Topics in the November 2012 Exam Paper for CHEM1612

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- Solutions
- Acids and Bases
- Chemical Equilibrium

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• Introduction to Chemical Energetics

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2012-N-15:

• Chemical Kinetics

• Explain the following terms or concepts.	Mark 3
a) Second law of thermodynamics	
All processes occur spontaneously in the direction that increases the total entropy of the universe.	
b) Vapour pressure	-
The partial pressure that builds up above the surface of a volatile liquid in a closed container due to evaporation.	
c) Isoelectric point	-
The pH at which a protein or amino acid has no net charge, <i>i.e.</i> it contains equal amounts of positive and negative charges.	
 The electron transfer reaction between NADH and oxygen is a spontaneous reaction at 37 °C 	3
NADH + $\frac{1}{2}O_2$ + H ⁺ \rightarrow NAD ⁺ + H ₂ O $\Delta G = -220 \text{ kJ mol}^{-1}$	
When this reaction is carried out in solution in a test tube via direct mixing of NADH with dissolved oxygen, the reaction releases a significant amount of heat. However, when the reaction occurs in mitochondria during respiration, it produces very little heat. Explain why the heat evolved is much less in mitochondria.	
According to the First Law of Thermodynamics, energy can be transferred in the form of heat or work. The amount of energy the reaction releases is constant, so if the heat released in mitochondria is reduced it means more work must be done. ΔG is the maximum amount of non- <i>PV</i> work obtainable from a system. The	
energy released by the oxidation of NADH in mitochondria is used to do non- PV work, <i>viz</i> . the pumping of H ⁺ ions across the inner mitochondrial membrane. By storing this energy in the form of an H ⁺ gradient, the amount of energy wasted as heat is reduced.	

- Marks 2
- Copper metal can be obtained by heating copper oxide, CuO, in the presence of carbon monoxide, CO, according to the following reaction.

$$CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)$$

Calculate ΔH° for this reaction in kJ mol⁻¹.

Data:	$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	$\Delta H^{\circ} = -566.1 \text{ kJ mol}^{-1}$
	$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$	$\Delta H^{\circ} = -310.5 \text{ kJ mol}^{-1}$

Using $\Delta_r H^\circ = \sum \Delta_f H^\circ$ (products) $-\sum \Delta_f H^\circ$ (reactants), the enthalpy changes in the 3 reactions are, respectively:

$$\Delta_{\mathbf{r}} H^{\circ}(1) = \Delta_{\mathbf{f}} H^{\circ}(\mathrm{CO}_{2}(\mathbf{g})) - [\Delta_{\mathbf{f}} H^{\circ}(\mathrm{CuO}(\mathbf{s})) + \Delta_{\mathbf{f}} H^{\circ}(\mathrm{CO}(\mathbf{g}))]$$

$$\Delta_{\rm r} H^{\circ}(2) = 2\Delta_{\rm f} H^{\circ}({\rm CO}_2({\rm g})) - 2\Delta_{\rm f} H^{\circ}({\rm CO}({\rm g})) = -566.1 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm r} H^{\circ}(3) = 2\Delta_{\rm f} H^{\circ}({\rm CuO}({\rm s})) = -310.5 \text{ kJ mol}^{-1}$$

Using $\Delta_f H^\circ = 0$ for Cu(s) and O₂(g) as these are elements in their standard states.

Rearranging (1) gives:

$$\Delta_{r}H^{\circ}(1) = \Delta_{f}H^{\circ}(CO_{2}(g)) - \Delta_{f}H^{\circ}(CO(g)) - \Delta_{f}H^{\circ}(CuO(s))$$

= ¹/₂ (\Delta_{r}H^{\circ}(2)) - ¹/₂ (\Delta_{r}H^{\circ}(3))
= [¹/₂ (-566.1) - ¹/₂ (-310.5)] kJ mol⁻¹ = -127.8 kJ mol⁻¹
Answer: -127.8 kJ mol⁻¹

• Acetylene burns in air according to the following equation:

 $C_2H_2(g) + {}^{5}/{}_{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g) \qquad \Delta H^{\circ} = -1255.8 \text{ kJ mol}^{-1}$

The $\Delta_f H^\circ$ of CO₂(g) = -393.5 kJ mol⁻¹, $\Delta_f H^\circ$ of H₂O(l) = -285.8 kJ mol⁻¹ and $\Delta_{vap} H^\circ$ of H₂O(l) = +44.0 kJ mol⁻¹. What is $\Delta_f H^\circ$ of C₂H₂(g)?

Using $\Delta_r H^\circ = \sum \Delta_f H^\circ$ (products) $-\sum \Delta_f H^\circ$ (reactants), the enthalpy of combustion of C₂H₂(g) is:

 $\Delta_{\text{comb}} H^{\circ}(C_{2}H_{2}(g)) = [2\Delta_{f} H^{\circ}(CO_{2}(g)) + \Delta_{f} H^{\circ}(H_{2}O(g))]$ $- \Delta_{f} H^{\circ}(C_{2}H_{2}(g)) = -1255.8 \text{ kJ mol}^{-1}$

The enthalpy of vaporisation for $H_2O(g)$ corresponds to $H_2O(l) \rightarrow H_2O(g)$:

$$\Delta_{\mathrm{vap}}H^{\circ}(\mathrm{H}_{2}\mathrm{O}(\mathrm{I})) = \Delta_{\mathrm{f}}H^{\circ}(\mathrm{H}_{2}\mathrm{O}(\mathrm{g})) - \Delta_{\mathrm{f}}H^{\circ}(\mathrm{H}_{2}\mathrm{O}(\mathrm{I})) = +44.0 \text{ kJ mol}^{-1}$$

and so,

$$\Delta_{f}H^{\circ}(H_{2}O(g)) = \Delta_{vap}H^{\circ}(H_{2}O(l)) + \Delta_{f}H^{\circ}(H_{2}O(l))$$

= (+44.0 + -285.8) kJ mol⁻¹ = -241.8 kJ mol⁻¹

ANSWER CONTINUES ON THE NEXT PAGE

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Substituting the data into the expression for $\Delta_{comb}H^{\circ}(C_2H_2(g))$

 $\Delta_{\text{comb}} H^{\circ}(C_{2}H_{2}(g)) = [(2 \times -393.5 + -241.8) - \Delta_{f} H^{\circ}(C_{2}H_{2}(g))] \text{ kJ mol}^{-1} = -1255.8 \text{ kJ mol}^{-1}$

So:

 $\Delta_{\rm f} H^{\circ}({\rm C}_{2}{\rm H}_{2}({\rm g}) = [(2 \times -393.5 + -241.8) + 1255.8] \text{ kJ mol}^{-1} = +227.0 \text{ kJ mol}^{-1}$

Answer: +227.0 kJ mol⁻¹

- Marks 3
- A sample of gas is found to exert a pressure of 7.00×10^4 Pa when it is in a 3.00 L flask at 10.00 °C. Calculate the new volume if the pressure becomes 1.01×10^5 Pa and the temperature is unchanged.

Using the ideal gas law, PV = nRT, the number of moles present is:

 $n = PV/RT = (7.00 \times 10^4 \text{ Pa})(3.00 \times 10^{-3} \text{ m}^3)/(8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1})(283.00 \text{ K})$ = 8.925 × 10⁻² mol

At the new pressure, the volume occupied by this amount is:

 $V = nRT/P = (8.925 \times 10^{-2} \text{ mol})(8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1})(283.00 \text{ K})/(1.01 \times 10^5 \text{ Pa})$ = 2.08 × 10⁻³ m³ = 2.08 L

More quickly, $P_1V_1 = P_2V_2$ can be used:

$$V_2 = P_1 V_1 / P_2 = (7.00 \times 10^4 \text{ Pa})(3.00 \text{ L}) / (1.01 \times 10^5 \text{ Pa}) = 2.08 \text{ L}$$

Answer: 2.08 L

Calculate the new pressure if the volume becomes 2.00 L and the temperature is unchanged.

From above, $n = 8.925 \times 10^{-2}$ mol. The pressure when V = 2.00 L and T = 283.00 K is:

P = nRT/V= (8.925 × 10⁻² mol)(8.314 m³ Pa K⁻¹ mol⁻¹)(283.00 K)/(2.00 × 10⁻³ m³) = 1.05 × 10⁵ Pa

 $P_1V_1 = P_2V_2$ can again be used without calculating *n*:

 $P_2 = P_1 V_1 / V_2 = (7.00 \times 10^4 \text{ Pa}) \times (3.00 \text{ L}) / (2.00 \text{ L}) = 1.05 \times 10^5 \text{ Pa}$

Answer: 1.05×10^5 Pa

Calculate the new pressure if the temperature is raised to 50.0 °C and the volume is unchanged, *i.e.* still 3.00 L.

From above, $n = 8.925 \times 10^{-2}$ mol. The pressure when V = 3.00 L and T = 323.0 K is:

P = nRT/V= (8.925 × 10⁻² mol)(8.314 m³ Pa K⁻¹ mol⁻¹)(323.0 K)/(3.00 × 10⁻³ m³) = 7.99 × 10⁴ Pa

The new pressure can be calculated directly using $P_1/T_1 = P_2/T_2$:

$$P_2 = P_1 \times T_2/T_1 = (7.00 \times 10^4 \text{ Pa}) \times 323.0/283.0 = 7.99 \times 10^4 \text{ Pa}$$

Answer: 7.99×10^4 Pa

• Consider the following reaction.

 $SO_2(g) + NO_2(g) \iff SO_3(g) + NO(g)$

An equilibrium mixture in a 1.00 L vessel was found to contain $[SO_2(g)] = 0.800$ M, $[NO_2(g)] = 0.100$ M, $[SO_3(g)] = 0.600$ M and [NO(g)] = 0.400 M. If the volume and temperature are kept constant, what amount (in mol) of NO(g) needs to be added to the reaction vessel to give an equilibrium concentration of NO₂(g) of 0.300 M?

From the chemical equation,

 $K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]}$

As the original mixture is at equilibrium:

 $K_{\rm eq} = \frac{[{\rm SO}_3({\rm g})][{\rm NO}({\rm g})]}{[{\rm SO}_2({\rm g})][{\rm NO}_2({\rm g})]} = \frac{(0.600)(0.400)}{(0.800)(0.100)} = 3.00$

This equilibrium is now disturbed by the addition of x M of NO(g). To reestablish equilibrium, the reaction will shift to the left by an unknown amount y. The reaction table for this is:

	SO ₂ (g)	$NO_2(g)$		SO ₃ (g)	NO(g)
initial	0.800	0.100	1	0.600	0.400 + x
change	+y	+y		-у	- <u>v</u>
equilibrium	0.800 + y	0.100 + y		0.600 - y	0.400 + <i>x</i> - y

As $[NO_2(g)] = 0.300$ M at the new equilibrium, y = (0.300 - 0.100) M = 0.200 M. Hence, the new equilibrium concentrations are:

$$\begin{split} [SO_2(g)] &= (0.800 + 0.200) \text{ M} = 1.000 \text{ M} \\ [NO_2(g)] &= 0.300 \text{ M} \\ [SO_3(g)] &= (0.600 - 0.200) \text{ M} = 0.400 \text{ M} \\ [NO(g)] &= (0.400 + x - 0.200) \text{ M} = (0.200 + x) \text{ M} \end{split}$$

As the system is at equilibrium,

 $K_{\rm eq} = \frac{[{\rm SO}_3({\rm g})][{\rm NO}({\rm g})]}{[{\rm SO}_2({\rm g})][{\rm NO}_2({\rm g})]} = \frac{(0.400)(0.200+x)}{(1.000)(0.300)} = 3.00$

Solving this gives x = 2.05 M. As the reaction is carried out in a 1.00 L container, this is also the number of moles required.

Marks • Phenylketonuria is an inherited disorder in which phenylacetic acid, C₆H₅CH₂COOH, (simplified here to HPAc) accumulates in the blood. If untreated, it can cause mental retardation and death. A study of the acid shows that the pH of a 0.12 M HPAc solution is 2.60. What is the pK_a of phenylacetic acid? As HPAc is a weak acid, the equilibrium for its dissociation can be studied using an 'ICE' table: \mathbf{H}^{+} HPAc -PAc⁻ 0 initial 0.12 0 -*x* change +x+xfinal 0.12 - xx х By definition, $pH = -log_{10}[H^+(aq)]$ so $[H^+(aq)] = 10^{-2.60}$ M. From the reaction table, $x = [\mathbf{H}^+(\mathbf{aq})]_{eq}$ so: $[HPAc]_{eq} = 0.12 - x = (0.12 - 10^{-2.60}) M = 0.12 M (to 2 s.f.)$ $[\mathrm{H}^{+}(\mathrm{aq})]_{\mathrm{eq}} = x = 10^{-2.60} \mathrm{M}$ $[PAc(aq)]_{eq} = x = 10^{-2.60} M$

The equilibrium constant K_a is given by:

$$K_{\rm a} = \frac{[{\rm HPac}^-][{\rm H}^+]}{[{\rm HPAc}]} = \frac{(10^{-2.60})(10^{-2.60})}{(0.12)} = 5.26 \times 10^{-5}$$

By definition, $pK_a = -\log_{10}K_a$ so:

$$pK_a = -\log_{10}(5.26 \times 10^{-5}) = 4.28$$

Answer: 4.28

• The concentration of NaCl used in intravenous drips is 150 mM. Explain why this particular concentration is used and what the consequences would be for a patient if pure water were used instead.

150 mM is used because this corresponds to the NaCl concentration in extracellular fluids and thus prevents any change in osmotic conditions in the blood. If water were used, water would flow into the red blood cells causing them to swell up and possibly burst. This may have fatal consequences for the patient.

2

4

• A calorimeter, consisting of an insulated coffee cup containing 50.0 g of water at 21.0 °C, has a total heat capacity of 9.4 J K⁻¹. When a 30.4 g sample of an alloy at 92.0 °C is placed into the calorimeter, the final temperature of the system is 31.2 °C. What is the specific heat capacity of the alloy? The calorimeter is heated from 21.0 °C to 31.2 °C corresponding to a temperature increase of: $\Delta T_{calorimeter} = (31.2 - 21.0) \text{ K} = +10.2 \text{ K}$

As the heat capacity of the calorimeter is 9.4 J K⁻¹, the heat change of the caloriometer is:

 $q_{\text{calorimeter}} = C_{\text{calorimeter}} \Delta T_{\text{calorimeter}} = (9.4 \text{ J K}^{-1})(10.2 \text{ K}) = +95.9 \text{ J}$

As this heat comes from the alloy:

 $q_{\text{alloy}} = -q_{\text{calorimeter}} = -95.9 \text{ J}$

The alloy cools from 92.0 °C to 31.2 °C corresponds to a temperature change of:

 $\Delta T_{\text{alloy}} = (31.2 - 92.0) \text{ K} = -60.8 \text{ K}$

Using $q = mC\Delta T$,

$$C = q / m\Delta T = -95.9 \text{ J} / (30.4 \text{ g} \times -60.8) = 0.052 \text{ J} \text{ g}^{-1} \text{ K}^{-1}$$

Answer: **0.052** J g^{-1} K⁻¹

• At 21.0 °C, a solution of 18.26 g of a non-volatile, non-polar compound in 33.25 g of bromoethane, CH₃CH₂Br, has a vapour pressure of 4.42×10^4 Pa. The vapour pressure of pure bromoethane at this temperature is 5.26×10^4 Pa. What is the molar mass of the compound?

The molar mass of CH₃CH₂Br is:

molar mass = $(2 \times 12.01 \text{ (C)} + 5 \times 1.008 \text{ (H)} + 79.90 \text{ (Br)}) \text{ g mol}^{-1}$ = 108.96 g mol⁻¹

The number of moles of CH₃CH₂Br in 18.26 g is therefore:

 $n_{\text{solvent}} = \text{mass} / \text{molar mass} = 33.25 \text{ g} / 108.96 \text{ g mol}^{-1} = 0.305 \text{ mol}$

From Raoult's law, the vapour pressure of a solution, P_{solution} , is related to the vapour pressure of the pure solvent, $P_{\text{solvent}}^{\circ}$ and its mole fraction, X_{solvent} :

 $P_{\text{solution}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$

ANSWER CONTINUES ON THE NEXT PAGE

Using $P_{\text{solution}} = 4.42 \times 10^4$ Pa and $P_{\text{solvent}}^0 = 5.26 \times 10^4$ Pa, the mole fraction must be:

 $X_{\text{solvent}} = P_{\text{solution}} / P^{0}_{\text{solvent}} = (4.42 \times 10^{4} / 5.26 \times 10^{4}) = 0.840$

The mole fraction of solvent is given by the number of moles of solvent divided by the total number of moles of solvent and solute:

 $X_{\text{solvent}} = n_{\text{solvent}} / (n_{\text{solvent}} + n_{\text{solute}}) = 0.840$

Using $n_{\text{solvent}} = 0.305 \text{ mol from above}$,

 $n_{\text{solvent}} / (n_{\text{solvent}} + n_{\text{solute}}) = 0.305 / (0.305 + n_{\text{solute}}) = 0.840$

 $n_{\text{solute}} = (0.305 / 0.840 - 0.305) \text{ mol} = 0.0581 \text{ mol}$

As this corresponds to a mass of 18.26 g, the molar mass is:

molar mass = mass / number of moles = $18.26 \text{ g} / 0.0581 \text{ mol} = 315 \text{ g mol}^{-1}$

Answer: **315 g mol**⁻¹

- Marks 4
- Buffer 1 is a solution containing 0.08 M NH₄Cl and 0.12 M NH₃. Buffer 2 is a solution containing 0.15 M NH₄Cl and 0.05 M NH₃. The acid dissociation constant of the ammonium ion is 5.50×10^{-10} . What are the pH values of each of the buffer solutions?

By definition, $pK_a = -\log_{10}K_a$ so:

 $pK_a = -\log_{10}(5.50 \times 10^{-10}) = 9.26$

Using the Henderson-Hasselbalch equation,

 $\mathbf{pH} = \mathbf{pK}_{\mathbf{a}} + \log \frac{[\mathsf{base}]}{[\mathsf{acid}]} = 9.290 + \log \frac{[\mathsf{NH}_3]}{[\mathsf{NH}_3\mathsf{CI}]}$

For buffer 1:

$$pH = 9.26 + \log \frac{0.12}{0.08} = 9.44$$

For buffer 2:

$$pH = 9.26 + \log \frac{0.05}{0.15} = 8.78$$

Buffer 1 pH = **9.44**

Buffer 2 pH = **8.78**

Which buffer is better able to maintain a steady pH on the addition of small amounts of both a strong acid and strong base? Explain.

Buffer 1 is better able to maintain a steady pH because its pH is closer to the pK_a of NH_4^+ . This is because it has relatively high concentrations of both NH_4^+ and NH_3 which can react with any added OH^- or H^+ respectively.

• Order the following salts from lowest to highest molar solubility.

Marks

4

Salt	CuCl	$Cd(IO_3)_2$	BaSO ₄	Ag ₂ CrO ₄
$K_{ m sp}$	$1.9 imes 10^{-7}$	$2.3 imes 10^{-8}$	1.1×10^{-10}	2.6×10^{-12}

(1) For CuCl, K_{sp} refers to the dissolution reaction:

$$CuCl(s) \iff Cu^{+}(aq) + Cl^{-}(aq) \qquad K_{sp} = [Cu^{+}(aq)][Cl^{-}(aq)]$$

If the solubility is x mol L⁻¹ then x mol of CuCl(s) dissolves in one litre. From the dissolution equation, this leads to $[Cu^+(aq)] = x$ M and $[C\Gamma(aq)] = x$ M. Hence,

$$K_{\rm sp} = (x)(x) = x^2 = 1.9 \times 10^{-7}$$
 or $x = (1.9 \times 10^{-7})^{1/2}$ M = 4.4 × 10⁻⁴ M

(2) For $Cd(IO_3)_2$, K_{sp} refers to the dissolution reaction:

$$Cd(IO_3)_2(s) \iff Cd^{2+}(aq) + 2IO_3(aq) \quad K_{sp} = [Cd^{2+}(aq)][IO_3(aq)]^2$$

If the solubility is x mol L⁻¹ then x mol of Cd(IO₃)₂ (s) dissolves in one litre. From the dissolution equation, this leads to $[Cd^{2+}(aq)] = x M$ and $[IO_3^-(aq)] = x M$. Hence,

$$K_{\rm sp} = (x)(2x)^2 = 4x^3 = 2.3 \times 10^{-8}$$
 or $x = (2.3 \times 10^{-8} / 4)^{1/3}$ M = 1.8×10^{-3} M

(3) For BaSO₄, K_{sp} refers to the dissolution reaction:

BaSO₄(s)
$$\implies$$
 Ba²⁺(aq) + **SO**₄²⁻(aq) $K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$

If the solubility is x mol L⁻¹ then x mol of BaSO₄(s) dissolves in one litre. From the dissolution equation, this leads to $[Ba^{2+}(aq)] = x M$ and $[SO_4^{2-}(aq)] = x M$. Hence,

$$K_{\rm sp} = (x)(x) = x^2 = 1.1 \times 10^{-10}$$
 or $x = (1.1 \times 10^{-10})^{1/2}$ M = 1.0×10^{-5} M

(4) For Ag_2CrO_4 , K_{sp} refers to the dissolution reaction:

$$Ag_2SO_4(s) \implies 2Ag^+(aq) + CrO_4^{2-}(aq) \quad K_{sp} = [Ag^+(aq)]^2 [CrO_4^{2-}(aq)]$$

If the solubility is x mol L^{-1} then x mol of Ag₂CrO₄(s) dissolves in one litre. From the dissolution equation, this leads to $[Ag^+(aq)] = 2x M$ and $[CrO_4^{2-}(aq)] = x M$. Hence,

$$K_{\rm sp} = (2x)^2(x) = 4x^3 = 2.6 \times 10^{-12}$$
 or $x = (2.6 \times 10^{-12} / 4)^{1/2}$ M = 8.7 × 10⁻⁵ M

Overall, solubility increases in the order:

 $BaSO_4 < Ag_2CrO_4 < CuCl < Cd(IO_3)_2$

ANSWER CONTINUES ON THE NEXT PAGE

- 3
- Give the equilibrium concentration of Ni²⁺(aq) ions in a solution formed by dissolving 0.15 mol of NiCl₂ in 0.500 L of 2.00 M KCN solution. The K_{stab} of [Ni(CN)₄]²⁻ = 1.7×10^{30} .

When the NiCl₂ is added to 0.500 L, the concentration of Ni²⁺(aq):

concentration = [Ni²⁺(aq)] = number of moles / volume = 0.15 mol / 0.500 L = 0.30 M

As K_{stab} is so large, essentially *all* of this will be complexed by the excess CN⁻(aq) ions:

 $Ni^{2+}(aq) + 4CN^{-}(aq) \implies [Ni(CN)_4^{2-}(aq)]$

As essentially all of the Ni²⁺(aq) becomes [Ni(CN)₄²⁻(aq)]:

 $[Ni(CN)_4^{2-}(aq)] = 0.30 \text{ M}$ $[CN^{-}(aq)] = (2.00 - 4 \times 0.30) \text{ M} = 0.80 \text{ M}$

 K_{stab} is the equilibrium constant for the reaction so:

 $K_{\text{stab}} = \frac{[\text{Ni}(\text{CN})_4^{2-}(\text{aq})]}{[\text{Ni}^{2+}(\text{aq})][\text{CN}^{-}(\text{aq})]^4}$

If the *tiny* amount of uncomplexed $Ni^{2+}(aq)$ has a concentration of x M then:

 $K_{\text{stab}} = \frac{(0.30)}{(x)(0.80)^4} = 1.7 \times 10^{30}$ so $x = 4.3 \times 10^{-31}$ M

Answer: 4.3×10^{-31} M



Marks 6

• A galvanic cell consists of a Cr^{3+}/Cr half-cell with unknown $[Cr^{3+}]$ and a Ni²⁺/Ni halfcell with $[Ni^{2+}] = 1.20$ M. The electromotive force of the cell at 25 °C was measured to be 0.55 V. What is the concentration of Cr^{3+} in the Cr^{3+}/Cr half-cell? From the standard reduction potentials, $\operatorname{Cr}^{3+}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Cr}(s)$ $\operatorname{Ni}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Ni}(s)$ $E^{0} = -0.74 \text{ V}$ $E^{0} = -0.24 \text{ V}$ The most negative is reversed to give an overall reaction and cell potential of $3Ni^{2+}(aq) + 2Cr(s) \rightarrow 3Ni(s) + 2Cr^{3+}(aq)$ $E^{0} = (+0.74 - 0.24) V = 0.50 V$ From the Nernst equation for this 6 electron reaction, $E = E^{\circ} - \frac{RT}{nF} \ln Q = E^{\circ} - \frac{RT}{nF} \ln \frac{[Cr^{3+}(aq)]^2}{[Ni^{2+}(aq)]^3}$ $= (0.50 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{6 \times 96485 \text{ mol}^{-1}} \ln \frac{[\text{Cr}^{3+}(\text{aq})]^2}{(120)^3}$ Solving this gives, $[Cr^{3+}(aq)] = 3.8 \times 10^{-3} M$ Answer: 3.8×10^{-3} M Calculate the equilibrium constant of the reaction at 25 °C. The equilibrium constant is related to the standard cell potential through: $E^{\circ} = \frac{RT}{mE} \ln K$ Using $E^{0} = +0.50$ V, $0.50 \text{ V} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{6 \times 96485 \text{ mol}^{-1}} \ln K$

Solving this gives:

 $K = 5.5 \times 10^{50}$

Answer: 5.5×10^{50}

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the standard Gibbs free energy of the reaction at 25 °C.

The Gibbs free energy change is related to the standard cell potential through:

 $\Delta G^{\circ} = -nFE^{\circ}$ = - 6 × (96485 mol⁻¹) × (0.50 V) = -290 kJ mol⁻¹

Answer: -290 kJ mol⁻¹

Express the overall reaction in the shorthand voltaic cell notation.

 $\operatorname{Cr}(s) | \operatorname{Cr}^{3+}(aq) || \operatorname{Ni}^{2+}(aq) | \operatorname{Ni}(s)$

Marks • A strip of copper and a strip of zinc are embedded in a lemon, and are connected by 3 wires to a voltmeter; a voltage is generated and can be read at the voltmeter. What chemical reactions are occurring that lead to the generation of current? $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ at the anode $2H^+(aq) + 2e^- \rightarrow H_2(g)$ at the cathode Assuming there are no losses in the circuit and the conditions are similar to standard, what voltage can be read at the voltmeter? The Zn^{2+} / Zn reduction potential is the more negative so is reversed to give E_{ox}^{o} = +0.76 V. The H⁺ / H₂ reduction potential is E°_{red} = 0.00 V. Overall $E^{0} = E^{0}_{ox} + E^{0}_{red} = (+0.76 + 0.00) V = +0.76 V$ 2 • The rate constant of a polymer cross-linking reaction was established as a function of temperature. How can we demonstrate that the kinetics of this reaction follow Arrhenius behaviour? If it does follow Arrhenius behaviour, how can we derive the activation energy for the reaction and the pre-exponential factor A? The Arrhenius equation relates the rate constant to the temperature, $k = Ae^{-Ea/RT}$ Taking natural logarithms of this gives $\ln k = \ln A - \frac{1}{T} \left(\frac{E_a}{P} \right)$ A plot of lnk (on y-axis) versus $\frac{1}{T}$ (on x-axis) will be a straight line if Arrhenius behaviour is followed. If so, it has a gradient of $-\frac{E_a}{D}$ and a y-intercept of lnA.

Marks • A 20.0 mL sample of 0.121 M Fe^{2+} in an acid solution was used to titrate 23.5 mL of 4 a KMnO₄ solution of unknown concentration. Write the balanced redox reaction that occurs in solution upon titration, and calculate the molarity of the KMnO₄ solution. From the standard reduction potentials, the two relevant half cells are: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(1)$ $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ Giving the overall reaction: $5Fe^{2+}(aq) + MnO_4(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(1)$ The number of moles of Fe^{2+} used in the titration is: number of moles of Fe^{2+} = concentration × volume $= 0.121 \text{ mol } L^{-1}) \times (0.0200 \text{ L}) = 2.42 \times 10^{-3} \text{ mol}$ From the balanced equation, the number of moles of $MnO_4^{-}(aq)$ is therefore: number of moles of MnO₄⁻ = $1/5 \times 2.42 \times 10^{-3}$ mol = 4.84×10^{-4} mol This amount is present in 23.5 mL so its concentration must be: concentration = number of moles / volume $= 4.82 \times 10^{-4} \text{ mol} / 0.0235 \text{ L} = 0.0206 \text{ M}$ Answer: 0.0206 M

• Why do phospholipids self-assemble in solution, what structures do they form, and why are they relevant to cell biology?

Phospholipids contain a hydrophilic head and 2 hydrophobic tails.

They self assemble in bilayers with the hydrophobic tails in the centre and the hydrophilic heads at the interface with the solution.

Lipid bilayers (intercalated with proteins) make up over 50 % of cell membranes in biology, as the bilayer arrangement makes an effective barrier against the free passage of water and ions into and out of cells.

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2012-N-14



• The major pollutants emitted by cars, NO(g), CO(g), NO₂(g) and CO₂(g), can react according to the following equation.

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The following rate data were collected at 215 °C.

Experiment	$[NO_2]_0(M)$	[CO] ₀ (M)	Initial rate $(d[NO_2]/dt, M s^{-1})$
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[NO_2]_0$ is kept constant and $[CO]_0$ is halved. There is no effect on the rate. The rate is not dependent on $[CO]_0$. It is zero order with respect to CO.

Between experiments (2) and (3), $[CO]_0$ is kept constant and $[NO]_0$ is doubled. This causes the rate to increase by a factor of $(5.76 \times 10^{-5} / 1.44 \times 10^{-5}) = 4$. The rate depends on the *square* of [NO]. It is second order with respect to NO.

Overall,

Rate =
$$k[NO_2]^2$$

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

The rate law is determined by the rate of the slowest step. The concentration of the species in this step are determined only by steps before it.

As the rate does not depend on [CO], it must be involved in steps *after* the rate determining step.

The rate depends on $[NO_2]^2$ which is consistent with two molecules of NO_2 colliding in the rate determining step.

The simplest mechanism which fits these points and is consistent with the overall chemical reaction is:

Step 1:	$NO_2 + NO_2 \rightarrow NO_3 + NO$	slow, rate determining step
Step 2:	$NO_3 + CO \rightarrow NO_2 + CO_2$	fast