Topics in the June 2013 Exam Paper for CHEM1903

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- Nuclear and Radiation Chemistry

2013-J-3:

- Filling Energy Levels in Atoms Larger than Hydrogen
- Periodic Table and the Periodic Trends

2013-J-4:

- Band Theory - MO in Solids

2013-J-5:

- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

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- Gas Laws

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- VSEPR

2013-J-8:

- Thermochemistry
- First and Second Law of Thermodynamics

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- Equilibrium and Thermochemistry in Industrial Processes

2013-J-12:

- First and Second Law of Thermodynamics

- Calculate the activity (in Bq) of a 1.00 g sample of $^{137}Cs^{131}I$, if the half lives of the caesium and iodine are 30.17 years and 8.02 days respectively.

The molar mass of $^{137}Cs^{131}I$ is (137 + 131) g mol^{-1} = 268 g mol^{-1}. As each mole of $^{137}Cs^{131}I$ contains one mole of ^{137}Cs and one moles of ^{131}I:

number of moles of ^{137}Cs = number of moles of ^{131}I = mass / molar mass
= 1.00 g / 268 g mol^{-1} = 0.00373 mol

Each mole contains Avogadro's number of nuclei so:

number of nuclei of ^{137}Cs = number of nuclei of ^{131}I = number of moles × N_A
= 0.00373 mol × 6.022 × 10^{23} mol^{-1}
= 2.25 × 10^{25}

The activity coefficient, λ, is related to the half life, $t_{1/2}$, through λ = ln 2 / $t_{1/2}$. Hence:

λ (^{137}Cs) = ln 2 / (30.17 × 365 × 24 × 60 × 60 s) = 7.28 × 10^{-10} s^{-1}
λ (^{131}I) = ln 2 / (8.02 × 24 × 60 × 60 s) = 1.00 × 10^{-6} s^{-1}

The activity, A, is related to the number of nuclei, N, through A = λN and so:

A (^{137}Cs) = (7.28 × 10^{-10} s^{-1}) × (2.25 × 10^{25} nuclei) = 1.64 × 10^{12} Bq
A (^{131}I) = (1.00 × 10^{-6} s^{-1}) × (2.25 × 10^{25} nuclei) = 2.25 × 10^{15} Bq

As might have been anticipated from the relative sizes of the half lives, the activity is completely dominated by ^{131}I:

Overall activity = A (^{137}Cs) + A (^{131}I) = 2.25 × 10^{15} Bq

Answer: **2.25 × 10^{15} Bq**

Both nuclides in $^{137}Cs^{131}I$ are beta emitters, and the daughter nuclides are stable. Describe the sample after it has been melted and allowed to resolidify after (a) 3 months and (b) 300 years.

The products formed by beta emission are:

$^{137}_{55}Cs \rightarrow {}^{137}_{56}Ba + {}^{0}_{-1}\beta$ $^{131}_{53}I \rightarrow {}^{131}_{54}Xe + {}^{0}_{-1}\beta$

The ^{131}I decays to ^{131}Xe which, being a gas, escapes on melting.

(a) As the half life of ^{131}I is only 8.02 days, after 3 months most of it will have decayed. As the half life of ^{137}Cs is 30.17 years, after 3 months little will have decay. The sample will be mainly ^{137}Cs with a little ^{137}Ba.

(b) After 300 years, the sample will be mainly ^{137}Ba with a little bit of ^{137}Cs remaining.

		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**

• 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?	**2**

The Periodic Table groups atoms into:
- **Groups (columns) based on the number of valence electrons they have and on the occupation of these electrons in *s*, *p*, *d* and *f* sub-shells, 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.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

**Marks
7**

Carbon, silicon, germanium and tin all adopt the diamond structure. Diamond has a band gap of 5.5 eV, while silicon absorbs wavelengths shorter than 1100 nm. Predict the band gaps of germanium and tin.

Tin is a metal. It is a conductor with no band gap.

The longest wavelength, λ, absorbed by silicon is 1100 nm. This corresponds to the *minimum* energy required to excite an electron: the band gap. The energy, E, is related to λ through Planck's equation $E = hc / \lambda$.

The band gap in silicon is therefore:

$E = hc / \lambda = (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{8} \text{ m s}^{-1}) / (1100 \times 10^{-9} \text{ m})$
$= 1.8 \times 10^{-19} \text{ J}$

As 1 eV = 1.602×10^{-19} J, this corresponds to:

$E = (1.8 \times 10^{-19} / 1.602 \times 10^{-19}) \text{ eV} = 1.1 \text{ eV}$

The band gap decreases down the group: 5.5 eV (C), 1.1 eV (Si) and 0 eV (Sn). The band gap in germanium will be between that for Si and Sn, around the average of 0 and 1.1 eV.

Predict the band gap of SiC, which also has a diamond like structure, but with Si bonded to 4 C atoms, and C bonded to 4 Si atoms.

It will be around an average of the values for C and Si:

predicted band gap = ½ (5.5 + 1.1) eV = 3.3 eV

Use the information in the following table to predict the density of tin.

Element	Atomic Mass	Density (g cm^{-3})	Bond length (pm)
Ge	72.64	5.323	244
Sn	118.7		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 = $(280 / 244)^{3}$ × volume of germanium

The mass will increase as the atomic mass increases:
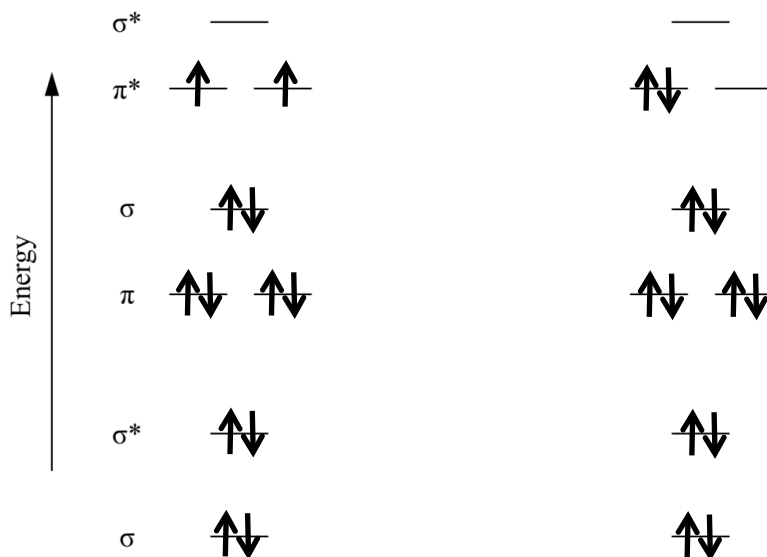
mass of tin = (118.7 / 72.64) × mass of germanium

As the density of germanium is 5.323 g cm^{-3}, the density of tin will therefore be:

density of tin = density of germanium × (118.7 / 72.64) / $(280 / 244)^{3}$
= 5.323 g cm^{-3} × (118.7 / 72.64) / $(280 / 244)^{3}$ = 5.76 g cm^{-3}

Answer: **5.76 g cm^{-3}**

**Marks
4**

- Oxygen exists in the troposphere as a diatomic molecule.

(a) Using arrows to indicate relative electron spin, fill the left-most **valence** orbital energy diagram for O_2, obeying Hund's Rule.

(b) Indicate on the right-most **valence** orbital energy diagram the lowest energy electronic configuration for O_2 which has no unpaired electrons.

Suggest a heteronuclear diatomic species, isoelectronic with O_2, that might be expected to have similar spectroscopic behaviour.

NO^-, NF

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 (b) *at the same time*. What wavelength photon would be emitted by one molecule returning from this state to the ground state?

635 nm excites two molecules. The energy emitted by one molecule will be half as much required to excite two molecules.

Energy, *E*, is inversely related to the wavelength, λ, through Plank's equation:

$E = hc / \lambda$.

Hence, if the energy is halved, the wavelength is *doubled*: 2 × 635 nm = 1270 nm.

Answer: **1270 nm**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

	Marks
The density of liquid oxygen is 1.141 g cm^{-3}. Calculate its molarity and compare to the molarity of oxygen in air. Air consists of 21% oxygen.	**4**

As density = mass / volume, the mass of 1 litre of liquid oxygen is:

mass = density × volume = (1.141 g cm^{-3}) × (1000. cm^3) = 1141 g

The molar mass of O$_2$ is 2 × 16.00 g mol^{-1} = 32.00 g mol^{-1}. This mass therefore corresponds to:

number of moles = 1141 g / 32.00 g mol^{-1} = 35.67 mol

As this is the number of moles in a litre, the molarity is 35.67 mol L^{-1}.

From the data sheet, 1 mole of an ideal gas at 1 atm and 25 °C occupies 24.5 L. As 21% of the air is oxygen, 0.21 mol of oxygen occupies 24.5 L. The concentration is therefore:

concentration = number of moles / volume
= 0.21 mol / 24.5 L = 8.6 × 10^{-3} mol L^{-1}

[O$_2$(l)]: **35.67 mol L^{-1}**	[O$_2$(g)]: **8.6 × 10^{-3} mol L^{-1}**

A 50.0 mL sample of liquid oxygen is transferred to an evacuated 1.25 L container and allowed to warm to room temperature (25 °C). What is the final pressure inside the container?

As the molarity of liquid oxygen is 35.67 mol L^{-1}, 50.0 mL of liquid oxygen corresponds to:

number of moles = concentration × volume
= (35.67 mol L^{-1}) × (0.0500 L) = 1.783 mol

When this amount becomes a gas in a container with V = 1.25 L, the pressure will be:

$P = nRT / V$
= (1.783 mol) × (0.08206 L atm K^{-1} mol^{-1}) × ((25 + 273) K) / (1.25 L)
= 34.9 atm

Answer: **34.9 atm (3500 kPa)**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

	Marks
• Complete the following table on the given oxides of nitrogen. Indicate the charge on all atoms with non-zero formal charge.	**9**

Molecule	Lewis Structure	Shape of molecule
NO_2		**bent**
N_2O		**linear**
NO_3		**trigonal planar**

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**Marks
5**

- The atmosphere of Venus contains 96.5 % CO_2 at 95 atm of pressure, leading to an average global surface temperature of 462 °C. The energy density of solar radiation striking Venus is 2625 J m^{-2} s^{-1}. The radius of Venus is 6052 km, and the average albedo (the fraction of solar radiation reflected back into space) of its surface is 0.90. Calculate the magnitude of the greenhouse effect on Venus.

An albedo of 0.90 means that 90% of the solar energy is reflected and only 10% is available to heat the planet. If Venus has a radius R, the energy input from the Sun is:

$$E_{in} = (2625 \times \pi R^2 \times 0.10) \text{ J}$$

The energy output from the surface area $4\pi R^2$ is:

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

At equilibrium, the energy input and output are equal and so the temperature can be calculated:

$$2625 \times \pi R^2 \times 0.10 = 4\pi R^2 \times 5.67 \times 10^{-8} \times T^4$$

$$T^4 = 0.10 \times 2625 / (4 \times 5.67 \times 10^{-8}) \text{ K} \qquad \text{so T = 184 K}$$

As the actual temperature on Venus is 462 °C = 735 K, the magnitude of the greenhouse effect is:

$$\text{greenhouse effect} = (735 - 185) \text{ K} = 551 \text{ K}$$

Answer: **551 K**

The main absorption bands of CO_2 lie in the energy range 600 – 750 cm^{-1}. What range of wavelengths (in nm) corresponds to this energy range?

600 cm^{-1} corresponds to a wavelength of (1/600) cm = 0.00167 cm. As 1 cm = 0.01 m and 1 nm = 10^{-9} m, this corresponds to 16700 nm.

750 cm^{-1} corresponds to a wavelength of (1/750) cm = 0.00133 cm. As 1 cm = 0.01 m and 1 nm = 10^{-9} m, this corresponds to 13300 nm.
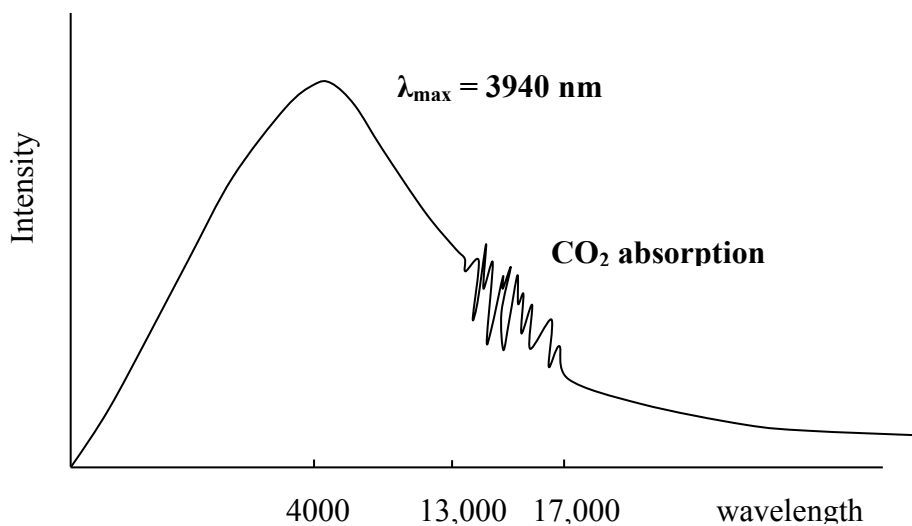
ANSWER CONTINUES ON THE NEXT PAGE

Sketch the emission spectrum of Venus on the axes below. Note the wavelength of maximum intensity, and point out any other important features.
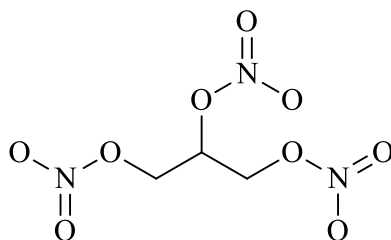
The wavelength corresponding to the intensity maximum is given by Wien's displacement law:

$$T \, \lambda_{max} \approx 2.898 \times 10^6 \text{ K nm}$$

Using $T = 735$ K, $\lambda_{max} \approx (2.898 \times 10^6$ K nm$) / (735$ K$) = 3940$ nm

Marks
5

- The structural formula of nitroglycerine, $C_3H_5N_3O_9$, is shown below.

The boiling point of nitroglycerine is 50 °C. What is the most important type of intermolecular force contributing to keeping nitroglycerine in the liquid state at room temperature, and which atoms in particular are involved?

Dipole-dipole forces involving N and O. The N-O bonds are very polar.

Write a balanced equation for the explosive decomposition of liquid nitroglycerine. The products are water, carbon dioxide, nitrogen and oxygen.

$2C_3H_5N_3O_9(l) \rightarrow 5H_2O(g) + 6CO_2(g) + 3N_2(g) + \frac{1}{2}O_2(g)$
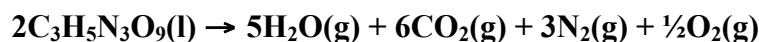
The standard enthalpy change associated with this explosive decomposition is -1414 kJ mol^{-1}. What other factor(s) would contribute to the free energy released in the decomposition of nitroglycerine?

As $\Delta G = \Delta H - T\Delta S$, a highly negative value for ΔG can arise through a highly negative ΔH value (as here) and also a positive ΔS value.

In the reaction, each mole of liquid reactant is converted into 7.25 mol of gases. This gives a highly positive ΔS value.

Briefly describe a calorimetry experiment that could reliably measure the enthalpy of decomposition of nitroglycerine.

A bomb calorimeter *(i.e.* **a constant volume calorimeter) of known heat capacity would be used.**

It would be charged with a known amount of water and nitroglycerine, which is then decomposed. By measuring the temperature of the water in the calorimeter before and after decomposition, the enthalpy change for the reaction can be calculated.

Marks
2

- The vapour pressure of mercury above its liquid at 25 °C is 0.265 Pa. Calculate the free energy of formation (in kJ mol^{-1}) of gaseous mercury at 25 °C.

Vapourisation corresponds to the process Hg(l) → Hg(g). As pure liquids do not appear in equilibrium constant expressions, for this process the equilibrium constant expression in terms of partial pressures is:
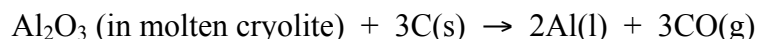
$$K_p = P_{Hg(g)} = 0.265$$

Using $\Delta G^o = -RT\ln K_p$:

$$\Delta G^o = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times \ln(0.265)$$
$$= +3300 \text{ J mol}^{-1} = +3.3 \text{ kJ mol}^{-1}$$

Answer: **+3.3 kJ mol^{-1}**

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Marks
4

- The principal chemical reaction in the Hall process, used to refine aluminium from its oxide, is:

$$Al_2O_3 \text{ (in molten cryolite)} + 3C(s) \rightarrow 2Al(l) + 3CO(g)$$

The free energy change for this reaction is $\Delta G° = 594$ kJ mol^{-1} at 1000 °C. Recycling aluminium essentially only requires enough energy to melt it. The melting point of aluminium is 660 °C, its heat of fusion is 10.7 kJ mol^{-1} and its heat capacity is 0.900 J K^{-1} g^{-1}. Calculate the percentage of energy saved by recycling aluminium *vs*. refining it from Al_2O_3. (Assume that the ambient temperature is 25 °C.)

To recycle aluminium requires energy to (i) heat it from 25 ^{o}C to 660 ^{o}C and (ii) the energy to melt it.

(i)   The mass of 1 mol of Al(s) is 26.98 g. The heat required to heat this quantity from 25 to 660 ^{o}C is therefore:

$$q = mC\Delta T = (26.98 \text{ g}) \times (0.900 \text{ J K}^{-1} \text{ g}^{-1}) \times ((660 - 25) \text{ K})$$
$$= 15400 \text{ J} = 15.4 \text{ kJ}$$

(ii)   The energy required to melt it is equal to the heat of fusion: 10.7 kJ.

The total energy required is therefore (10.7 + 15.4) kJ = 26.1 kJ

From the chemical equation, 594 kJ will form 2 mol of Al so 297 kJ will form 1 mol.

The percentage energy saved is:

percentage saved = (297 - 26.1) / 297 × 100% = 91 %

Answer: **91%**

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<div align="right">Marks
8</div>

- Differential scanning calorimetry (DSC) is an experimental technique that measures the temperature of a sample as a function of the heat supplied to it. Negative or positive peaks on a DSC curve therefore indicate endothermic or exothermic processes respectively. The figure below shows a series of DSC curves collected for methane at different pressures. The scales of all the heat flow curves are the same, but they have been offset from zero for clarity. Clearly identify the type of phase change associated with every peak in the DSC curve.
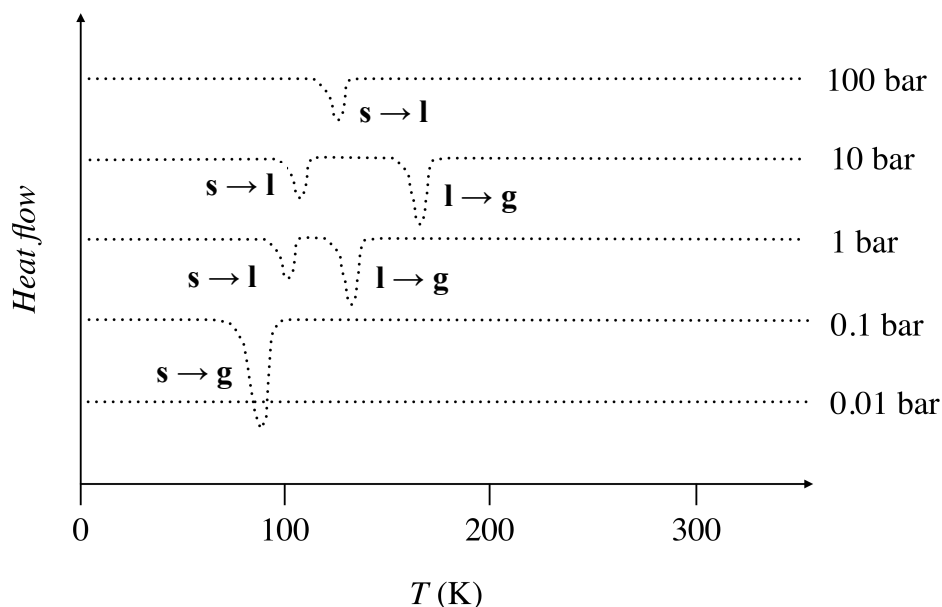

On the 0.1, 1 and 10 bar curves, there are two phase transitions observed so melting and boiling occurs. From the size of the peak is consistent with the single peak in the 100 bar being melting. The size of the peak in the 0.01 bar curve is not consistent with melting or boiling so it must correspond to sublimation.

ANSWER CONTINUES ON THE NEXT PAGE

Use the DSC data shown to sketch a pressure-temperature phase diagram on the graph below (note that pressure is on a log scale). Label all the important regions of the phase diagram.

**Marks
8**
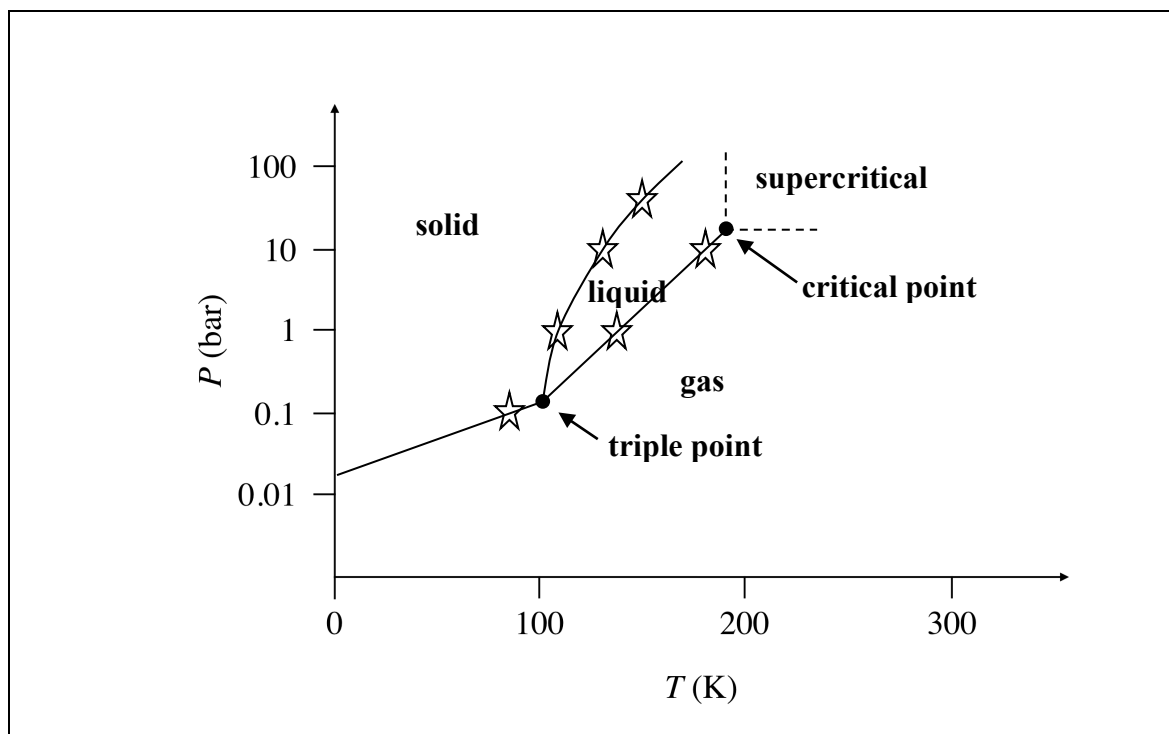
- Consider the following aqueous voltaic cell at 25 °C:

$$Pb(s) \mid Pb^{2+} \text{ (0.0010 M)} \parallel Sn^{2+} \text{ (2.0 M)} \mid Sn(s)$$
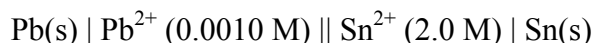
Write balanced equations for the reactions occurring at the anode, cathode and overall.

anode: | $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

cathode: | $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

overall: | $Sn^{2+}(aq) + Pb(s) \rightarrow Pb^{2+}(aq) + Sn(s)$

Calculate the potential of the cell under the stated conditions.

From the standard reduction potentials:

$E^o(Pb^{2+} / Pb) = -0.126$ **V and** $E^o(Sn^{2+} / Sn) = -0.136$ **V**

As the Pb^{2+} / Pb **is the oxidation half cell in the cell described, this is reversed and the standard cell potential is:**

$E^o{}_{cell} = E_{red}{}^o + E_{ox}{}^o = (-0.136 + (0.126)$ **V** $= -0.010$ **V**

As non-standard concentrations are used in the cell, the Nernst equation must be used to calculate the cell potential:

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

From the reaction, $Q = \dfrac{[Pb^{2+}(aq)]}{[[Sn^{2+}(aq)]} = \dfrac{0.0010}{2.0} = 0.00050$

For this 2 electron reaction, $n = 2$ **and the cell potential is:**

$$E_{cell} = (-0.010) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})((25+273) \text{ K})}{(2)(96485 \text{ C mol}^{-1})}\ln(0.00050) = +0.088 \text{ V}$$

Answer: **+0.088 V**

What will be the concentrations of $Pb^{2+}(aq)$ and $Sn^{2+}(aq)$ in the cell when it comes to equilibrium?

At equilibrium, $E^o = \dfrac{RT}{nF}\ln K$**, hence:**

$$-0.010 \text{ V} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})((25+273) \text{ K})}{(2)(96485 \text{ C mol}^{-1})}\ln K$$

$\ln K = -0.779$ **so** $K = e^{-0.779} = 0.459$

ANSWER CONTINUES ON THE NEXT PAGE

A reaction table can be used to work out the equilibrium concentrations.

	$Sn^{2+}(aq)$	Pb(s)		$Pb^{2+}(aq)$	Sn(s)
initial	2.0	-	$\rightleftharpoons$	0.0010	-
change	-x			+x	
equilibrium	$2.0 - x$			$0.0010 + x$	

Hence,

$$K = \frac{0.0010 + x}{2.0 - x} = 0.459$$

$0.0010 + x = 0.459(2.0 - x) = 0.918 - 0.459x$
$1.459x = 0.917$
$x = 0.63$

The concentrations are therefore:

$[Sn^{2+}(aq)] = (2.0 - x)$ M $= (2.0 - 0.63)$ M $= 1.4$ M

$[Sn^{2+}(aq)] = (0.0010 + x)$ M $= (0.0010 + 0.63) = 0.63$ M

$[Pb^{2+}(aq)] = $ **0.63 M**	$[Sn^{2+}(aq)] = $ **1.4 M**