Topics in the November 2013 Exam Paper for CHEM1612

Click on the links for resources on each topic.

2013-N-2:

- Introduction to Chemical Energetics
- Solutions
- Acids and Bases

2013-N-3:

- Introduction to Chemical Energetics
- Solubility

2013-N-4:

Gas Laws

2013-N-5:

Chemical Equilibrium

2013-N-6:

- Introduction to Chemical Energetics
- Solutions

2013-N-7:

- Chemical Equilibrium
- Introduction to Chemical Energetics

2013-N-8:

- Introduction to Chemical Energetics
- Chemical Equilibrium

2013-N-9:

- Radiochemistry
- Acids and Bases

2013-N-10:

• Complexes

2013-N-11:

• Redox Reactions and Introduction to Electrochemistry

2013-N-12:

• Introduction to Colloids and Surface Chemistry

2013-N-13:

• Chemical Kinetics

• Explain the following terms or concepts.

Third law of thermodynamics

A perfect pure crystal at absolute zero (0 K) has zero entropy. It is not possible to reduce the temperature of any system to absolutel in a finite number of finite operations.

Osmotic pressure

The pressure that needs to be applied to prevent water from flowing across a semipermeable membrane due to osmosis.

Lewis base

A species that can form a bond by donating a lone pair of electrons, *e.g.* H₂O.

• The specific heat capacity of water at 0 °C is undefined. Explain why this is so.

2

Marks

3

At 0 °C, any heat transferred into or out of the system is either causing the ice to melt or the water to freeze – there is no change in the temperature. Specific heat capacity is defined as $c = q/m\Delta T$. As there is no change in temperature, $\Delta T = 0$ and c is undefined.

Marks • Consider the following reaction: 3 $2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$ Calculate ΔG° for this reaction given the following data. $\Delta G^{\circ} = -139.56 \text{ kJ mol}^{-1}$ $4NO(g) \rightarrow 2N_2O(g) + O_2(g)$ $\Delta G^{\circ} = -69.70 \text{ kJ mol}^{-1}$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ Using $\Delta_r G^\circ = \sum \Delta_f G^\circ$ (products) $- \sum \Delta_f G^\circ$ (reactants), the free energy changes in the 3 reactions are, respectively: $\Delta_{\rm r}G^{\circ}(1) = 4\Delta_{\rm f}G^{\circ}({\rm NO}_2({\rm g})) - 2\Delta_{\rm f}G^{\circ}({\rm N}_2{\rm O}({\rm g}))$ $\Delta_{\rm r} G^{\circ}(2) = 2\Delta_{\rm f} G^{\circ}({\rm N}_2{\rm O}({\rm g})) - 4\Delta_{\rm f} G^{\circ}({\rm NO}({\rm g})) = -139.56 \text{ kJ mol}^{-1}$ $\Delta_r G^{\circ}(3) = 2\Delta_f G^{\circ}(NO_2(g)) - 2\Delta_f G^{\circ}(NO(g)) = -69.70 \text{ kJ mol}^{-1}$ Mathematically, the combination $2\Delta_r G^{\circ}(3) - \Delta_r G^{\circ}(2)$ leads to $\Delta_r G^{\circ}(1)$: $2\Delta_{\rm r}G^{\circ}(3) = 4\Delta_{\rm f}G^{\circ}({\rm NO}_2({\rm g})) - 4\Delta_{\rm f}G^{\circ}({\rm NO}({\rm g}))$ $\Delta_{\rm r}G^{\circ}(2) = 2\Delta_{\rm f}G^{\circ}({\rm N}_2{\rm O}({\rm g})) - 4\Delta_{\rm f}G^{\circ}({\rm NO}({\rm g}))$ $2\Delta_{\rm r}G^{\circ}(3) - \Delta_{\rm r}G^{\circ}(2) = 4\Delta_{\rm f}G^{\circ}({\rm NO}_2({\rm g})) - 2\Delta_{\rm f}G^{\circ}({\rm N}_2{\rm O}({\rm g})) = \Delta_{\rm f}G^{\circ}(1)$ $\Delta_{\rm f} G^{\circ}(1) = 2\Delta_{\rm r} G^{\circ}(3) - \Delta_{\rm r} G^{\circ}(2) = [(2 \times -69.70) - (-139.56)] \text{ kJ mol}^{-1}$ $= 0.16 \text{ kJ mol}^{-1}$ Answer: 0.16 kJ mol^{-1} • Calculate the molar solubility of silver sulfide, Ag₂S, given that K_{sp} is 8×10^{-51} 3 at 25 °C. The dissolution reaction and solubility product are:

 $Ag_2S(s) \implies 2Ag^+(aq) + S^{2-}(aq) \qquad K_{sp} = [Ag^+(aq)]^2[S^{2-}(aq)]$

If x mol of Ag₂S dissolve in one litre, then $[Ag^+(aq)] = 2x M$ and $[S^{2-}(aq)] = x M$. Hence:

$$K_{\rm sp} = (2x)^2(x) = 4x^3 = 8 \times 10^{-51}$$
 so $x = 1 \times 10^{-17}$

Answer: 1×10^{-17}

- Marks
 - 5
- Calcium carbide, CaC_2 , reacts with water to produce a gas and a solution containing OH⁻ ions. A sample of CaC₂ was treated with excess water and the resulting gas was collected in an evacuated 5.00 L glass bulb. At the completion of the reaction, the pressure inside the bulb was 1.00×10^5 Pa at a temperature of 26.8 °C. Calculate the amount (in mol) of the gas produced.

5.00 L corresponds to 5.00×10^{-3} m³ and 26.8 °C corresponds to (26.8 + 273.0) K = 299.8 K. Using the ideal gas law:

$$PV = nRT$$

n = PV / RT= (1.00 ×10⁵ Pa)(5.00 × 10⁻³ m³) / ((8.314 Pa m³ mol⁻¹ K⁻¹)(299.8 K)) = 0.201 mol

Answer: 0.201 mol

Given that the mass of the gas collected was 5.21 g, show that the molar mass of the gas is 25.9 g mol^{-1} .

As the number of moles = mass / molar mass:

molar mass = mass / number of moles = $5.21 \text{ g} / 0.201 \text{ mol} = 25.9 \text{ g mol}^{-1}$

Suggest a molecular formula for the gas and write a balanced equation for the reaction that occurred.

As the gas was produced from CaC_2 which contains C_2^{2-} , a likely formula is C_2H_2 :

molar mass = $(2 \times 12.01 \text{ (C)} + 2 \times 1.008 \text{ (H)}) \text{ g mol}^{-1} = 26.0 \text{ g mol}^{-1}$

This is formed by addition of H₂O:

 $CaC_2(s) + 2H_2O(l) \rightarrow Ca^{2+}(aq) + 2OH^{-}(aq) + C_2H_2(g)$

- Marks • Methane, CH₄, reacts with hydrogen sulfide, H₂S, according the following 5 equilibrium: $CH_4(g) + 2H_2S(g) \iff CS_2(g) + 4H_2(g)$ In an experiment 1.00 mol of CH₄, 2.00 mol of H₂S, 1.00 mol of CS₂ and 2.00 mol of H₂ are mixed in a 250 mL vessel at 960 °C. At this temperature, $K_c = 0.034$ (based on a standard state of 1 mol L^{-1}). Calculate the reaction quotient, Q, and hence predict in which direction the reaction will proceed to reach equilibrium? Explain your answer. Using concentration = number of moles / volume, the concentrations when the gases are mixed are: $[CH_4(g)] = 1.00 \text{ mol} / 0.250 \text{ L} = 4.00 \text{ mol} \text{ L}^{-1}$ $[H_2S(g)] = 2.00 \text{ mol} / 0.250 \text{ L} = 8.00 \text{ mol} \text{ L}^{-1}$ $[CS_2(g)] = 1.00 \text{ mol} / 0.250 \text{ L} = 4.00 \text{ mol} \text{ L}^{-1}$ $[H_2(g)] = 2.00 \text{ mol} / 0.250 \text{ L} = 8.00 \text{ mol} \text{ L}^{-1}$ From the chemical equation, the reaction quotient is: $Q = \frac{[CS_2(g)][H_2(g)]^4}{[CH_4(g)][H_2S(g)]^2} = \frac{(4.00)(8.00)^4}{(4.00)(8.00)^2} = 64.0$ As $Q > K_c$, therefore the reaction will shift to the left until $Q = K_c$ Show that the system is at equilibrium when $[CH_4(g)] = 5.56$ M. A reaction table can be constructed to calculate the equilibrium concentrations: $CH_4(g) +$ - $2H_2S(g)$ $CS_2(g) +$ $4H_2(g)$ Initial 4.00 8.00 8.00 4.00 +2x-4xChange +x-x Equilibrium 4.00 + x8.00 + 2x8.00 - 4x4.00 - xIf $[CH_4(g)]_{equilibrium} = 5.56$ M then 4.00 + x = 5.56 M and x = 1.56 M. Hence: $[CH_4(g)]_{equilibrium} = (4.00 + x) M = 5.56 M$ $[H_2S(g)]_{equilibrium} = (8.00 + 2x) M = 11.12 M$ $[CS_2(g)]_{equilibrium} = (4.00 - x) M = 2.44 M$ $[H_2(g)]_{equilibrium} = (8.00 - 4x) M = 1.76 M.$ With these concentrations:
 - $K_{\rm c} = \frac{[\rm CS_2(g)][\rm H_2(g)]^4}{[\rm CH_4(g)][\rm H_2S(g)]^2} = \frac{(2.44)(1.76)^4}{(5.56)(11.12)^2} = 0.034$

- Marks
 - 2

• Isooctane, an important constituent of petrol, has a boiling point of 99.3 °C and a standard enthalpy of vaporisation of 37.7 kJ mol⁻¹. What is ΔS° (in J K⁻¹ mol⁻¹) for the vaporisation of isooctane? At the boiling point, $\Delta_{vap}G^{\circ} = \Delta_{vap}H^{\circ} - T\Delta_{vap}S^{\circ} = 0$. Hence: $\Delta_{\text{vap}}S^{\circ} = \Delta_{\text{vap}}H^{\circ} / T = (37.7 \times 10^3 \text{ J mol}^{-1}) / (99.3 + 273) \text{ K} = +101 \text{ J K}^{-1} \text{ mol}^{-1}$ Answer: $+101 \text{ J K}^{-1} \text{ mol}^{-1}$ • An aqueous solution with a volume of 10.0 mL contains 0.025 g of a purified protein 3 of unknown molecular weight. The osmotic pressure of the solution was measured in an osmometer to be 0.0036 atm at 20.0 °C. Assuming ideal behaviour and no dissociation of the protein, estimate its molar mass in $g \text{ mol}^{-1}$. A pressure of 0.0036 atm corresponds to $(0.0036 \times 101.3 \times 10^3)$ Pa = 360 Pa. The osmotic pressure, Π , is related to the concentration of the solute through $\Pi = cRT$ Hence: $c = \Pi / RT = 360 \text{ Pa} / ((8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1})((20.0 + 273) \text{ K}))$ $= 0.15 \text{ mol m}^{-3} = 0.15 \times 10^{-3} \text{ mol L}^{-1}$ The number of moles in 10.0 mL is therefore: number of moles = concentration × volume = $(0.15 \times 10^{-3} \text{ mol } \text{L}^{-1}) \times (0.0100 \text{ L}) = 1.5 \times 10^{-6} \text{ mol}$ As this is the number of moles in 0.025 g, the molar mass is: molar mass = mass / number of moles $= 0.025 \text{ g} / 1.5 \times 10^{-6} \text{ mol} = 17000 \text{ g mol}^{-1}$ Answer: 17000 g mol⁻¹

Marks

3

• Ammonia is synthesised according to the following reaction.

$$N_2(g) + 3H_2(g) \implies 2NH_3(g)$$

At 500 °C this reaction has a K_c of 6.0×10^{-2} . ΔH° for this reaction is -92 kJ mol⁻¹. Calculate the value of K_c at 200 °C.

The equilibrium constant varies with temperature according to the van't Hoff equation:

$$\ln\frac{K_2}{K_1}=\frac{-\Delta H^{\circ}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Hence:

$$\ln \frac{K_2}{6.0 \times 10^{-2}} = \frac{+92 \times 10^3}{8.314} \left(\frac{1}{(200 + 273)} - \frac{1}{(500 + 273)} \right)$$

 $K_2 = 530$

Answer: 530

• Good wine will turn to vinegar if it is left exposed to air because the alcohol is oxidised to acetic acid. The equation for the reaction is

 $C_2H_5OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$

Calculate ΔS° for this reaction in J K⁻¹ mol⁻¹.

Data:		$\Delta S^{\circ} (J K^{-1} mol^{-1})$
	$C_2H_5OH(1)$	161
	$O_2(g)$	205.0
	CH ₃ COOH(1)	160
	$H_2O(l)$	69.96

Using $\Delta_r S^\circ = \sum S^\circ$ (products) $-\sum S^\circ$ (reactants):

$$\Delta_r S^\circ = ((160 + 69.96) - (161 + 205.0)) J K^{-1} mol^{-1} = -136 J K^{-1} mol^{-1}$$

Answer: -136 J K⁻¹ mol⁻¹

2



Relance the following nuclear reactions	and name the decay process occurring	Marks		
Equation				
Equation	Name of decay process	_		
$^{15}_{8}$ O $\rightarrow ^{15}_{7}$ N + $^{0}_{1}e$	positron emission			
$^{238}_{92}$ U $\rightarrow ^{234}_{90}$ Th + $^{4}_{2}$ He	a decay			
$^{40}_{19}\mathrm{K}$ + $^{0}_{-1}e$ \rightarrow $^{40}_{18}\mathrm{Ar}$	electron capture			
• What amount of NaOH (in mol) needs t give a solution with a pH of 5.00? The	• What amount of NaOH (in mol) needs to be added to 250 mL of 0.10 M acetic acid to give a solution with a pH of 5.00? The pK_a of acetic acid is 4.76.			
If the concentration of OH ⁻ which is a acid to produce its conjugate base, ac	added is <i>x</i> M then this will react with acetic etate, so that:			
[acid] = (0.10 - x) M and [base] = x M				
The Henderson-Hasselbalch equation can be used to work out the ratio of these needed for a pH of 5.00:				
$pH = pK_a + \log\frac{[base]}{[acid]}$				
$5.00 = 4.76 + \log \frac{x}{0.10 - x}$				
Hence:				
$\frac{x}{0.10-x} = 10^{0.24} \text{so } x = 0.0634$				
To achieve [OH ⁻ (aq)] = 0.0634 mol L ⁻ that must be added is:	⁻¹ in 250 mL, the number of moles of NaOH			
number of moles = concentration × volume = $0.0634 \text{ mol } \text{L}^{-1} \times 0.250 \text{ L} = 0.016 \text{ mol}$				
	Answer: 0.016 mol			

CHEM1612

• Complete the follow	te the following table. Marks 9				
Coordination compound	Oxidation number of transition metal	Number of <i>d</i> electrons around transition metal	Arrangement of <i>d</i> electrons		
K ₂ [PtCl ₄]	+2	<i>d</i> ⁸	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$		
Na[MnO ₄]	+7	d^0			
(NH ₄) ₂ [CoCl ₄]	+2	d^7	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$		
[Cr(NH ₃) ₅ (OH ₂)]Cl ₃	+3	d^3	$\uparrow \uparrow \uparrow$		
Identify one paramagnetic and one diamagnetic species from the above table.					
Paramagnetic: (NH ₄) ₂ [Cr(NH	[CoCl4] and H3)5(OH2)]Cl3	Diamagnetic: I	K ₂ [PtCl ₄] and Na[MnO ₄]		

2013-N-11



• What is the electrochemical potential of the following cell at 25 °C? Fe | FeSO₄ (0.010 M) || (FeSO₄ (0.100 M) | Fe

As this is a concentration cell, $E^{\circ} = 0$ V. The cell notation corresponds to the 0.100 M solution being the cathode, where reduction occurs, and the 0.010 M solution being the anode, where oxidation occurs. The two half cells are:

Anode: $Fe(s) \rightarrow Fe^{2+}(aq, 0.010 \text{ M}) + 2e^{-}$ Cathode: $Fe^{2+}(aq, 0.100 \text{ M}) + 2e^{-} \rightarrow Fe(s)$ Overall: $Fe^{2+}(aq, 0.100 \text{ M}) \rightarrow Fe^{2+}(aq, 0.010 \text{ M})$

The potential is given by the Nernst equation for this two electron reaction:

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

 $= (0 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{2 \times 96485 \text{ mol}^{-1}} \ln \frac{(0.010)}{(0.100)} = +0.0296 \text{ V}$

Answer: +0.0296 V

• Calculate the mass of aluminium which can be produced with the same quantity of electricity that is used to produce 1.00 kg of copper metal.

2

As the molar mass of Cu is 63.55 g mol⁻¹, 1.00 kg corresponds to:

number of moles = mass / molar mass = 1.00×10^3 g / 63.55 g mol⁻¹ = 15.7 mol.

Reduction of Cu²⁺ requires 2 mol of electrons. Hence, the number of electrons requires to produce 15.7 mol is:

number of moles of electrons = 2×15.7 mol = 31.5 mol

Reduction of a mole of Al^{3+} requires 3 mol of electrons. Hence, the number of moles of aluminium produced by 31.5 mol of electrons is:

number of moles of aluminium = 31.5 / 3 mol = 10.5 mol

As the molar mass of aluminium is 26.98 g mol⁻¹, this corresponds to:

mass = number of moles \times molar mass = 10.5 mol \times 26.98 g mol⁻¹ = 283 g.

Answer: 283 g

ANSWER CONTINUES ON THE NEXT PAGE

• Explain why Na(s) cannot be obtained by the electrolysis of aqueous NaCl solutions.

From the table of standard reduction potentials:

 $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83 V$ $Na^+(aq) + e^- \rightarrow Na(s) \qquad E^\circ = -2.71 V$

Water has a much greater reduction potential than Na⁺ and hence is preferentially reduced, even when the overpotential of water is considered.

• Give a brief definition or explanation of the following concepts in colloid science.
louble layer
The layers of ions on a colloidal particle. The inner (Stern) layer consists of ions that are electrostatically attracted to the charged particle. The outer (diffuse) layer consists of counter ions.
counter ion
An ion of opposite charge to another chemical species.
isoelectric point
The pH value at which an amino acid or peptide has zero net charge.
zeta potential
The zeta potential is a measure of repulsion between adjacent, similarly charged particles in a colloid (<i>i.e.</i> the stability of a colloid). Colloids with high zeta potentials are electrically stabilized, whilst those with low potentials tend to coagulate.
flocculation
The process in which colloidal particles clump together to form larger particles causing separation of the colloid.
electrokinetic mobility
The movement of colloidal particles in response to the application of an electric field.

•	The following	reaction is	run from 4	different	starting positions	5.
	The following	reaction is	run nom i	uniterent	suiting positions	·•

$H_2SeO_3 + 6I^- + 4H^- \rightarrow Se + 2I_3^- + 3H_2O$					
Experiment	Initial [H ₂ SeO ₃] (mol L ⁻¹)	Initial $[I^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Initial rate of increase of $[I_3^-]$ (mol L ⁻¹ s ⁻¹)	
1	0.100	0.100	0.100	1.000	
2	0.100	0.075	0.100	0.422	
3	0.075	0.100	0.100	0.750	
4	0.100	0.075	0.075	0.237	

Determine the rate law for the reaction.

The rate law is of the form:

 $rate = k[H_2SeO_3]^x[I^-]^y[H^+]^z$

Between experiments (1) and (3), $[I^-]$ and $[H^+]$ are both constant. The change in rate is due to the change in $[H_2SeO_3]$:

$$\frac{\operatorname{rate}(3)}{\operatorname{rate}(1)} = \frac{k(0.075)^{x}(0.100)^{\frac{y}{2}}(0.100)^{\frac{x}{2}}}{k(0.100)^{x}(0.100)^{\frac{y}{2}}(0.100)^{\frac{x}{2}}} = \frac{(0.075)^{x}}{(0.100)^{x}} = \frac{0.750}{1.000} \text{ so } x = 1$$

Between experiments (1) and (2), $[H_2SeO_3]$ and $[H^+]$ are both constant. The change in rate is due to the change in $[I^-]$:

$$\frac{\operatorname{rate}(2)}{\operatorname{rate}(1)} = \frac{k(0.100)^{\underline{x}}(0.075)^{y}(0.100)^{\underline{x}}}{k(0.100)^{\underline{x}}(0.100)^{y}(0.100)^{\underline{x}}} = \frac{(0.075)^{y}}{(0.100)^{y}} = \frac{0.422}{1.000} \text{ so } y = 3$$

Between experiments (2) and (4), $[H_2SeO_3]$ and $[\Gamma]$ are both constant. The change in rate is due to the change in $[H^+]$:

$$\frac{\operatorname{rate}(4)}{\operatorname{rate}(2)} = \frac{k(0.100)^{\frac{2}{3}}(0.075)^{\frac{2}{3}}}{k(0.100)^{\frac{2}{3}}(0.075)^{\frac{2}{3}}} = \frac{(0.075)^{z}}{(0.100)^{z}} = \frac{0.237}{0.422} \text{ so } z = 2$$

Overall:

 $rate = k[H_2SeO_3][I^-]^3[H^+]^2$

What is the value of the rate constant?

Using, for example, experiment (1), the initial rate of increase of $[I_3^-] = 1.000$ mol $L^{-1} s^{-1}$. As $2I_3^-$ are produced in the reaction:

rate of reaction = $\frac{1}{2}$ × rate of increase of I_3^- = 0.5000 mol L⁻¹ s⁻¹

Marks 4 $rate = k[H_2SeO_3][\Gamma]^3[H^+]^2$ = k (0.100 mol L⁻¹)(0.100 mol L⁻¹)^3(0.100 mol⁻¹)^2 = 0.5000 mol L⁻¹ s⁻¹ Hence: k = (0.5000 mol L⁻¹ s⁻¹) / (1.00 × 10⁻⁶ mol⁶ L⁻⁶) = 5.00 × 10⁵ L⁵ mol⁻⁵ s⁻¹ Answer: 5.00 × 10⁵ L⁵ mol⁻⁵ s⁻¹