks

4

- Use the figure below to help answer the following.



Write a balanced equation for the smelting of NiO by coke. In what temperature range will this process be spontaneous?



The reaction is spontaneous at temperatures where the C-CO line is above the Ni-NiO line.

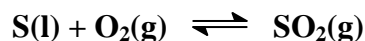
As marked on the diagram, this occurs at temperatures above ~620 K.

Why are (a) aluminium and (b) tungsten not recovered from their oxides by smelting with coke? What alternative processes are used and why?

Tungsten forms tungsten carbide if smelted with coke. The oxide is usually reduced using another reductant such as H₂.

Aluminium is usually recovered electrolytically as smelting only occurs at temperatures well above 1800 K, which are not readily achieved.

- The first step in the production of sulfuric acid is the production of SO₂ by one of three main routes. Give the equation for SO₂ production by sulfur burning.



What is the equilibrium constant for this reaction?

In terms of partial pressures: $K_p = \frac{p_{\text{SO}_2}}{p_{\text{O}_2}}$

In terms of concentrations, $K_c = \frac{[\text{SO}_2(\text{g})]}{[\text{O}_2(\text{g})]}$

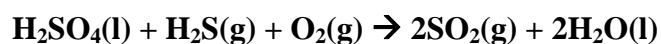
Explain why this is done industrially using compressed air and at high temperatures.

$$\Delta H_f^\circ(\text{SO}_2) = -297 \text{ kJ mol}^{-1}$$

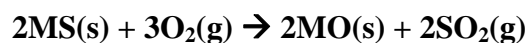
Using a high partial pressure (high concentration) of O₂ drives the reaction to the right.

Although, as the reaction is exothermic, use of a high temperature favours reactants, it is used to increase the reaction rate.

Give the equation for the production of SO₂ by spent acid regeneration using a 1:1 ratio of H₂SO₄ and H₂S.



Give the equation for the roasting of a metal sulphide, MS, in a metallurgical plant.



In the final step, H₂SO₄ is produced by adding SO₃ to concentrated H₂SO₄ to produce "oleum". Why is the reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ not used directly?

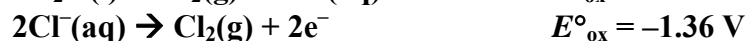
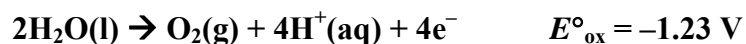
The direct reaction between SO₃ and H₂O is very exothermic. The heat generated causes the water to boil, ceating a mist of sulfuric acid.



Marks
2

- 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. On the basis of reduction potentials, $\text{O}_2(\text{g})$ should be produced at the anode instead of $\text{Cl}_2(\text{g})$. Explain the formation of Cl_2 .

The overpotential for the formation of $\text{O}_2(\text{g})$ is much greater than that for the formation of $\text{Cl}_2(\text{g})$. Hence Cl_2 produced preferentially, despite the E° values of the two oxidations which suggest O_2 should form:



3

- A certain aluminium refinery produces $\text{Al}(\text{s})$ via the Hall-Herault process using ten electrolytic cells in parallel, each operating at a current of 220,000 A. What mass of aluminium (in tonnes) is produced each day?

The total charge passed, $Q = It$. Hence, for ten cells:

$$Q = 10 \times 220000 \times (24 \times 60 \times 60) = 1.90 \times 10^{11} \text{ C}$$

The number of moles of electrons in this charge is:

$$\text{number of moles of electrons} = \frac{Q}{F} = \frac{1.90 \times 10^{11}}{96485} = 1.97 \times 10^6 \text{ mol}$$

As reduction of Al^{3+} requires 3e^- , the number of moles of aluminium produced is $\frac{1}{3} \times 1.97 \times 10^6 = 6.56 \times 10^5 \text{ mol}$.

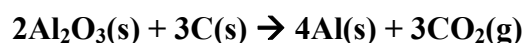
The atomic mass of aluminium is 26.98 so the mass produced is:

$$\text{mass} = \text{number of moles} \times \text{atomic mass} = (6.56 \times 10^5) \times (26.98) = 1.77 \times 10^7 \text{ g} \\ = 17.7 \text{ tonnes}$$

Answer: 17.7 tonnes

Calculate the mass of carbon anodes consumed each day in such a process.

The overall reaction is:



To produce $6.56 \times 10^5 \text{ mol}$ requires $(\frac{3}{4} \times 6.56 \times 10^5) = 4.92 \times 10^5 \text{ mol}$ of C. The atomic mass of carbon is 12.01 so the consumed is:

$$\text{mass} = \text{number of moles} \times \text{atomic mass} = (4.92 \times 10^5) \times (12.01) = 5.91 \times 10^6 \text{ g} \\ = 5.91 \text{ tonnes}$$

Answer: 5.91 tonnes

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

Marks
5

In any spontaneous reaction, the entropy of the universe always increases. The enthalpy of reaction defines the heat released into or absorbed from the surroundings at constant temperature and pressure. The entropy change of the surroundings arises from the heat released.

By definition, $\Delta_{\text{surr}}S = \frac{q_{\text{surr}}}{T}$

As the heat from the reaction is lost to the surroundings, $q_{\text{surr}} = -\Delta_{\text{rxn}}H$ at constant P.

Hence, $\Delta_{\text{surr}}S = \frac{-\Delta_{\text{rxn}}H}{T}$

Formic acid HCOOH, can dimerise in the gas phase according to the reaction



with a standard enthalpy and entropy of dimerisation of $\Delta H^\circ = -62 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -150 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Predict the temperature-dependence of the dimerisation reaction.

$$\Delta_{\text{universe}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S = \Delta_{\text{sys}}S - \frac{\Delta_{\text{rxn}}H}{T}$$

Assuming that ΔS° and ΔH° do not change greatly with temperature, this becomes:

$$\Delta_{\text{universe}}S = (-150) - \frac{(-62 \times 10^3)}{T} = -150 + \frac{(62 \times 10^3)}{T} \text{ J K}^{-1} \text{ mol}^{-1}$$

Dimerization is spontaneous if $\Delta_{\text{universe}}S > 0$. This occurs when $T < \frac{(62 \times 10^3)}{(150)}$.

Hence, dimerization is spontaneous at $T < 413 \text{ K}$ and the reverse process is spontaneous at $T > 413 \text{ K}$. More dimer is formed at low temperature.

Draw a structure that shows the bonding in the dimer.

