Topics in the November 2006 Exam Paper for CHEM1612

Click on the links for resources on each topic.

Marks
6

- The final step in the industrial production of urea, $(NH_2)_2CO$, is:

$CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + (NH_2)_2CO(s)$　　　　$\Delta H° = \text{-90.1 kJ mol}^{-1}$
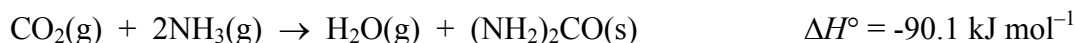
Using the following data, calculate the standard enthalpy of formation of solid urea.
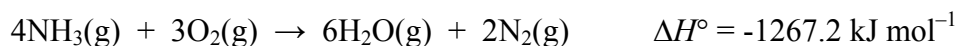
$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g)$　　　$\Delta H° = \text{-1267.2 kJ mol}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$　　　　　　　　　$\Delta H° = \text{-393.5 kJ mol}^{-1}$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$　　　　　　　$\Delta H° = \text{-483.6 kJ mol}^{-1}$

Using $\Delta_{rxn}H^0 = \sum m\Delta_f H^0 (\text{products}) - \sum n\Delta_f H^0 (\text{reac} \tan \text{ts})$ for the reaction,

$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g)$
$\Delta_{rxn}H^0 = [6\Delta_f H^0 (H_2O(g))] - [4\Delta_f H^0 (NH_3(g))]$
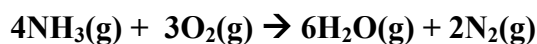
as $\Delta_f H^0 (N_2(g))$ and $\Delta_f H^0 (O_2(g))$ are both zero for elements in the standard states. Using $\Delta_{rxn}H^0 = \text{-1267.2 kJ mol}^{-1}$ and $\Delta_f H^0 (H_2O(g)) = 0.5 \times \text{-483.6 kJ mol}^{-1}$,

$\Delta_{rxn}H^0 = [6 \times 0.5 \times -483.6] - [4\Delta_f H^0 (NH_3(g))] = -1267.2 \text{ kJ mol}^{-1}$

$\Delta_f H^0 (NH_3(g)) = \text{-45.9 kJ mol}^{-1}$

Using $\Delta_{rxn}H^0 = \sum m\Delta_f H^0 (\text{products}) - \sum n\Delta_f H^0 (\text{reac} \tan \text{ts})$ for the reaction,

$CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + (NH_2)_2CO(s)$
$\Delta_{rxn}H^0 = [\Delta_f H^0 (H_2O(g)) + \Delta_f H^0 ((NH_2)_2CO(g))]$
　　　　　$-[\Delta_f H^0 (CO_2(g)) + 2\Delta_f H^0 (NH_3(g))]$

As $\Delta_{rxn}H^0 = \text{-90.1 kJ mol}^{-1}$ and $\Delta_f H^0 (H_2O(g))$, $\Delta_f H^0 (CO_2(g))$ and

$\Delta_f H^0 (NH_3(g))$ are $0.5 \times$ -483.6 , -393.5 and -45.9 kJ mol^{-1} respectively,

$\Delta_{rxn}H^0 = [(0.5 \times -483.6) + \Delta_f H^0 ((NH_2)_2CO(g))]$
　　　　　$-[-393.5 + (2 \times -45.9)] = -90.1 \text{ kJ mol}^{-1}$

$\Delta_f H^0 ((NH_2)_2CO(g)) = \text{-333.6 kJ mol}^{-1}$

Answer: **-333.6 kJ mol⁻¹**

ANSWER CONTINUES ON THE NEXT PAGE

The formation of urea in the industrial process is only spontaneous below 821 °C. What is the value of the entropy change $\Delta S°$ (in J K^{-1} mol^{-1}) for the reaction?

The reaction is spontaneous when $\Delta G° < 0$. As $\Delta G° = \Delta H° - T\Delta S$ and assuming that $\Delta H°$ and $\Delta S°$ are independent of temperature, this occurs at temperatures below T = 821 °C

$$\Delta H° - T\Delta S < 0$$

Using $\Delta H° = -90.1$ kJ mol^{-1} for the industrial, at T = (821 + 273) = 1094 K,

$$(-90.1 \times 10^3) - (1094)\Delta S° = 0 \quad \text{so } \Delta S° = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer: **-82.4 J K^{-1} mol^{-1}**

Rationalise the sign of $\Delta S°$ in terms of the physical states of the reactants and products.

The reaction,

$$CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + (NH_2)_2CO(s)$$

involves the conversion of 3 moles of gas $\rightarrow$ 1 mole of gas. This corresponds to an increase in ordering which is consistent with a reduction in entropy (so $\Delta S° < 0$).

Marks
2

- The specific heat capacity of water is 4.18 J g^{-1} K^{-1} and the specific heat capacity of copper is 0.39 J g^{-1} K^{-1}. If the same amount of energy were applied to a 1.0 mol sample of each substance, both initially at 25 °C, which substance would get hotter? Show all working.

Using q = C × m × ΔT, the temperature change for a substance of mass m and specific heat capacity C when an amount of heat equal to q is supplied is given by:

$$\Delta T = \frac{q}{C \times m}$$

The atomic mass of copper is 63.55. Hence, the temperature change for 1.0 mol of copper is

$$\Delta T \text{ (copper)} = \frac{q}{(0.39 \times 63.55)} = \frac{q}{24.8} \text{ °C}$$

The molar mass of H$_2$O is (2 × 1.008 (H)) + 16.00 (O) = 18.016. Hence, the temperature change for 1.0 mol of water is

$$\Delta T \text{ (water)} = \frac{q}{(4.18 \times 18.016)} = \frac{q}{75.3} \text{ °C}$$

Hence,

$$\Delta T \text{ (copper)} > \Delta T \text{ (water)}$$

Answer: **Copper**

3

- Explain why the acidity of hydrogen halides *increases* with increasing halogen size (*i.e.*, K_a (HCl) < K_a (HBr) < K_a (HI)), while the acidity of hypohalous acids *decreases* with increasing halogen size (*i.e.*, K_a (HOCl) > K_a (HOBr) > K_a (HOI)).

For the hydrogen halides, the length of the H-X bond increases and hence gets weaker as the halogen gets bigger,. The weaker the bond, the more easily the H$^+$ dissociates.

For the hypohalous acids, as the electronegativity of the halide increases, the more electron density it pulls from the O-H bond towards itself. This results in the O-H bond becoming more polar and increasing the ease with which the H$^+$ will be lost.

- The K_a of benzoic acid is 6.3×10^{-5} M at 25 °C.

  Calculate the pH of a 0.0100 M aqueous solution of sodium benzoate (C_6H_5COONa).

As benzoic acid is a weak acid, its conjugate base, $C_6H_5COO^-$, is a weak base and so [OH⁻] must be calculated using the reaction table:

	$C_6H_5COO^-$	H_2O	$\rightleftharpoons$	OH^-	C_6H_5COOH
initial	0.0100	large		0	0
change	-x	negligible		+x	+x
final	0.0100 – x	large		x	x

The equilibrium constant K_b is given by:

$$K_b = \frac{[OH^-][C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{x^2}{0.0100 - x}$$

For an acid and its conjugate base in aqueous solution, $K_a \times K_b = K_w = 10^{-14}$. Hence,

$$K_b = \frac{10^{-14}}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$$

As K_b is very small, $0.0100 - x \sim 0.0100$ and hence:

$$x^2 = 0.0100 \times (1.6 \times 10^{-10}) \quad \text{or} \quad x = 1.3 \times 10^{-6} \text{ M} = [OH^-(aq)]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = -\log_{10}[1.3 \times 10^{-6}] = 5.9$$

Finally, pH + pOH = 14.0 so

$$pH = 14.0 - 5.9 = 8.1$$

Answer: **pH = 8.1**
Answer: **pH = 4.1**

ANSWER CONTINUES ON THE NEXT PAGE

A buffer solution is prepared by adding 375 mL of this 0.0100 M aqueous solution of sodium benzoate to 225 mL of 0.0200 M aqueous benzoic acid. Calculate the pH of the buffer solution.

375 mL of a 0.0100 of benzoate contains,

moles of benzoate = volume×concentration = 0.375×0.0100 = 3.75×10^{-3} mol

225 mL of a 0.0200 of benzoic acid contains,

moles of benzoic acid = 0.225×0.0200 = 4.50×10^{-3} mol

The mixture has a volume of (375 + 225) = 600 mL so the concentrations of benzoate (base) and benzoic acid (acid) are:

$$[\text{base}] = \frac{\text{number of moles}}{\text{volume}} = \frac{3.75\times10^{-3}}{0.600} = 6.25\times10^{-3} \text{ M}$$

$$[\text{acid}] = \frac{4.50\times10^{-3}}{0.600} = 7.50\times10^{-3} \text{ M}$$

As pK_a = -log$_{10}K_a$,
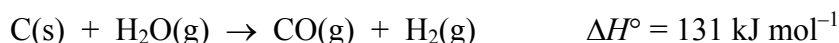
pK_a = -log$_{10}$(6.3 × 10^{-5}) = 4.2

The pH of the buffer can be calculated using the Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 4.2 + \log_{10}\left(\frac{6.25\times10^{-3}}{7.50\times10^{-3}}\right) = 4.1$$

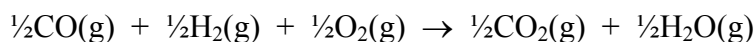Answer: **pH = 4.1**

- "Water gas" is a mixture of combustible gases produced from steam and coal according to the following reaction:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \qquad \Delta H° = 131 \text{ kJ mol}^{-1}$$

The equation for the complete combustion of 1 mol of water gas (*i.e.* 0.5 mol CO(g) and 0.5 mol H_2(g)) can be written as:

$$\tfrac{1}{2}CO(g) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow \tfrac{1}{2}CO_2(g) + \tfrac{1}{2}H_2O(g)$$

Calculate the standard enthalpy of combustion of water gas, given the following thermochemical data.

$$\Delta H°_{vap} (H_2O) = 44 \text{ kJ mol}^{-1}$$
$$\Delta H°_f (H_2O(l)) = -286 \text{ kJ mol}^{-1}$$
$$\Delta H°_f (CO_2(g)) = -393 \text{ kJ mol}^{-1}$$

Using $\Delta_{rxn}H^o = \sum m\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reac tan ts})$ for the vaporization of water ($H_2O(l) \rightarrow H_2O(g)$) gives

$$\Delta_{vap}H^o = [\Delta_f H^o(H_2O(g))] - [\Delta_f H^o(H_2O(l))]$$

$$= [\Delta_f H^o(H_2O(g))] - (-286) = +44$$

Hence $\Delta_f H^o(H_2O(g)) = (+44) + (-286) = -242 \text{ kJ mol}^{-1}$

Using $\Delta_{rxn}H^o = \sum m\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reac tan ts})$ for the reaction,

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \text{ gives}$$
$$\Delta_{rxn}H^o = [\Delta_f H^o(CO(g)] - [\Delta_f H^o(H_2O(g))]$$

$$= [\Delta_f H^o(CO(g)] - (-242) = +131$$

as $\Delta_f H^o(H_2(g))$ and $\Delta_f H^o(C(s))$ are both zero for elements in their standard states. Hence $\Delta_f H^o(CO(g) = -111 \text{ kJ mol}^{-1}$

Using $\Delta_{rxn}H^o = \sum m\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reac tan ts})$ for the reaction,

$$\tfrac{1}{2}CO(g) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow \tfrac{1}{2}CO_2(g) + \tfrac{1}{2}H_2O(g) \text{ gives}$$
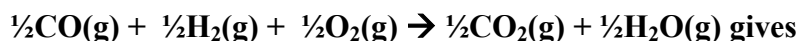
$$\Delta_{comb}H^o = [\tfrac{1}{2}\Delta_f H^o(CO_2(g)) + \tfrac{1}{2}\Delta_f H^o(H_2O(g))] - [\tfrac{1}{2}\Delta_f H^o(CO(g))]$$

as the enthalpy of formation of H_2(g) and O_2(g) are both zero for elements in their standard states. Hence,

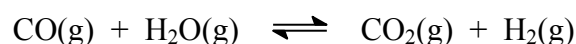$$\Delta_{comb}H^o = [(\tfrac{1}{2} \times -393) + (\tfrac{1}{2} \times -242)] - [(\tfrac{1}{2} \times -111)] = -262 \text{ kJ mol}^{-1}$$

Answer: **-262 kJ mol^{-1}**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
4

The $CO(g)$ in water gas can be reacted further with $H_2O(g)$ in the so-called "water-gas shift" reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At 900 K, $K_c = 1.56$ for this reaction. A sample of water gas flowing over coal at 900 K contains a 1:1 mole ratio of $CO(g)$ and $H_2(g)$, as well as 0.250 mol L^{-1} $H_2O(g)$. This sample is placed in a sealed container at 900 K and allowed to come to equilibrium, at which point it contains 0.070 mol L^{-1} $CO_2(g)$. What was the initial concentration of $CO(g)$ and $H_2(g)$ in the sample?

The reaction table is

	$CO(g)$	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	$H_2(g)$
initial	x	0.250		0	x
change	-0.070	-0.070		+0.070	+0.070
equilibrium	x – 0.070	0.250 – 0.070		0.070	x + 0.070

The equilibrium constant in terms of concentrations, K_c, is:

$$K_c = \frac{[CO_2(g)][H_2(g)]}{[H_2O(g)][CO(g)]} = \frac{(0.070)(x + 0.070)}{(0.180)(x - 0.070)} = 1.56$$

$x = [CO(g)]_{initial} = [H_2(g)]_{initial} = $ **0.12 mol L^{-1}**

$[CO] = [H_2] = $ **0.12 mol L^{-1}**

If the walls of the container are chilled to below 100 ºC, what will be the effect on the concentration of $CO_2(g)$?

At temperatures below 100 °C, the water vapour will condense to form $H_2O(l)$. Following Le Chatelier's principle, the equilibrium will shift to the left as $[H_2O(g)]$ is reduced by this process and so $[CO_2(g)]$ will decrease.

**Marks
6**

- The isomerisation of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P) is a key step in the metabolism of glucose for energy. At 298 K,

$$G6P \rightleftharpoons F6P \qquad \Delta G° = 1.67 \text{ kJ mol}^{-1}$$

Calculate the equilibrium constant for this process at 298 K.

Using ΔG° = -RTlnK,

1.67 × 10³ = -(8.314) × (298) × lnK

K = 0.510

Answer: **K = 0.510**

What is the free energy change (in kJ mol⁻¹) involved in a mixture of 3.00 mol of F6P and 2.00 mol of G6P reaching equilibrium at 298 K?
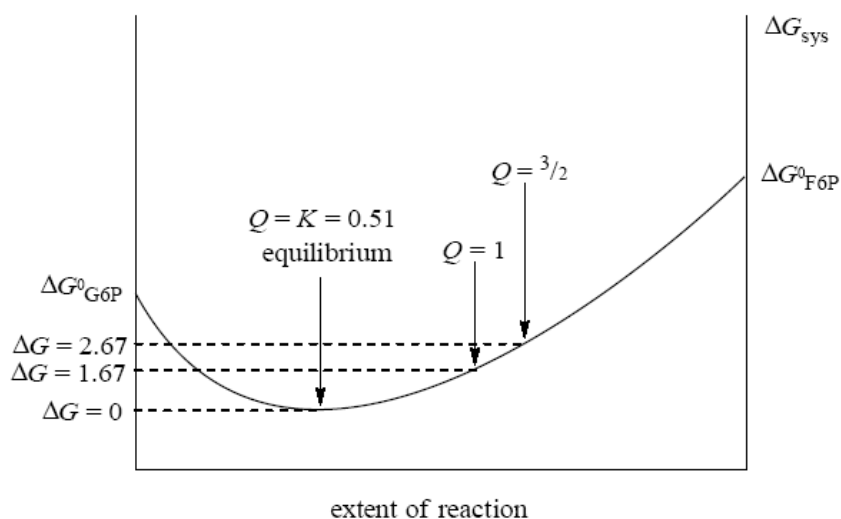
The reaction quotient, for the reaction, is Q = $\dfrac{[F6P]}{[G6P]} = \dfrac{3.00}{2.00} = 1.50$.

Using ΔG = ΔG° + RTlnQ,

ΔG = (1.67 × 10³) + (8.314 × 298) × ln(1.50) = +2670 J mol⁻¹ = +2.67 kJ mol⁻¹

Answer: **+2.67 kJ mol⁻¹**

Sketch a graph of G_{sys} *versus* "extent of reaction", with a curve showing how G_{sys} varies as G6P is converted to F6P. Indicate the position on this curve corresponding to 3.00 mol of F6P and 2.00 mol of G6P.

Marks
6

- Assume that NaCl is the only significant solute in seawater. A 1.000 L sample of seawater at 25 ºC and 1 atm has a mass of 1.0275 kg and contains 33.0 g of NaCl. At what temperature would this seawater freeze? The freezing point depression constant of water is 1.86 ºC kg mol^{-1}.

The formula mass of NaCl is 22.99 (Na) + 35.45 (Cl) = 58.44. Therefore, 33.0 g corresponds to:

$$\text{number of moles of NaCl} = \frac{\text{mass}}{\text{formula mass}} = \frac{33.0}{58.44} = 0.565 \text{ mol}$$

As each mole of NaCl dissolves to give 2 moles of particles (Na$^+$(aq) and Cl$^-$(aq)), the number of moles of solute is 2 × 0.565 = 1.129 mol.

If salt water contains only water and NaCl,

mass of water = 1.0275 – 0.0330 = 0.995 kg

Hence, the molality is

$$m = \frac{\text{moles of solute}}{\text{mass of solvent}} = \frac{1.129}{0.995} = 1.136 \text{ mol kg}^{-1}$$

The freezing point depression is then:

$$\Delta T_f = K_f \, m = 1.86 \times 1.136 = 2.11 \text{ °C}$$

As water normally freezes at 0°C, this saltwater will freeze at -2.11 °C.

Answer: **-2.11 °C**

ANSWER CONTINUES ON THE NEXT PAGE

The vapour pressure above pure H_2O is 23.76 mmHg at 25 ºC and 1 atm. Calculate the vapour pressure above this seawater under the same conditions.

The molar mass of H_2O is (2 × 1.008 (H)) + 16.00 (O) = 18.016. Therefore, 0.995 kg of water corresponds to

$$\text{moles of water} = \frac{\text{mass}}{\text{molar mass}} = \frac{(0.995 \times 10^3)}{18.016} = 55.3 \, \text{mol}$$

As 1.129 mol of solute is also present, the mole fraction, X, of water is

$$X_{water} = \frac{\text{number of moles of water}}{\text{total number of moles}} = \frac{55.3}{(55.3 + 1.129)} = 0.980$$

From Raoult's law,

$$P_{water} = X_{water} P_{water}{}^o = 0.980 \times 23.76 = 23.3 \, \text{mmHg}$$

Answer: **23.3 mmHg**

The desalination of seawater by reverse osmosis has been suggested as a way of alleviating water shortages in Sydney. What pressure (in Pa) would need to be applied to this seawater in order to force it through a semi-permeable membrane, yielding pure H_2O?

The concentration of solute is:

$$\text{concentration} = c = \frac{\text{number of moles of solute}}{\text{volume}} = \frac{1.129}{1.000} = 1.129 \, \text{M}$$

The osmotic pressure, Π, required is given by

$$\Pi = cRT = (1.129) \times (0.08206) \times (25 + 273) = 27.6 \, \text{atm}$$
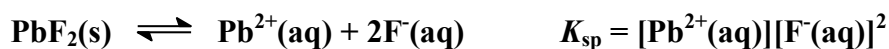
As 1 atm = 101.3 × 10³ Pa,

$$\Pi = 27.6 \times (101.3 \times 10^3) = 2800000 \, \text{Pa} = 2.80 \times 10^6 \, \text{Pa}$$

Answer: **2.80×10^6 Pa**

• The molar solubility of lead(II) fluoride, PbF_2, is found to be 2.6×10^{-3} M at 25 °C. Calculate the value of K_{sp} for this compound at this temperature.

Marks 2

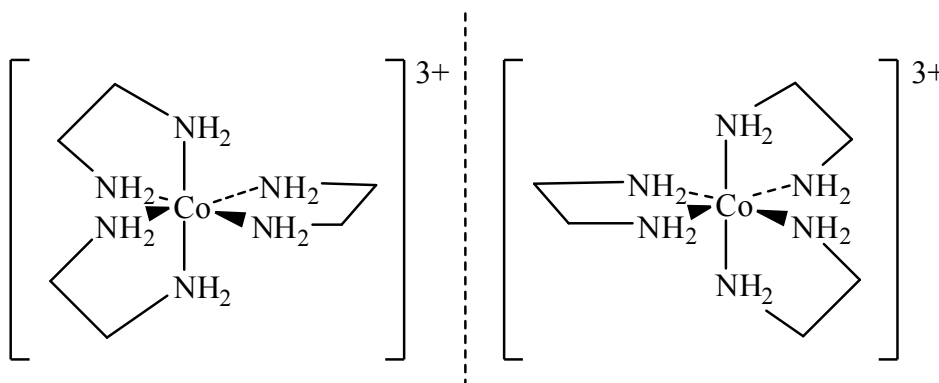**The solubility equilibrium and constant for PbF_2(s) are,**

$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$ $K_{sp} = [Pb^{2+}(aq)][F^-(aq)]^2$

As one moles of Pb^{2+}(aq) and two moles of F^-(aq) are produced for every mole of PbF_2(s) which dissolves, $[Pb^{2+}(aq)] = 2.6 \times 10^{-3}$ M and $[F^-(aq)] = (2 \times 2.6 \times 10^{-3}) = 5.2 \times 10^{-3}$ M. Hence,

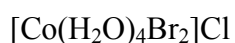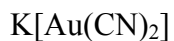**$K_{sp} = (2.6 \times 10^{-3}) \times (5.2 \times 10^{-3})^2 = 7.0 \times 10^{-8}$**

$K_{sp} = 7.0 \times 10^{-8}$

• Draw all stereoisomers of the complex ion of $[Co(en)_3]Br_3$.
  (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

2

• Name the following complexes.

2

| $[Co(H_2O)_4Br_2]Cl$ | **tetraaaquadibromocobalt(III) chloride** |
| $K[Au(CN)_2]$ | **potassium dicyanoaurate(I)** |

	Marks
• Write the chemical equation for the formation of the complex ion $[Cd(NH_3)_4]^{2+}$.	**2**

$$Cd^{2+} + 4NH_3 \; \rightleftharpoons \; [Cd(NH_3)_4]^{2+}$$
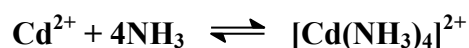
Write the associated stability constant expression (K_{stab}).

$$K_{stab} = \frac{[[Cd(NH_3)_4]^{2+}]}{[Cd^{2+}][NH_3]^4}$$

3

• The physiological properties of chromium depend on its oxidation state. Consider the half reaction in which Cr(VI) is reduced to Cr(III).

$$CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \rightarrow Cr(OH)_3(s) + 5OH^-(aq) \qquad E^o = -0.13 \text{ V}$$

Calculate the potential for this half reaction at 25 ^{o}C, where pH = 7.40 and $[CrO_4^{2-}(aq)] = 1.0 \times 10^{-6}$ M.

As pH + pOH = 14.00 and pOH = $-\log_{10}([OH^-(aq)])$, at pH = 7.40,

pOH = 14.00 – 7.40 = 6.60 = $-\log_{10}([OH^-(aq)])$

$[OH^-(aq)] = 10^{-6.60}$

The reaction quotient for the half-cell reaction is,

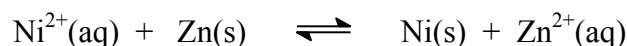$$Q = \frac{[OH^-(aq)]^5}{[CrO_4^{2-}(aq)]} = \frac{(10^{-6.60})^5}{(1.0 \times 10^{-6})} = 1.0 \times 10^{-27}$$

Using the Nernst equation for this three electron process,

$$E = E^o - \frac{RT}{nF}\ln Q = (-0.13) - \frac{8.314 \times (25+273)}{3 \times 96485}\ln(1.0 \times 10^{-27}) = +0.40 \text{ V}$$
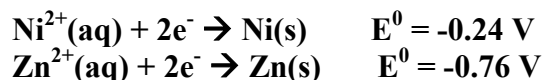
Answer: $E = +0.40$ V

- Consider the following reaction at 298 K.

$$Ni^{2+}(aq) + Zn(s) \rightleftharpoons Ni(s) + Zn^{2+}(aq)$$

Calculate ΔG^o for the cell. (Relevant electrode potentials can be found on the data page.)

The half-cell reduction reactions and potentials are:

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E^0 = -0.24$ V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^0 = -0.76$ V

In the reaction above, the Zn is undergoing oxidation so its potential is reversed and the overall cell potential is:

$E^0_{cell} = (-0.24) - (-0.76) = +0.52$ V

Using $\Delta G^0 = -nFE^0$ for this two electron reaction:

$\Delta G^0 = -(2) \times (96485) \times (+0.52) = -100000$ J mol^1 = **-100 kJ mol^1**

Answer: **-100 kJ mol^{-1}**

What is the value of the equilibrium constant for the reaction at 298 K?

Using $E^0 = \dfrac{RT}{nF}\ln K$,

$+0.52 = \dfrac{(8.314)\times(298)}{(2)\times(96485)}\ln K$ **so K = 3.89 × 10^{17}**

Alternatively, using $\Delta G^0 = -RT\ln K$,

$-100 \times 10^3 = -(8.314) \times (298) \times \ln K$ **so K = 3.89 × 10^{17}**

Answer: **3.89 × 10^{17}**

Express the overall reaction in voltaic cell notation.

In the reaction, Zn is being oxidized and hence is the anode. Ni^{2+} is being reduced and so Ni is the cathode. In the standard cell notation, the anode is written on the left and the cathode on the right:

Zn(s) | Zn^{2+}(aq) || Ni^{2+}(aq) | Ni(s)

ANSWER CONTINUES ON THE NEXT PAGE

2
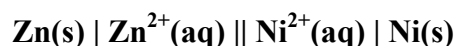
- Using a current of 2.00 A, how long (in minutes) will it take to plate out all of the silver from 0.250 L of a 1.14×10^{-2} M Ag^+(aq) solution?

The number of moles of Ag^+(aq) in a 0.250 L of a 1.14×10^{-2} M solution is,

number of moles = volume×concentration = $0.250 \times 1.14 \times 10^{-2}$ = 2.85×10^{-3} mol

The reduction of Ag^+(aq) is a one electron process, Ag^+(aq) + e^- → Ag(s), so this number of moles of electrons are required.

As the number of moles of electrons delivered by a current I in a time t is,

number of moles of electrons = $\dfrac{It}{F} = \dfrac{2.00 \times t}{96485} = 2.85 \times 10^{-3}$

t = 137 s = 2.29 minutes

**Marks
2**

- If a medical procedure calls for 2.0 mg of ^{48}V, what mass of isotope would be required to be able to use it exactly one week later? The half life of ^{48}V is 1.61 days.

The decay constant is related to the half life as $t_{1/2} = \dfrac{\ln 2}{\lambda}$. Thus,

$$\lambda = \frac{\ln 2}{1.61} = 0.431 \text{ days}^{-1}$$

The number of radioactive nuclei decreases with time according to the equation,

$$\ln\left(\frac{N_0}{N_t}\right) = \lambda t$$

If N_t = 2.0 mg after t = 7 days,

$$\ln\left(\frac{N_0}{2.0 \times 10^{-3}}\right) = (0.431) \times 7.00 \qquad \text{so } N_0 = 0.041 \text{ g} = 41 \text{ mg}$$

Answer: **41 mg**

3

- Describe how hydrophilic and hydrophobic colloids are stabilised in water.

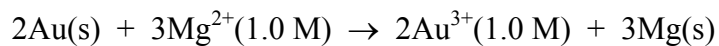**They can be stabilised via electrostatic and steric stabilisation.**

Hydrophilic colloids may have a charge on their surface that attracts oppositely charged ions (H^+ or OH^- present in water) to form a tightly bound layer known as the Stern Layer. The Stern layer is surrounded by a diffuse layer which contains an excess of counter-ions (opposite in charge to the Stern layer) and a deficit of co-ions. The Stern layer and diffuse layer are collectively known as a double layer. Coagulation of a hydrophilic colloid is prevented by mutual repulsion of the double layers.

Hydrophobic colloids may be stabilised by the use of a surfactant, e.g. a long chain fatty acid with a polar head and a non-polar tail. When dispersed in water these molecules arrange themselves spherically so that the polar (hydrophilic) heads are interacting with the polar water molecules and the non-polar (hydrophobic) tails are interacting with each other. This arrangement is called a micelle. The hydrophobic colloid can be stabilized by dissolving in the non-polar interior of the micelle.
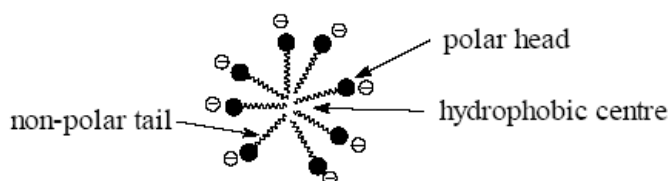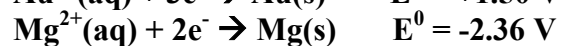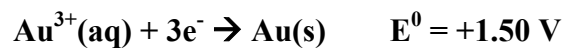

ANSWER CONTINUES ON THE NEXT PAGE

- Calculate the standard free-energy change for the following reaction at 298 K.

$$2Au(s) + 3Mg^{2+}(1.0\ M) \rightarrow 2Au^{3+}(1.0\ M) + 3Mg(s)$$

The half-cell reduction reactions and potentials are:

$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$ $E^0 = +1.50$ V
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $E^0 = -2.36$ V

In the reaction above, the Au is undergoing oxidation so its potential is reversed and the overall cell potential is:
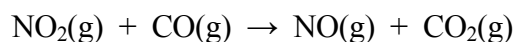
$E^0_{cell} = (-2.36) - (+1.50) = -3.86$ V

Using $\Delta G^0 = -nFE^0$ for this six electron reaction:

$\Delta G^0 = -(6) \times (96485) \times (-3.86) = +2.23 \times 10^6$ J mol^1 = +2.23 × 10^3 kJ mol^1

Answer: **+2.23 × 10^3 kJ mol^{-1}**

**Marks
5**

- The major pollutants $NO(g)$, $CO(g)$, $NO_2(g)$ and $CO_2(g)$, which are emitted by cars, 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 225 ^{o}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 constant and $[CO]_0$ is halved. The rate does not change. The rate is independent of $[CO]$: zero order with respect to $[CO]$.

Between experiments (2) and (3), $[CO]_0$ is kept constant and $[NO_2]_0$ is doubled. The rate increases by a factor of four: the rate is second order with respect to $[NO_2]$. Overall,

rate α $[NO_2]^2$ = k$[NO_2]^2$

Calculate the value of the rate constant at 225 ^{o}C.

Answer: **2.08×10^{-4} M^{-1} s^{-1}**

Calculate the rate of appearance of CO_2 when $[NO_2] = [CO] = 0.500$ M.

When $[NO_2] = 0.500$ M, rate $= \dfrac{d[NO_2]}{dt} = (2.08 \times 10^{-4}) \times (0.500)^2 = 5.20 \times 10^{-5}$ M s^{-1}

From the chemical equation, one mole of CO_2 is produced for every mole of NO_2 that is removed. Thus, rate of appearance of CO_2 = rate of loss of NO_2.

Answer: **5.20×10^{-5} M s^{-1}**

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

A possible mechanism is:

$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ (slow)

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$.............(fast)
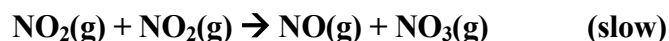
The first step is slow and is rate determining. For this step, rate α $[NO_2]^2$, as observed. The second step is fast and does not affect the overall rate of the reaction and so the rate is independent of $[CO(g)]$.