Topics in the June 2013 Exam Paper for CHEM1101

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2013-J-2:

- Ionic Bonding

2013-J-3:

- Types of Intermolecular Forces
- First and Second Law of Thermodynamics

2013-J-4:

- Filling Energy Levels in Atoms Larger than Hydrogen
- Nuclear and Radiation Chemistry

2013-J-5:

- Periodic Table and the Periodic Trends
- Wave Theory of Electrons and Resulting Atomic Energy Levels

2013-J-6:

- Bonding - MO theory (larger molecules)

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- Lewis Structures
- VSEPR

2013-J-8:

- Thermochemistry
- Nitrogen Chemistry and Compounds
- Nitrogen in the Atmosphere

2013-J-9:

- Chemical Equilibrium

2013-J-10:

- First and Second Law of Thermodynamics
- Gas Laws
- Nitrogen Chemistry and Compounds

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- Equilibrium and Thermochemistry in Industrial Processes

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- Electrolytic Cells
- Electrochemistry
- Batteries and Corrosion

2013-J-13:

- Electrochemistry
- Batteries and Corrosion

Marks
6

- What is an ionic bond?

An ionic bond is the electrostatic attraction between a cation and an anion.

Why does ionic bonding favour the formation of macroscopic crystals rather than molecules?

Electrostatic attractions are long range and isotropic. Stronger interactions can be built up by packing as many anions around each cation (and vice versa) as will fit. This leads to large crystals which are lower in energy and hence favoured over small molecules.

What information do you need to estimate the relative lattice energies of two chemically different salts?

The relative lattice energy depends on:

- **the charges on the anions and cations, requiring information on the identity of the cation and anion and their charges,**
- **the size of the cations and anions, requiring information on their ionic radii, and**
- **the Madelung constant, requiring information on the coordination numbers and the crystal structure type.**

	Marks
• Intermolecular forces are responsible for the physical properties of many compounds. What are dispersion forces?	3
Transient unsymmetrical electron distribution around an atom results in an instantaneous dipole that causes an induced dipole in an adjacent molecule. Dispersion forces are the attractions between the instantaneous dipoles and the induced dipoles.	
The boiling points of F_2, Cl_2 and Br_2 are 85, 239 and 338 K, respectively. Where would you expect the boiling point of I_2? Give reasons.	
All the molecules are non-polar, so dispersion forces are the only ones relevant. Iodine is the biggest atom with the most electrons and hence its electron cloud is the most polarisable. I_2 therefore has the strongest dispersion forces and the highest boiling point. Its boiling point will be higher than 338 K.	
• The Second Law states that all observable processes must involve a net increase in entropy. When liquid water freezes into ice at 0 °C, the entropy of the water decreases. Explain how this is consistent with the Second Law.	2
The freezing of water is exothermic and the heat evolved is passed to the surroundings. This causes an *increase* in the entropy of the surroudings with $\Delta_{surrounding}S = \Delta q/T$ where Δq is the heat passed to the surroundings from the freezing of the water. **At low temperatures (below 0 °C), the increase in the entropy of the surroundings is larger than the reduction in entropy of the water itself. There is a net increase in entropy of the universe (system + surroundings) therefore increases, consistent with the Second Law.** **Above 0 °C, $\Delta_{surrounding}S = \Delta q/T$ is smaller and not enough to overcome the decrease in the entropy of the freezing water.**	

Marks

- Write down the ground state electron configurations for the following species. Na is given as an example. **4**

Na	[Ne] $3s^1$
K	**[Ar] $4s^1$**
As	**[Ar] $4s^2\ 3d^{10}\ 4p^3$**
Sr	**[Kr] $5s^2$**
C^+	**[He] $2s^2\ 2p^1$**

Name the elements described by the following configurations.

[Kr] $5s^2\ 4d^6$	**ruthenium**
[Xe] $6s^2\ 5d^1\ 4f^{11}$	**erbium**

- Radioactivity may have damaging effects on humans but can also be used for medical imaging to potentially save lives. Which of alpha and gamma radiation is better suited for medical imaging? Give reasons. **4**

Gamma radiation is more useful as it is more penetrating (so can be detected by detector placed outside the body) and is less damaging to human tissue than alpha radiation. As alpha radiation is charged, it leads ionisation and causes more damage and is less penetrating.

Given nuclides with half-lives of minutes, hours or years, which would be best used for medical imaging? Explain.

Nuclides with half-lives of hours are best suited. This allows time for production of nuclide, administration to patient, and for it to accumulate in the tissue of interest. Activity is high enough to give good quality image with small amount of nuclide. A long half-life means a lower activity and hence more nuclide needs to be used to generate a quality image.

Marks
5

- The Periodic Table as arranged by Mendeleev allows us to make predictions about the behaviours of elements based on those around them. Briefly describe why the Periodic Table works.

The Periodic Table groups atoms into:

- **Groups (columns) based on the number of valence electrons they have, and**
- **Periods (rows) based on the shell and sub-shell.**

Chemical reactivity is based on the number of valence electrons and the size of the element. Elements in the same group have similar chemical properties as they have the same number of valence electrons. Differences in the reactivity of elements in the same group are due to their size – elements get larger down each group leading to decreased electronegativity.

Silicon and tin have the same structure as diamond. Use the information in the following table to predict the density of tin.

Element	Atomic Mass	Density (g cm^{-3})	Bond length (pm)
Si	28	2.329	233
Sn	118		280

Density depends on the mass and the volume:

density = mass / volume

The volume of a crystal will increase as the cube of the bond length:

volume of tin = $(280 / 233)^3$ × volume of silicon

The mass will increase as the atomic mass increases:

mass of tin = (118 / 28) × mass of silicon

As the density of silicon is 2.329 g cm^{-3}, the density of tin will therefore be:

density of tin = density of silicon × (118 / 28) / $(280 / 233)^3$
= 2.329 g cm^{-3} × (118 / 28) / $(280 / 233)^3$ = 5.7 g cm^{-3}

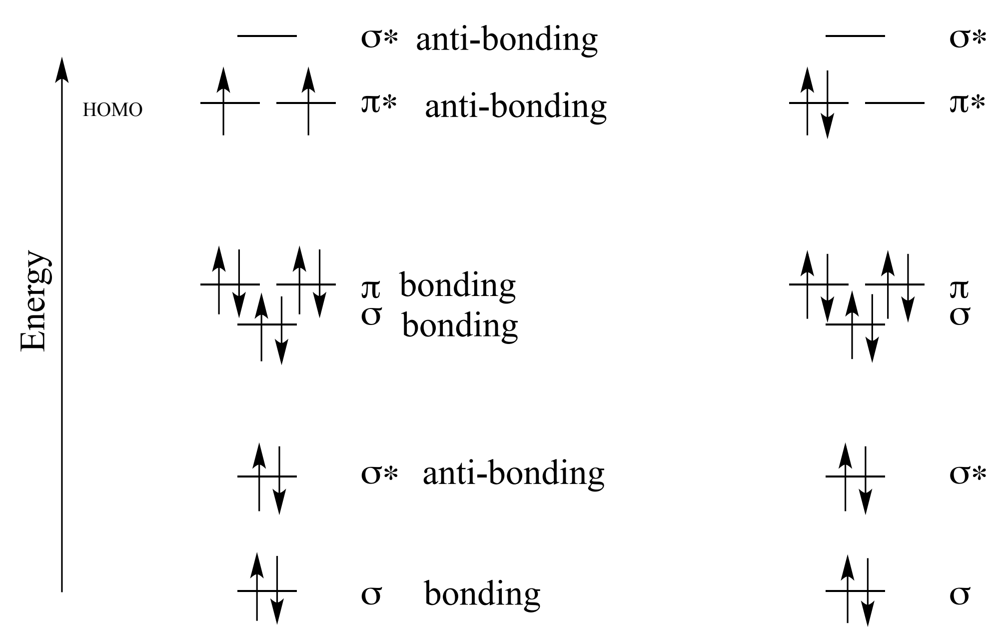
Answer: **5.7 g cm^{-3}**

Marks
8

- Oxygen exists in the troposphere as a diatomic molecule.

  How many valence electrons in the O_2 molecule? **12**

  The molecular orbital energy levels for O_2 are shown below. On the left-hand diagram, fill in the **valence** electrons for oxygen, O_2, in the ground state.



(a) What is the bond order for O_2? **½ (8 – 4) = 2**

(b) Clearly label a bonding orbital and an anti-bonding orbital on the left-hand diagram.

(c) Clearly label the HOMO of O_2 on the left-hand diagram.

(d) On the right-hand diagram, indicate the lowest energy electronic configuration for O_2 which has no unpaired electrons.

The blue colour of liquid O_2 arises from an electronic transition whereby one 635 nm photon excites two molecules to the state indicated by the configuration in (d) *at the same time*. What wavelength photon would be emitted by one molecule returning from this state to the ground state?

If one 635 nm photon excites two molecules, then half as much energy is will be emitted when one molecule returns to the ground state.

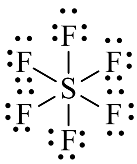
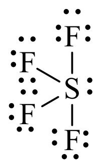
As $E = hc / \lambda$, if the energy is *halved*, the wavelength *doubles*: λ = 1270 nm.

Answer: **1270 nm**

Suggest a heteronuclear diatomic species, isoelectronic with O_2, that might be expected to have similar spectroscopic behaviour. **NO^-, NF**

Marks 6

- Complete the following table for the molecules SF_6 and SF_4.

Molecule	Total number of valence electrons	Lewis structure	Shape of molecule
SF_6	**48**		**octahedral**
SF_4	**34**		**"see saw"**

Sulfur hexafluoride (SF_6) is quite inert, whilst sulfur tetrafluoride (SF_4) is highly reactive. Suggest a reason for the difference in reactivity between SF_6 and SF_4.

There is a lone pair of electrons on the S that can participate in reactions for SF_4, but not for SF_6.

Marks

- 1.00 L of water is heated to 95 ^{o}C and then solid copper, initially at 25 ^{o}C, is immersed in it. What mass of copper was added if the final temperature of the water was 84 ^{o}C? Show all working. 3

Data: Specific heat capacity of Cu(s) is 0.39 J g^{-1} K^{-1}.
Specific heat capacity of H_2O(l) is 4.184 J g^{-1} K^{-1}.
The density of water is 1.0 g mL^{-1}.

1.00 L of water corresponds to 1.00 × 10^3 g. When this quantity cools from 95 ^{o}C to 84 ^{o}C, the heat change is:

$$q_{\text{water}} = mC\Delta T = (1.00 \times 10^3 \text{ g}) \times (4.184 \text{ J g}^{-1} \text{ K}^{-1}) \times ((84 - 95) \text{ K}) = -46 \times 10^3 \text{ J}$$

If the mass of copper used is *x* g, the heat change when it warms from 25 ^{o}C to 84 ^{o}C is:

$$q_{\text{copper}} = mC\Delta T = (x) \times (0.39 \text{ J g}^{-1} \text{ K}^{-1}) \times ((84 - 25) \text{ K}) = +23x \text{ J}$$

The heat lost by the water is gained by the copper so these two quantities must be equal in magnitude:

$$23x = 46 \times 10^3 \qquad \text{so } x = 2.0 \text{ kg}$$

Answer: **2.0 kg**

- Atmospheric nitrogen is converted into ammonia or various oxides by both natural processes and those associated with human activity. Identify one process (either natural or due to human activity) that results in the conversion of N_2 to either NH_3 or an oxide of nitrogen and identify the nitrogen compound produced in that process. 2

Natural processes:

- **Nitrogen fixing bacteria in plants (legumes) and blue-green algae produces NH_3.**
- **Lightning (high temperatures) causes the reaction of N_2 with O_2 to produce NO(g).**

Human activity:

- **Haber process produces NH_3(g) from N_2(g) and H_2(g).**
- **Reaction of N_2 with O_2 in internal combustion engines produces NO(g).**

Marks 4

- Consider the following reaction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

An equilibrium mixture in a 1.00 L container is found to contain $[N_2O_4]$ = 1.00 M and $[NO_2]$ = 0.46 M. The vessel is then compressed to half its original volume while the temperature is kept constant. Calculate the concentration $[N_2O_4]$ when the compressed system has come to equilibrium. Show all working.

For this reaction, the equilibrium constant expression is given by:

$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4]}$$

As mixture is at equilibrium when $[N_2O_4]$ = 1.00 M and $[NO_2]$ = 0.46 M:

$$K_c = \frac{(0.46)^2}{(1.00)} = 0.21$$

If the volume of the vessel is halved, the initial concentrations will *double*: $[N_2O_4]$ = 2.00 M and $[NO_2]$ = 0.92 M. The reaction is no longer at equilibrium and Le Chatelier's principle predicts it will shift towards the side with fewer moles: it will shift towards reactants.

A reaction table needs to be used to calculate the new equilibrium concentrations.

	$N_2O_4(g)$		$2NO_2(g)$
initial	**2.00**	$\rightleftharpoons$	**0.92**
change	$+x$		$-2x$
equilibrium	$2.00 + x$		$0.92 - 2x$

Hence,

$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4]} = \frac{(0.92-2x)^2}{(2.00+x)} = 0.21$$

So,

$$(0.92 - 2x)^2 = 0.21\ (2.00 + x)$$

$$0.8464 - 3.68x + 4x^2 = 0.42 + 0.21x$$

$$4x^2 - 3.89x + 0.43 = 0$$

ANSWER CONTINUES ON THE NEXT PAGE

With a = 4, b = -3.89 and c = 0.43, this quadratic equation has roots:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{3.89 \pm \sqrt{(-3.89)^2 - 4 \times 4 \times 0.43}}{2 \times 4}$$

This gives x = 0.13 or 0.85. The latter makes no chemical sense as it gives a negative concentration for NO_2.

Hence using x = 0.13:

$[N_2O_4] = (2.00 + x)$ M = (2.00 + 0.13) M = 2.13 M

$[NO_2] = (0.92 - 2x)$ M = (0.92 – 2 × 0.13) M = 0.66 M

Answer: **$[N_2O_4]$ = 2.13 M**

Marks

- Use the standard heats of formation provided to calculate the molar heat of combustion of liquid methanol, CH_3OH, in oxygen to produce CO_2 and water. Your answer must include a balanced chemical equation for this reaction. Show all working. **2**

Data:

Compound	$H_2O(l)$	$CH_3OH(l)$	$CO_2(g)$
$\Delta_f H^o$ / kJ mol^{-1}	–285.9	–238.6	–393.5

The chemical equation for the combustion of methanol is:

$$CH_3OH(l) + 3/2\ O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Using $\Delta_{rxn}H° = \Sigma m\Delta_f H°$(products) - $\Sigma n\Delta_f H°$(reactants), the enthalpy of this reaction is:

$$\Delta H° = (\Delta_f H°(CO_2(g) + 2\Delta_f H°(H_2O(l)) - (\Delta_f H°(CH_3OH(l)) + 3/2\ \Delta_f H°(O_2(g))$$
$$= [(-393.5 + 2 \times -285.9) – (-238.6 + 0)] \text{ kJ mol}^{-1} = -726.7 \text{ kJ mol}^{-1}$$

where $\Delta_f H°(O_2(g))$ is zero for an element in its standard state.

Answer: **-726.7 kJ mol^{-1}**

- Calculate the volume change when 10.0 g of solid trinitrotoluene $C_7H_5N_3O_6(s)$ explosively decomposes via the following process at 2000. °C and 1.0 atm. **3**

$$2C_7H_5N_3O_6(s) \rightarrow 12CO(g) + 5H_2(g) + 3N_2(g) + 2C(s)$$

Assume all gases behave as ideal gases and neglect the volume of any solid phases. Show all working.

The molar mass of $C_7H_5N_3O_6$ is:

$$\text{molar mass} = (7 \times 12.01 (C) + 5 \times 1.008 (H) + 3 \times 14.01 (N) + 6 \times 16.00 (O)) \text{ g mol}^{-1}$$
$$= 227.14 \text{ g mol}^{-1}$$

The number of moles in 10.0 g is therefore:

$$\text{number of moles} = \text{mass / molar mass} = 10.0 \text{ g} / 227.14 \text{ g mol}^{-1} = 0.0440 \text{ mol}$$

The chemical reaction, when 2 mol of $C_7H_5N_3O_6$ decomposes, 12 mol of CO(g), 5 mol of H_2(g) and 3 mol of N_2(g) are produced. When 0.0440 mol decomposes,

$$\text{moles of gas} = 0.0440 \times (12 / 2 (CO) + 5/2 (H_2) + 3/2 (N_2)) \text{ mol} = 0.44 \text{ mol}$$

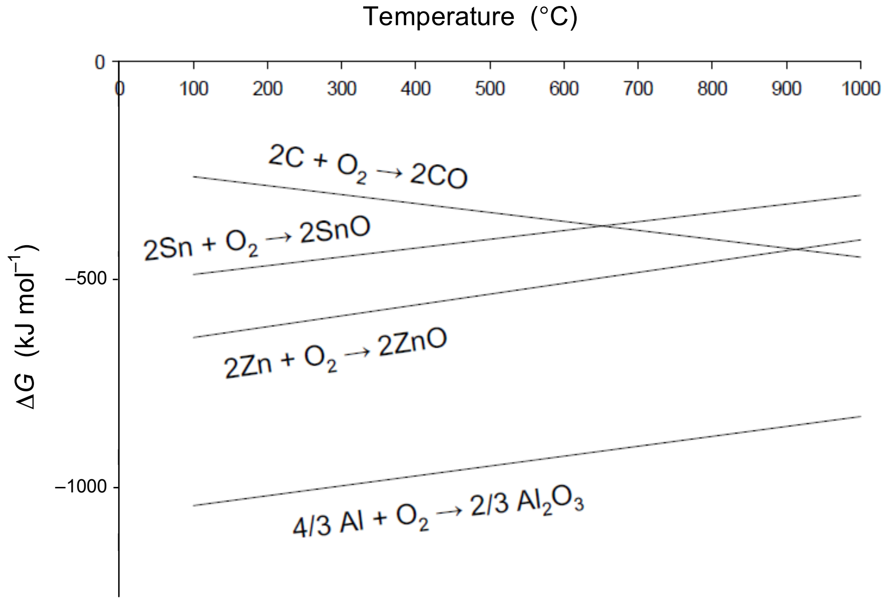
Using $PV = nRT$, the volume of this amount at 2000. °C (2273 K) and 1.0 atm is:

$$V = nRT / P$$
$$= (0.44 \text{ mol} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 2273 \text{ K}) / (1.0 \text{ atm}) = 82 \text{ L}$$

Answer: **82 L**

Marks
4

- The diagram below represents the Gibbs free energy change associated with the formation of four different oxides.



Using the free energy data above, write down the equation and indicate with an arrow the direction of the expected spontaneous reaction under the following conditions. If no reaction occurs, write "no reaction".

CO and Sn are mixed at 400 °C **At 400 ^{o}C, the Sn / SnO line is below the C / CO line:** **$Sn(s) + CO(g) \rightarrow SnO(s) + C(s)$**
Al and ZnO are mixed at 400 °C **At 400 ^{o}C, the Al / Al_2O_3 line is below the Zn / ZnO line:** **$2Al(s) + 3ZnO(g) \rightarrow Al_2O_3(s) + 3Zn(s)$**
CO and Sn are mixed at 900 °C **At 900 ^{o}C, the Sn / SnO line is above the C / CO line:** **No reaction**

ANSWER CONTINUES ON THE NEXT PAGE

Which oxide has the smallest (least negative) enthalpy of formation?

As $\Delta G = \Delta H - T\Delta S$, the enthalpy is $\Delta H = \Delta G + \mathrm{T}\Delta S$.

The smallest (least negative) value of ΔG is for $C(s) + O_2(g) \rightarrow 2CO(g)$.

This reaction involves an increase in the number of moles of gas so ΔS will be positive. As $\Delta H = \Delta G + \mathrm{T}\Delta S$, this means that $\Delta H > \Delta G$.

For the other reactions, there is a decrease in the number of moles of has so ΔS is negative. $\Delta H = \Delta G + \mathrm{T}\Delta S$, this means that $\Delta H < \Delta G$.

Hence, the smallest (least negative) value of ΔH must be for the formation of CO.

Marks

- How many hours does it take to form 10.0 L of O_2 measured at 99.8 kPa and 28 °C from water if a current of 1.3 A passes through the electrolysis cell? **3**

10.0 L corresponds to 0.0100 m^3. Using *PV* = *nRT*, this corresponds to:

$$n = PV / RT$$
$$= (99.8 \times 10^3 \text{ Pa}) \times (0.0100 \text{ m}^3) / (8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}) \times ((28 + 273) \text{ K})$$
$$= 0.399 \text{ mol}$$

O_2(g) is formed by electrolysis of water according to the reaction:

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

Hence, 4 × 0.399 mol = 1.60 mol of electrons are required. As the number of moles of electrons passed by a current *I* in a time *t* is:

number of moles of electrons = *It* / *F*

$$1.60 \text{ mol} = (1.3 \text{ A})t / (96485 \text{ C mol}^{-1})$$

$$t = 1.2 \times 10^5 \text{ s} = (1.2 \times 10^5 / 3600) \text{ hours} = 33 \text{ hours}$$

Answer: **33 hours**

- In concentration cells no net chemical conversion occurs, however a measurable voltage is present between the two half-cells. Explain how the voltage is produced. **2**

In concentration cells, the same solution and electrode are present in both half cells but with different concentrations. For example, both half cells could contain a copper electrode in a copper(II) sulfate solution but these solutions have different concentrations. In order to equalise the concentrations:

- **In the cell with the lower concentration, oxidation occurs to increase the concentration of the Cu^{2+}(aq) in solution,**
- **In the other cell, reduction occurs to decrease the concentration of ions in solution.**

This requires the transfer of electrons between the two half-cells occurs to try and equalise the concentrations in each half-cell and hence to maximise the entropy.

- Is H_2 a stronger reducing agent under acidic or basic conditions? Give reasons for your answer. **2**

When H_2 acts as a reducing agent, it is itself oxidised:

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

Under acidic conditions, this equilibrium will be pushed to the left due to Le Chatelier's principle. Similarly, it will be pulled to the right under basic conditions as the H^+ ions produced will react with the OH^- ions. Therefore H_2 is a better reducing agent under basic conditions.

Marks 7

- A galvanic cell utilises the following redox reaction.

$$NH_4^+(aq) + 8Ce^{4+}(aq) + 3H_2O(l) \rightarrow NO_3^-(aq) + 8Ce^{3+}(aq) + 10H^+(aq)$$

What species is the reducing agent in this reaction?	**$NH_4^+(aq)$**
How many electrons are transferred in the redox reaction?	**8**

Calculate the standard cell potential, $E°_{cell}$, for this electrochemical cell.

From the reduction potential table,

$\boldsymbol{E_{cell}^o}$ **($NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow NH_4^+(aq) + 3H_2O$) = +0.88 V**

$\boldsymbol{E_{cell}^o}$ **($Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$) = +1.72 V**

The former is reversed and becomes the oxidation half cell:

$\boldsymbol{E_{cell}^o = (-0.88 + 1.72)\ \text{V} = 0.84\ \text{V}}$

Answer: **+0.84 V**

Calculate $\Delta G°$ for the redox reaction at 25 °C.

Using $\Delta G° = -nFE^o$

$\boldsymbol{\Delta G° = -(8) \times (96485\ \text{C mol}^{-1}) \times (0.84\ \text{V}) = -650\ \text{kJ mol}^{-1}}$

Answer: **-650 kJ mol^{-1}**

What is the effect on the E_{cell} of decreasing the concentration of $NO_3^-(aq)$ in the anode compartment?

If [$NO_3^-(aq)$] is reduced, the reaction will shift to increase it (Le Chatelier's reaction). The reaction will shift towards products and E_{cell} will increase.

Calculate the cell potential, E_{cell}, when $[NH_4^+] = 0.35$ M, $[Ce^{4+}] = 0.25$ M, $[NO_3^-] = 5.0 \times 10^{-2}$ M, $[Ce^{3+}] = 6.0 \times 10^{-2}$ M, and the pH is 2.0.

As pH = -log[$H^+(aq)$], a pH of 2.0 corresponds to [$H^+(aq)$] = $10^{-2.0}$ M. Using the Nernst equation,

$$E_{cell} = E° - \frac{RT}{nF}\ln Q$$

$$= E° - \frac{RT}{nF}\ln\frac{[NO_3^-(aq)][Ce^{3+}(aq)]^8[H^+(aq)]^{10}}{[NH_4^+(aq)][Ce^{4+}(aq)]^8}$$

$$= (0.84\ \text{V}) - \frac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ K)}{8(96485\ \text{C mol}^{-1})}\ln\frac{(5.0\times10^{-2})(6.0\times10^{-2})^8(10^{-2.0})}{(0.35)(0.25)^8}$$

$$= +1.03\ \text{V}$$

Answer: **+1.03 V**