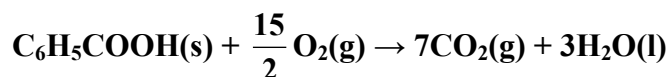


Marks
6

- High-purity benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, ($\Delta H^\circ_{\text{comb}} = -3227 \text{ kJ mol}^{-1}$) is used to calibrate a bomb calorimeter that has a 1.000 L capacity. A 1.000 g sample of $\text{C}_6\text{H}_5\text{COOH}$ is placed in the bomb calorimeter, along with 750 mL of pure $\text{H}_2\text{O}(\text{l})$, and the remaining 250 mL cavity is filled with pure $\text{O}_2(\text{g})$ at 10.00 atm. The $\text{C}_6\text{H}_5\text{COOH}$ is ignited and completely burned, causing the temperature of the water and the bomb calorimeter to rise from 27.20 °C to 33.16 °C. Write the chemical equation corresponding to the standard enthalpy of combustion ($\Delta H^\circ_{\text{comb}}$) of $\text{C}_6\text{H}_5\text{COOH}$.



Given that $\text{H}_2\text{O}(\text{l})$ has a heat capacity of $4.184 \text{ J K}^{-1} \text{ g}^{-1}$ and a density of 0.997 g mL^{-1} , calculate the heat capacity of the bomb calorimeter itself (in units of J K^{-1}). Ignore the heat capacity of the gases and of $\text{C}_6\text{H}_5\text{COOH}$.

The molar mass of $\text{C}_6\text{H}_5\text{COOH}$ is $(7 \times 12.01 \text{ (C)}) + (6 \times 1.008 \text{ (H)}) + (2 \times 16.00 \text{ (O)}) = 122.118$. Therefore 1.000 g corresponds to:

$$\text{amount of } \text{C}_6\text{H}_5\text{COOH} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.000}{122.118} = 0.008189 \text{ mol}$$

As combustion of 1 mol gives out 3227 kJ of heat, this amount gives out:

$$q = 0.008189 \times 3227 = 26.42 \text{ kJ} = 26.43 \times 10^3 \text{ J}$$

This heat leads to a temperature increase of $(33.16 - 27.20) = 5.96 \text{ }^\circ\text{C}$ for the combination of the calorimeter and the water. As water has a density of 0.997 g mL^{-1} , 750 mL has a mass of $750 \times 0.997 \text{ g}$.

$$q = (mC_{\text{water}} + C_{\text{calorimeter}}) \times \Delta T$$

$$= ((750 \times 0.997 \times 4.184) + (C_{\text{calorimeter}})) \times 5.96 = 26.42 \times 10^3$$

$$C_{\text{calorimeter}} = 1305 \text{ J K}^{-1}$$

Answer: **1305 J K⁻¹**

ANSWER CONTINUES ON THE NEXT PAGE

If 30.0% of the CO₂ produced dissolves in the water, calculate the final total pressure (in atm) inside the 250 mL cavity of the bomb calorimeter. Assume oxygen is insoluble in water and ignore the vapour pressure of water.

Initially, 10.00 atm of oxygen is present in a volume of 250 mL and a temperature of 27.20 °C. Using the ideal gas equation, $PV = nRT$,

$$\text{initial } n_{\text{O}_2(\text{g})} = \frac{PV}{RT} = \frac{(10.00) \times (0.250)}{(0.08206) \times (273 + 27.20)} = 0.1015 \text{ mol}$$

From the chemical equation, $\frac{15}{2}$ mol of O₂ are required for the combustion of every mole of C₆H₅COOH. As 0.008189 mol of C₆H₅COOH is present,

$$\text{consumed } n_{\text{O}_2(\text{g})} = 0.008189 \times \frac{15}{2} = 0.06142 \text{ mol}$$

Therefore,

$$\text{final } n_{\text{O}_2(\text{g})} = 0.1015 - 0.06142 = 0.0400 \text{ mol}$$

From the chemical equation, 7 moles of CO₂ are produced for the combustion every mole of C₆H₅COOH. As 0.008189 mol of C₆H₅COOH is present,

$$\text{total } n_{\text{CO}_2} = 0.008189 \times 7 = 0.05732 \text{ mol}$$

As 30% of this dissolves,

$$n_{\text{CO}_2(\text{g})} = 0.70 \times 0.05732 = 0.04013 \text{ mol}$$

The total number of moles of O₂(g) and CO₂(g) is therefore 0.0400 + 0.04013 = 0.0801. This is present in 250 mL at 33.16 °C. Using the ideal gas law,

$$P = \frac{nRT}{V} = \frac{(0.0801) \times (0.08206) \times (273 + 33.16)}{0.250} = 8.05 \text{ atm}$$

Answer: 8.05 atm

Marks
2

- The specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and the specific heat capacity of copper is $0.39 \text{ J g}^{-1} \text{ K}^{-1}$. 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 $q = C \times m \times \Delta T$, 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

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

The molar mass of H_2O is $(2 \times 1.008 (\text{H})) + 16.00 (\text{O}) = 18.016$. Hence, the temperature change for 1.0 mol of water is

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

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.*, $K_a (\text{HCl}) < K_a (\text{HBr}) < K_a (\text{HI})$), while the acidity of hypohalous acids *decreases* with increasing halogen size (*i.e.*, $K_a (\text{HOCl}) > K_a (\text{HOBr}) > K_a (\text{HOI})$).

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.

Marks
5

- 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,

$$\text{moles of benzoate} = \text{volume} \times \text{concentration} = 0.375 \times 0.0100 = 3.75 \times 10^{-3} \text{ mol}$$

225 mL of a 0.0200 of benzoic acid contains,

$$\text{moles of benzoic acid} = 0.225 \times 0.0200 = 4.50 \times 10^{-3} \text{ mol}$$

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

$$[\text{base}] = \frac{\text{number of moles}}{\text{volume}} = \frac{3.75 \times 10^{-3}}{0.600} = 6.25 \times 10^{-3} \text{ M}$$

$$[\text{acid}] = \frac{4.50 \times 10^{-3}}{0.600} = 7.50 \times 10^{-3} \text{ M}$$

As $pK_a = -\log_{10}K_a$,

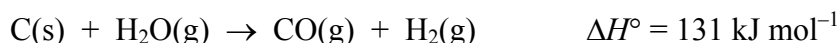
$$pK_a = -\log_{10}(6.3 \times 10^{-5}) = 4.2$$

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

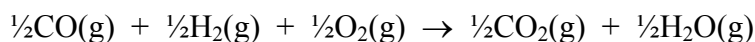
$$\text{pH} = pK_a + \log_{10} \left(\frac{[\text{base}]}{[\text{acid}]} \right) = 4.2 + \log_{10} \left(\frac{6.25 \times 10^{-3}}{7.50 \times 10^{-3}} \right) = 4.1$$

Answer: pH = 4.1

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



The equation for the complete combustion of 1 mol of water gas (*i.e.* 0.5 mol CO(g) and 0.5 mol H₂(g)) can be written as:



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

$$\Delta H^\circ_{\text{vap}}(\text{H}_2\text{O}) = 44 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{H}_2\text{O(l)}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{CO}_2\text{(g)}) = -393 \text{ kJ mol}^{-1}$$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_{\text{f}}H^\circ(\text{products}) - \sum n\Delta_{\text{f}}H^\circ(\text{reactants})$ for the vaporization of water ($\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$) gives

$$\begin{aligned} \Delta_{\text{vap}}H^\circ &= [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})] - [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(l)})] \\ &= [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})] - (-286) = +44 \end{aligned}$$

Hence $\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)}) = (+44) + (-286) = -242 \text{ kJ mol}^{-1}$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_{\text{f}}H^\circ(\text{products}) - \sum n\Delta_{\text{f}}H^\circ(\text{reactants})$ for the reaction,

$\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2\text{(g)}$ gives

$$\begin{aligned} \Delta_{\text{rxn}}H^\circ &= [\Delta_{\text{f}}H^\circ(\text{CO(g)})] - [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})] \\ &= [\Delta_{\text{f}}H^\circ(\text{CO(g)})] - (-242) = +131 \end{aligned}$$

as $\Delta_{\text{f}}H^\circ(\text{H}_2\text{(g)})$ and $\Delta_{\text{f}}H^\circ(\text{C(s)})$ are both zero for elements in their standard states. Hence $\Delta_{\text{f}}H^\circ(\text{CO(g)}) = -111 \text{ kJ mol}^{-1}$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_{\text{f}}H^\circ(\text{products}) - \sum n\Delta_{\text{f}}H^\circ(\text{reactants})$ for the reaction,

$\frac{1}{2}\text{CO(g)} + \frac{1}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \frac{1}{2}\text{CO}_2\text{(g)} + \frac{1}{2}\text{H}_2\text{O(g)}$ gives

$$\Delta_{\text{comb}}H^\circ = \left[\frac{1}{2}\Delta_{\text{f}}H^\circ(\text{CO}_2\text{(g)}) + \frac{1}{2}\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})\right] - \left[\frac{1}{2}\Delta_{\text{f}}H^\circ(\text{CO(g)})\right]$$

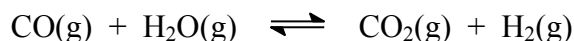
as the enthalpy of formation of H₂(g) and O₂(g) are both zero for elements in their standard states. Hence,

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

Answer: -262 kJ mol⁻¹

THIS QUESTION CONTINUES ON THE NEXT PAGE.

The CO(g) in water gas can be reacted further with H₂O(g) in the so-called “water-gas shift” reaction:



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 H₂(g), as well as 0.250 mol L⁻¹ H₂O(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 CO₂(g). What was the initial concentration of CO(g) and H₂(g) in the sample?

Marks
4

The reaction table is

	CO(g)	H ₂ O(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:

$$K_c = \frac{[\text{CO}_2\text{(g)}][\text{H}_2\text{(g)}]}{[\text{H}_2\text{O(g)}][\text{CO(g)}]} = \frac{(0.070)(x + 0.070)}{(0.180)(x - 0.070)} = 1.56$$

$$x = [\text{CO(g)}]_{\text{initial}} = [\text{H}_2\text{(g)}]_{\text{initial}} = 0.12 \text{ mol L}^{-1}$$

$$[\text{CO}] = [\text{H}_2] = 0.12 \text{ mol L}^{-1}$$

If the walls of the container are chilled to below 100 °C, what will be the effect on the concentration of CO₂(g)?

At temperatures below 100 °C, the water vapour will condense to form H₂O(l). Following Le Chatelier’s principle, the equilibrium will shift to the left as [H₂O(g)] is reduced by this process and so [CO₂(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,



Calculate the equilibrium constant for this process at 298 K.

Using $\Delta G^\circ = -RT \ln K$,

$$1.67 \times 10^3 = -(8.314) \times (298) \times \ln K$$

$$K = 0.510$$

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?

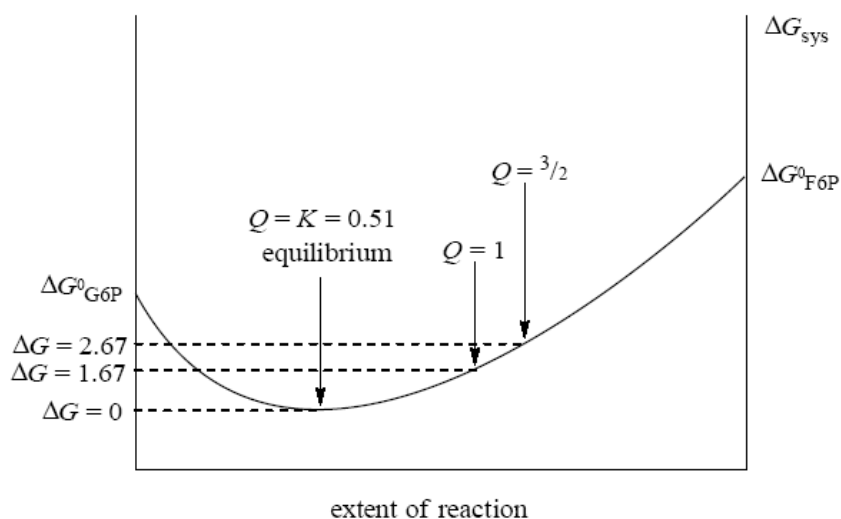
The reaction quotient, for the reaction, is $Q = \frac{[\text{F6P}]}{[\text{G6P}]} = \frac{3.00}{2.00} = 1.50$.

Using $\Delta G = \Delta G^\circ + RT \ln Q$,

$$\Delta G = (1.67 \times 10^3) + (8.314 \times 298) \times \ln(1.50) = +2670 \text{ J mol}^{-1} = +2.67 \text{ kJ mol}^{-1}$$

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 °C 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 °C 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,

$$\text{mass of water} = 1.0275 - 0.0330 = 0.995 \text{ kg}$$

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 H₂O is 23.76 mmHg at 25 °C and 1 atm. Calculate the vapour pressure above this seawater under the same conditions.

The molar mass of H₂O is $(2 \times 1.008 \text{ (H)}) + 16.00 \text{ (O)} = 18.016$. 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

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

From Raoult's law,

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

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 H₂O?

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 = 101.3×10^3 Pa,

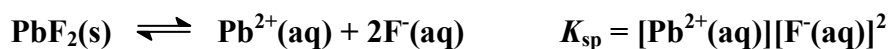
$$\Pi = 27.6 \times (101.3 \times 10^3) = 2800000 \text{ Pa} = 2.80 \times 10^6 \text{ Pa}$$

Answer: **2.80×10^6 Pa**

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

Marks
2

The solubility equilibrium and constant for $\text{PbF}_2(\text{s})$ are,



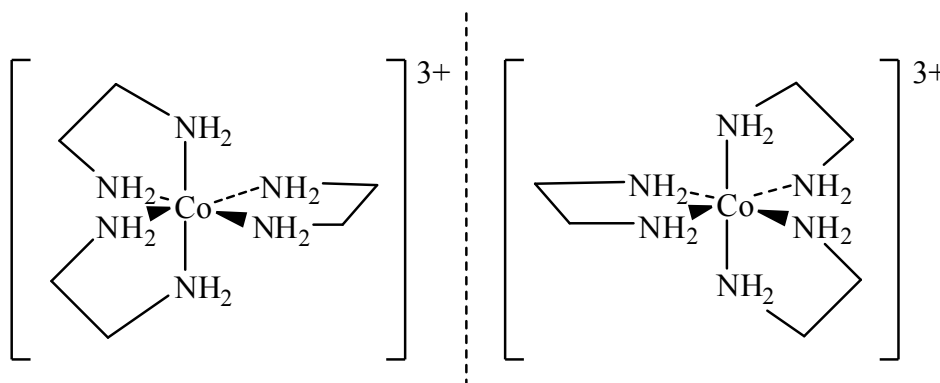
As one moles of $\text{Pb}^{2+}(\text{aq})$ and two moles of $\text{F}^{-}(\text{aq})$ are produced for every mole of $\text{PbF}_2(\text{s})$ which dissolves, $[\text{Pb}^{2+}(\text{aq})] = 2.6 \times 10^{-3} \text{ M}$ and $[\text{F}^{-}(\text{aq})] = (2 \times 2.6 \times 10^{-3}) = 5.2 \times 10^{-3} \text{ M}$. Hence,

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

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

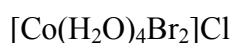
- Draw all stereoisomers of the complex ion of $[\text{Co}(\text{en})_3]\text{Br}_3$. (en = ethylenediamine = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

2

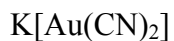


- Name the following complexes.

2



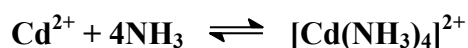
tetraaquadibromocobalt(III) chloride



potassium dicyanoaurate(I)

- Write the chemical equation for the formation of the complex ion $[\text{Cd}(\text{NH}_3)_4]^{2+}$.

Marks
2



Write the associated stability constant expression (K_{stab}).

$$K_{\text{stab}} = \frac{[[\text{Cd}(\text{NH}_3)_4]^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4}$$

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

3



Calculate the potential for this half reaction at 25 °C, where pH = 7.40 and $[\text{CrO}_4^{2-}(\text{aq})] = 1.0 \times 10^{-6} \text{ M}$.

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

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

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

The reaction quotient for the half-cell reaction is,

$$Q = \frac{[\text{OH}^-(\text{aq})]^5}{[\text{CrO}_4^{2-}(\text{aq})]} = \frac{(10^{-6.60})^5}{(1.0 \times 10^{-6})} = 1.0 \times 10^{-27}$$

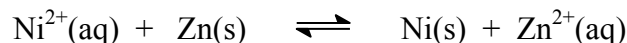
Using the Nernst equation for this three electron process,

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

Answer: $E = +0.40 \text{ V}$

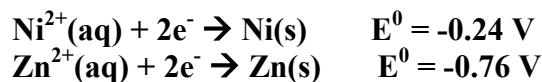
Marks
5

- Consider the following reaction at 298 K.



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

The half-cell reduction reactions and potentials are:



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

$$E_{\text{cell}}^0 = (-0.24) - (-0.76) = +0.52 \text{ V}$$

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

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

Answer: **-100 kJ mol⁻¹**

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

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

$$+0.52 = \frac{(8.314) \times (298)}{(2) \times (96485)} \ln K \quad \text{so } K = 3.89 \times 10^{17}$$

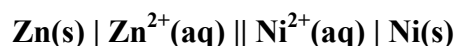
Alternatively, using $\Delta G^0 = -RT \ln K$,

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

Answer: **3.89 × 10¹⁷**

Express the overall reaction in voltaic cell notation.

In the reaction, Zn is being oxidized and hence is the anode. Ni²⁺ 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:



ANSWER CONTINUES ON THE NEXT PAGE

- 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 $\text{Ag}^+(\text{aq})$ solution?

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

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

The reduction of $\text{Ag}^+(\text{aq})$ is a one electron process, $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$, 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,

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

$$t = 137 \text{ s} = 2.29 \text{ minutes}$$

- 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.

Marks
2

The decay constant is related to the half life as $t_{1/2} = \frac{\ln 2}{\lambda}$. 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 $N_t = 2.0 \text{ mg}$ after $t = 7 \text{ days}$,

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

Answer: **4.1 mg**

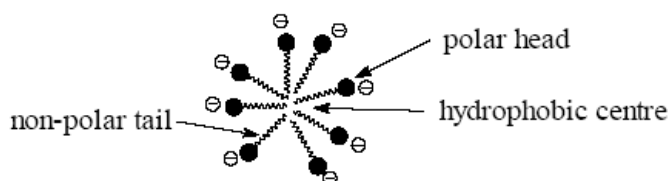
- Describe how hydrophilic and hydrophobic colloids are stabilised in water.

3

They can be stabilised via electrostatic and steric stabilisation.

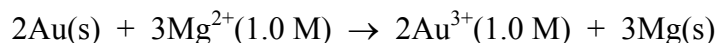
Hydrophilic colloids may have a charge on their surface that attracts oppositely charged ions (H^+ or OH^- present in water) to form a tightly bound layer known as the Stern Layer. The Stern layer is surrounded by a diffuse layer which contains an excess of counter-ions (opposite in charge to the Stern 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.

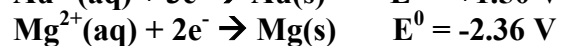
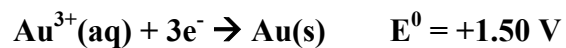


ANSWER CONTINUES ON THE NEXT PAGE

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



The half-cell reduction reactions and potentials are:



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

$$E_{\text{cell}}^{\circ} = (-2.36) - (+1.50) = -3.86\text{ V}$$

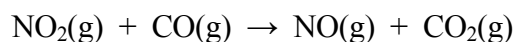
Using $\Delta G^{\circ} = -nFE^{\circ}$ for this six electron reaction:

$$\Delta G^{\circ} = -(6) \times (96485) \times (-3.86) = +2.23 \times 10^6\text{ J mol}^{-1} = +2.23 \times 10^3\text{ kJ mol}^{-1}$$

Answer: $+2.23 \times 10^3\text{ kJ mol}^{-1}$

Marks
5

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



The following rate data were collected at 225 °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), [NO₂]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 [NO₂]₀ is doubled. The rate increases by a factor of four: the rate is second order with respect to [NO₂]. Overall,

$$\text{rate} \propto [\text{NO}_2]^2 = k[\text{NO}_2]^2$$

Calculate the value of the rate constant at 225 °C.

Answer: $2.08 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

Calculate the rate of appearance of CO₂ when [NO₂] = [CO] = 0.500 M.

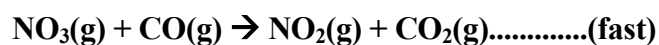
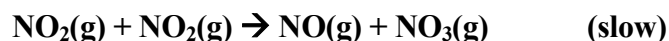
When [NO₂] = 0.500 M, rate = $\frac{d[\text{NO}_2]}{dt} = (2.08 \times 10^{-4}) \times (0.500)^2 = 5.20 \times 10^{-5} \text{ M s}^{-1}$

From the chemical equation, one mole of CO₂ is produced for every mole of NO₂ that is removed. Thus, rate of appearance of CO₂ = rate of loss of NO₂.

Answer: $5.20 \times 10^{-5} \text{ M s}^{-1}$

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

A possible mechanism is:



The first step is slow and is rate determining. For this step, rate \propto [NO₂]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)].

