

Topics in the November 2013 Exam Paper for CHEM1101

Click on the links for resources on each topic.

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- [Filling Energy Levels in Atoms Larger than Hydrogen](#)

2013-N-3:

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

2013-N-4:

- [Wave Theory of Electrons and Resulting Atomic Energy Levels](#)
- [Atomic Electronic Spectroscopy](#)

2013-N-5:

- [Bonding - MO theory \(larger molecules\)](#)

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- [VSEPR](#)

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- [Nuclear and Radiation Chemistry](#)

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2013-N-14:

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

2013-N-15:

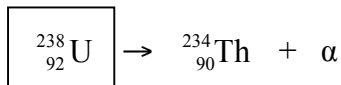
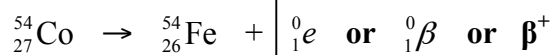
- [Electrochemistry](#)

<ul style="list-style-type: none">Name the element described by the following configuration.	Marks 1
<div><div data-bbox="164 230 336 282">$[\text{Kr}] 5s^2 4d^{10}$</div><div data-bbox="360 226 1318 300">Cadmium</div></div>	
<ul style="list-style-type: none">Write out the valence electron configuration of the following anions and in each case explain why the anion is less stable than the separated atom and electron.	4
<p>Ne⁻</p> <p>$1s^2 2s^2 2p^6 3s^1$</p> <p>Ne has a noble gas configuration. The extra electron needs to go into the 3s orbital which is in the next shell: it is high in energy as the electron is far from the nucleus.</p>	
<p>N⁻</p> <p>$1s^2 2s^2 2p^4$</p> <p>N has all 3 electrons in different <i>p</i> orbitals with parallel spins. Adding an extra electrons forces one of these electrons to become paired which is a higher energy situation.</p>	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks**2**

- Complete the blanks in the following nuclear equations.

**3**

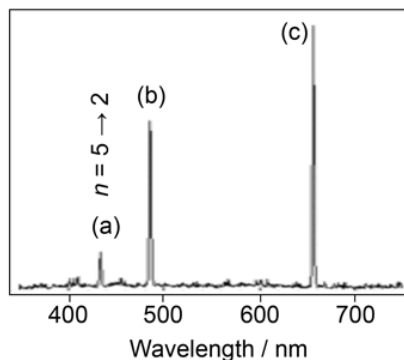
- Explain why the electron on an H atom does not crash into the nucleus.

The negatively charged electron is attracted to the positively charged nucleus. The electron behaves like a standing wave (a matter wave) and as it approaches the nucleus it becomes more confined (or localised) and its wavelength decreases. As shown by the de Broglie equation ($\lambda = h/mv$), as the wavelength of a matter wave decreases, its momentum (and hence kinetic energy) increases. If it were at nucleus, its wavelength would become zero and its position would be known exactly. To do this, it would need to have infinite kinetic energy.

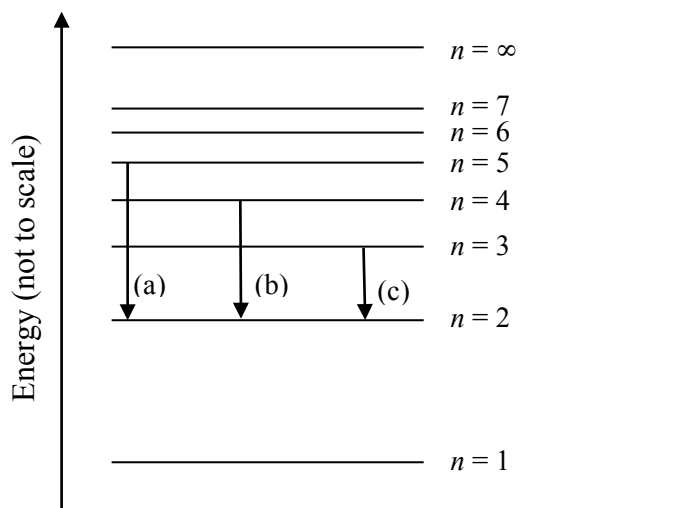
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Marks
4

- The emission spectrum of an H atom in the visible region of the electromagnetic spectrum is shown below, showing three clear transitions, labelled (a), (b) & (c). The quantum numbers associated with one of the transitions is assigned for you.



Complete the energy level diagram below to illustrate the energy levels of an H atom associated with all three transitions



Calculate the wavelength (in nm) of transition (a).

The energy levels of the electron in a H atom vary with the n quantum number according to the Rydberg relationship, $E_n = -Z^2 E_R(1/n^2)$ where $Z = 1$ for hydrogen and $E_R = 2.18 \times 10^{-18}$ J.

Transition (a) corresponds to $n = 5 \rightarrow n = 2$ and its energy is the difference between $E_{n=2}$ and $E_{n=5}$:

$$E_{n=2} = -(1)^2 \times (2.18 \times 10^{-18} \text{ J}) \times (1/2^2) = 5.45 \times 10^{-19} \text{ J}$$

$$E_{n=5} = -(1)^2 \times (2.18 \times 10^{-18} \text{ J}) \times (1/5^2) = 8.72 \times 10^{-20} \text{ J}$$

$$\Delta E = E_{n=2} - E_{n=5} = (5.45 \times 10^{-19} - 8.72 \times 10^{-20}) \text{ J} = 4.58 \times 10^{-19} \text{ J}$$

ANSWER CONTINUES ON THE NEXT PAGE

The wavelength of light is related to the energy through Planck's relationship, $E = hc/\lambda$:

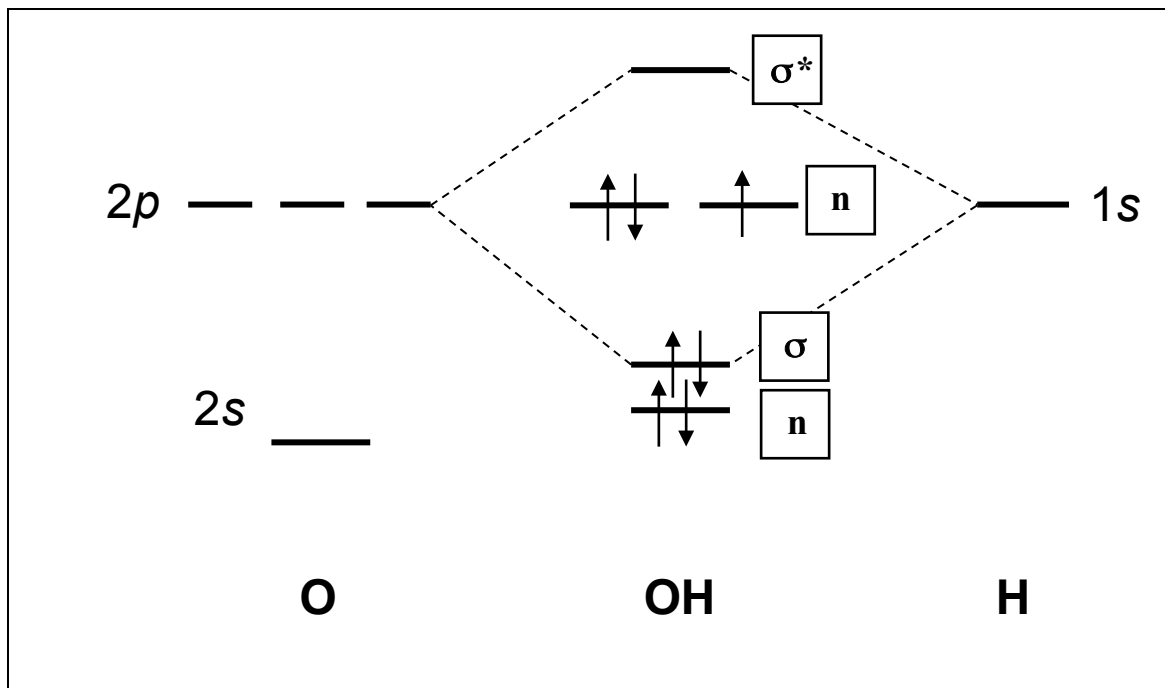
$$4.58 \times 10^{-19} \text{ J} = (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) / \lambda$$

$$\lambda = 4.34 \times 10^{-7} \text{ m} = 434 \text{ nm}.$$

Answer: **434 nm**

- The OH radical is the most important species in the atmosphere for removing pollutants. A molecular orbital diagram of this species is shown below. Core orbitals are omitted.

Marks
8



Using arrows to indicate electrons with their appropriate spin, indicate on the above diagram the ground state occupancy of the atomic orbitals of O and H, and of the molecular orbitals of OH.

In the provided boxes on the above diagram, label the molecular orbitals as n , σ , σ^* , π , π^* , etc.

What is the bond order of the O–H bond?

There are 2 bonding and no anti-bonding electrons. The bond order is 1.

Why do we call OH a “radical”? How does the MO diagram support this?

It has an unpaired electron in a non-bonding orbital. This electron is found in the higher energy n orbital on the above MO diagram

- Complete the following table. The central atom is underlined. Carbon dioxide is given as an example. Where applicable, give all resonance structures and identify the major contributors according to the theory of formal charges.

Marks
5

Molecule	Lewis structure	Shape of molecule	Dipole? (Y/N)
<u>C</u> O ₂	$\text{:}\ddot{\text{O}}=\text{C}=\ddot{\text{O}}\text{:}$	linear	N
<u>P</u> F ₃	$ \begin{array}{c} \text{:}\ddot{\text{F}}-\ddot{\text{P}}-\ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{F}}\text{:} \end{array} $	trigonal pyramidal	Yes
<u>N</u> NO	$ \begin{array}{c} \text{:}\text{N}\equiv\text{N}^{\oplus}-\ddot{\text{O}}^{\ominus}\text{:} \\ \updownarrow \\ \text{:}\ddot{\text{N}}^{\ominus}=\text{N}^{\oplus}=\ddot{\text{O}}\text{:} \end{array} $	linear	Yes

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Marks
5

- The generation of energy in a nuclear reactor is largely based on the fission of either ^{235}U or ^{239}Pu . The fission products include every element from zinc through to the f -block. Explain why most of the radioactive fission products are β -emitters.

The optimal n:p ration increases as Z increases. Splitting a large nucleus in two will almost certainly 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 β emitters.

The radioactivity of spent fuel rods can be modelled by the exponential decay of ^{137}Cs , which has a half-life of 30.23 years. What is the specific activity of ^{137}Cs , in Bq g^{-1} ?

The number of nuclei, N , in 1.00 g of ^{137}Cs is:

number of nuclei = number of moles \times Avogadro's constant

$$N = \left(\frac{1.00}{137} \text{ mol}\right) \times (6.022 \times 10^{23} \text{ nuclei mol}^{-1}) = 4.40 \times 10^{21} \text{ nuclei}$$

The activity (A) is related to N by $A = \lambda N$ where λ is the decay constant. The half life, $t_{1/2}$, is related to the decay constant, λ , by $t_{1/2} = \ln 2 / \lambda$. Hence,

$$\lambda = \ln 2 / (30.23 \times 365 \times 24 \times 60 \times 60 \text{ s}) = 7.271 \times 10^{-10} \text{ s}^{-1}$$



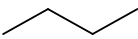
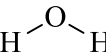
The activity is thus,

$$\begin{aligned} A &= \lambda N = (7.271 \times 10^{-10} \text{ s}^{-1}) \times (4.40 \times 10^{21} \text{ nuclei}) \\ &= 3.19 \times 10^{12} \text{ nuclei s}^{-1} = 3.19 \times 10^{12} \text{ Bq} \end{aligned}$$

Answer: $3.19 \times 10^{12} \text{ Bq g}^{-1}$

- In terms of the type and size of intermolecular forces involved, explain the trend in boiling points of the following compounds.

Marks
4

Substance	Stick structure	Boiling Point (°C)
ethane, C ₂ H ₆		-89
2-methylpropane, C ₄ H ₁₀		-12
butane, C ₄ H ₁₀		-1
water, H ₂ O		100

Water has hydrogen bonds, so has the highest boiling point.

All the others just have dispersion forces, so the number of electrons and the surface area determine the overall magnitude of the dispersion forces.

Ethane is smallest molecule, so has lowest boiling point. Butane is a longer molecule than 2-methylpropane (which has a spherical shape). Butane is better able to entangle with other butane molecules and has larger contact surface area, so its boiling point is greater than that of 2-methylpropane.

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|--|--------------------------|
| <ul style="list-style-type: none">Two samples of iron are prepared so that the heavier has a heat capacity of 50.0 J K^{-1} and the lighter has a heat capacity of 19 J K^{-1}. Initially, the heavier sample is at a temperature of 100.0°C and the lighter sample is at 20.0°C. Calculate the final equilibrium temperature after the two samples have been placed in thermal contact. Show working. | Marks
2 |
|--|--------------------------|

The heat lost by the heavier sample is gained by the lighter sample until they reach the same final temperature, T_f .

For the heavier sample, the heat change is:

$$\begin{aligned} q_{\text{heavier}} &= C_{\text{heavier}} \times \Delta T_{\text{heavier}} \\ &= 50.0 \times (T_f - 100.0) \text{ J} \end{aligned}$$

For the lighter sample, the heat change is:

$$\begin{aligned} q_{\text{lighter}} &= C_{\text{lighter}} \times \Delta T_{\text{lighter}} \\ &= 19 \times (T_f - 20.0) \text{ J} \end{aligned}$$

As $q_{\text{heavier}} = -q_{\text{lighter}}$:

$$\begin{aligned} 50.0 \times (T_f - 100.0^\circ\text{C}) &= -19 \times (T_f - 20.0^\circ\text{C}) \\ 69 T_f &= 5380 \end{aligned}$$

So, $T_f = 78^\circ\text{C}$.

Answer: 78°C
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- Paraffin wax candles primarily consist of long, saturated, hydrocarbon chains such as triacontane ($C_{30}H_{62}$). Assuming a 1.00 kg candle is made of pure triacontane, how many moles of triacontane will it contain?

Marks
6

The molar mass of $C_{30}H_{62}$ is $(30 \times 12.01 \text{ (C)} + 62 \times 1.008 \text{ (H)}) \text{ g mol}^{-1} = 422.80 \text{ g mol}^{-1}$. The number of moles in 1.00 kg is therefore:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} \\ &= 1.00 \times 10^3 \text{ g} / 422.80 \text{ g mol}^{-1} = 2.37 \text{ mol} \end{aligned}$$

Answer: **2.37 mol**

Estimate the atomisation enthalpy, $\Delta_{\text{atom}}H$, for triacontane, based on the following tabulated average bond enthalpies.

bond	$\Delta H / \text{kJ mol}^{-1}$	bond	$\Delta H / \text{kJ mol}^{-1}$
C–C	346	C–H	414
C–O	358	O–H	463
C=O	804	O=O	498

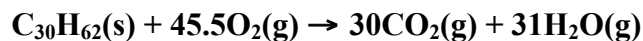
We are told that $C_{30}H_{62}$ is a long, saturated hydrocarbon: it contains a chain of C–C bonds with no branches or double bonds.

As there are 30 C atoms in the chain, there must be 29 C–C bonds. If there are 62 H in the molecule, there must be 62 C–H bonds.

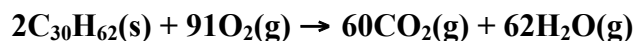
$$\begin{aligned} \Delta_{\text{atom}}H &= 29 \times \Delta H (\text{C–C}) + 62 \times \Delta H (\text{C–H}) \\ &= (29 \times 346 + 62 \times 414) \text{ kJ mol}^{-1} = 3.57 \times 10^4 \text{ kJ mol}^{-1} \end{aligned}$$

Answer: **$3.57 \times 10^4 \text{ kJ mol}^{-1}$**

Write out a chemical equation for the complete combustion of triacontane.



or



ANSWER CONTINUES ON THE NEXT PAGE

Using the same table of average bond enthalpies, estimate the atomisation enthalpy of each product of the complete combustion.

CO₂ contains 2 C=O bonds:

$$\Delta_{\text{atom}}H = 2 \times \Delta H (\text{C=O}) = 2 \times 804 \text{ kJ mol}^{-1} = 1608 \text{ kJ mol}^{-1}$$

H₂O contains 2 O-H bonds:

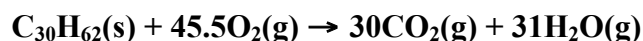
$$\Delta_{\text{atom}}H = 2 \times \Delta H (\text{O-H}) = 2 \times 463 \text{ kJ mol}^{-1} = 926 \text{ kJ mol}^{-1}$$

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Estimate the molar enthalpy of combustion of triacontane, $\Delta_c H$.

Marks
4

The balanced equation for the combustion is:



The reaction involves (i) atomising $\text{C}_{30}\text{H}_{62}(\text{s})$ and $45.5\text{O}_2(\text{g})$ and (ii) forming 30CO_2 and $31\text{H}_2\text{O}$ from the atoms. Hence:

$$\begin{aligned}\Delta_c H &= \Delta_{\text{atom}} H (\text{C}_{30}\text{H}_{62}) + 45.5 \Delta_{\text{atom}} H (\text{O}_2) \\ &\quad - 30 \Delta_{\text{atom}} H (\text{CO}_2) - 31 \Delta_{\text{atom}} H (\text{H}_2\text{O}) \\ &= ((3.57 \times 10^4) + 45.5 \times (498) \\ &\quad - 30 \times (1608) - 31 \times (926)) \text{ kJ mol}^{-1} \\ &= -1.86 \times 10^4 \text{ kJ mol}^{-1}\end{aligned}$$

Answer: $-1.86 \times 10^4 \text{ kJ mol}^{-1}$

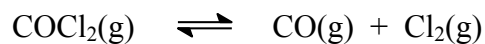
Using this enthalpy of combustion, calculate the energy released by the combustion of the candle.

As $1.86 \times 10^4 \text{ kJ}$ is released per mol, 2.37 mol will release:

$$\Delta H = (1.86 \times 10^4 \text{ kJ mol}^{-1}) \times (2.37 \text{ mol}) = 4.40 \times 10^4 \text{ kJ}$$

Answer: $4.40 \times 10^4 \text{ kJ}$

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



What is the expression for the equilibrium constant, K_p , for this reaction?

$$K_p = \frac{p(\text{Cl}_2)p(\text{CO})}{p(\text{COCl}_2)}$$

Calculate the value of the equilibrium constant at 298 K.

As $\Delta G^\circ = -RT \ln K$,

$$69.73 \times 10^3 = -(8.314 \times 298) \times \ln K$$

$$K = 5.98 \times 10^{-13}$$

$$K_p = 5.98 \times 10^{-13}$$

In which direction will this reaction proceed if a mixture of gases is made with:
 $P_{\text{COCl}_2} = 1.00 \text{ atm}$; $P_{\text{Cl}_2} = 0.01 \text{ atm}$; $P_{\text{CO}} = 0.50 \text{ atm}$? Show working.

The reaction quotient, Q_p , is:

$$Q_p = \frac{p(\text{Cl}_2)p(\text{CO})}{p(\text{COCl}_2)} = \frac{(0.01)(0.50)}{(1.00)} = 0.005$$

As $Q_p > K_p$, the reaction proceeds to decrease Q_p . It moves to reduce the amount of produce and increase the amount of reactant: it shifts to the left (towards reactants).

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
5

This reaction mixture is now allowed to come to equilibrium at 298 K in a fixed volume container. Calculate the equilibrium pressure of Cl_2 .

Marks
4

As shown in 2013-N-12, the reaction will shift towards reactants to reach equilibrium. The equilibrium constant for the forward reaction is *very* small: $K = 5.98 \times 10^{-13}$. With $P_{\text{Cl}_2} = 0.01$ atm initially, it is easiest to assume that (i) *all* of the Cl_2 reacts and (ii) a little of the COCl_2 then reacts to reach equilibrium.

(i) All of the Cl_2 reacts with CO to make COCl_2 :

$$P_{\text{COCl}_2} = (1.00 + 0.01) \text{ atm} = 1.01 \text{ atm}$$

$$P_{\text{Cl}_2} = (0.01 - 0.01) \text{ atm} = 0.00 \text{ atm}$$

$$P_{\text{CO}} = (0.50 - 0.01) \text{ atm} = 0.49 \text{ atm}$$

(iii) This reaction will then shift to equilibrium:

	$\text{COCl}_2(\text{g})$	\rightleftharpoons	$\text{CO}(\text{g}) +$	$\text{Cl}_2(\text{g})$
initial	1.01		0.49	0.00
change	-x		+x	+x
equilibrium	$1.01 - x$		$0.49 + x$	x

$$K_p = \frac{p(\text{Cl}_2)p(\text{CO})}{p(\text{COCl}_2)} = \frac{x(0.49 + x)}{(1.01 - x)}$$

As the equilibrium constant is so small, x will be tiny. In this case, $0.49 + x \sim 0.49$ and $1.01 - x \sim 1.01$. Hence:

$$K_p \sim \frac{x(0.49)}{(1.01)} = 5.98 \times 10^{-13}$$

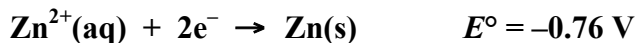
$$x = 5.98 \times 10^{-13} \times \frac{1.01}{0.49} = 1.23 \times 10^{-12}$$

Answer: 1.23×10^{-12}

Marks
2

- Both magnesium oxide and zinc oxide can be reduced to their respective metals by carbon at temperatures of over 1200 K. Which oxide requires the higher temperature for reaction? Give reasons for your answer.

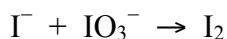
Mg is much more electropositive than Zn, so MgO is more ionic in character than ZnO. As the electrons in Mg are more readily given up than those of Zn, the K_p of formation for MgO will be higher than that of ZnO. This can be confirmed from the table of electrode reduction potentials on the data page:



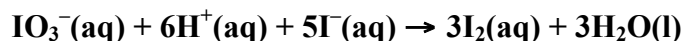
Conversely, it should require less energy (and hence lower temperature) to convert ZnO into Zn and $\text{O}_2(\text{g})$

3

- Balance the following redox reaction, which is carried out in an acidic solution.



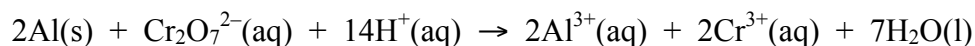
Working



- The unbalanced has I^{-} being oxidised to I_2 . This involves 1 e^{-} as the oxidation number is changing from -1 in I^{-} to 0 in I_2 .
- The unbalanced equation has IO_3^{-} being reduced to I_2 . This involves 5 e^{-} as the oxidation number is changing from +5 in IO_3^{-} to 0 in I_2 .
- To balance the oxidation and reduction processes, 5I^{-} are therefore required.
- This gives a total charge of -6 on the left hand side (from IO_3^{-} and 5I^{-}) and no charged species on the right hand side.
- To balance the charges, 6H^{+} are added to the left hand side. Note that the solution is acidic so there are H^{+} in the solution.
- Lastly, there are now 6H and 3O on the left hand side so $3\text{H}_2\text{O}$ is added to the right hand side to ensure atom balance.

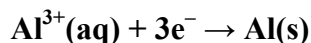
Marks
7

- The following redox reaction occurs in a voltaic cell:

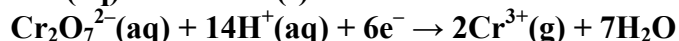


Calculate the standard cell potential, E°_{cell} , for the cell at 25 °C.

From the standard reduction potentials table:



$$E^\circ_{\text{red}} = -1.68 \text{ V}$$



$$E^\circ_{\text{red}} = +1.36 \text{ V}$$

In the reaction, the $\text{Al}^{3+} / \text{Al}$ half cell is reversed and is acting as the oxidation half cell with $E^\circ_{\text{ox}} = +1.68 \text{ V}$. Hence:

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = (+1.68 \text{ V}) + (1.36 \text{ V}) = +3.04 \text{ V}$$

Answer: **+3.04 V**

Calculate the cell potential, E_{cell} , at 25 °C when $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})] = 7.2 \times 10^{-5} \text{ M}$, $[\text{Al}^{3+}(\text{aq})] = 0.55 \text{ M}$, $[\text{Cr}^{3+}(\text{aq})] = 0.75 \text{ M}$ and the pH is 2.35.

As $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$, when $\text{pH} = 2.35$, $[\text{H}^+(\text{aq})] = 10^{-2.35}$.

The reaction involves transfer of 6 e⁻: $n = 6$. Using the Nernst equation for this reaction:

$$\begin{aligned} E_{\text{cell}} &= E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Al}^{3+}(\text{aq})]^2 [\text{Cr}^{3+}(\text{aq})]^2}{[\text{Cr}_2\text{O}_7^{2-}(\text{aq})] [\text{H}^+(\text{aq})]^{14}} \\ &= (+3.04) - \frac{(8.314)(298 \text{ K})}{(6)(96485)} \ln \frac{(0.55)^2 (0.75)^2}{(7.2 \times 10^{-5})(10^{-2.35})^{14}} = +2.68 \text{ V} \end{aligned}$$

Answer: **+2.68 V**

What is the effect on the E_{cell} of decreasing the concentration of $\text{Cr}_2\text{O}_7^{2-}$ in the cathode compartment?

From the Nernst equation, decreasing $[\text{Cr}_2\text{O}_7^{2-}]$ will increase Q and decrease E_{cell} . In the concentration of this reactant is decreased, the reaction will shift slightly towards reactants and E_{cell} will decrease.

What is the effect on the E_{cell} of adding a 0.35 M solution of $\text{Al}(\text{NO}_3)_3$ to the anode compartment?

Adding a 0.35 M solution of Al^{3+} to a 0.55 M solution of Al^{3+} will increase the number of moles of Al^{3+} but *decrease* the concentration. It is a dilution.

This will reduce Q and increase E_{cell} . In the concentration of this product is decreased, the reaction will shift slightly towards products and E_{cell} will increase.