Problem of the Day 1

A 500 cm³ solution of hydrobromic acid has a pH of 3.00. 80cm³ of the solution was found to be completely neutralized by 20.0 cm³ of ammonia solution. Determine the concentration of the ammonia solution and the mass concentration of the salt formed.

[N = 14 g/mol; Br = 80 g/mol; H = 1.0 g/mol]

SOLUTION:

 $[HBr] = 0.0010 \text{ moldm}^{-3}$

Moles of HBr = $0.0010 \times 80 = 0.080$ mmol

From equation of reaction: $HBr + NH_3 \rightarrow NH_4Br$

Mole ratio = 1:1

Hence $[NH_3] = 0.080/20 = 0.0040 \text{ moldm}^{-3}$

[NH₄Br] formed = $0.080/100 = 8.0 \times 10^{-4}$

Mass concentration of $NH_4Br = 8.0 \times 10^{-4} \times 98$

 $= 0.0784 \text{ gdm}^{-3} = 78.4 \text{ mgdm}^{-3}$

Problem of the Day 2

The reaction $2A + B \rightarrow 2C$ was studied at 25 °C and the following data were obtained.

Experiment	Initial [A]/ mol dm ⁻³	Initial [B]/ mol dm ⁻³	Rate of formation of
			C/ mol dm ⁻³ s ⁻¹
Ι	0.24	0.24	$2.20 imes10^{-4}$
II	0.48	0.24	$8.80 imes10^{-4}$
III	0.48	0.48	1.76×10^{-3}

Calculate the rate of formation of C for an experiment conducted at 25 °C with reactant concentrations of A = B = 0.20 mol dm⁻³.

SOLUTION

Determine the rate law expression

From expt. 1 and 2, when [B] remains constant, and [A] is doubled, rate increases four times

From expt. 2 and 3, when [A] remains constant, and [B] is doubled, rate doubles

Hence rate law expression = **Rate** = **K**[**A**]²[**B**]

 $\mathbf{R} = \mathbf{K}[\mathbf{A}]^2[\mathbf{B}]$

Hence, K = $\frac{R}{[A]^2[B]}$. Using the values of experiment, I (or II or III) K= $\frac{2.2 \times 10^{-4} \ mol \ dm^{-3} \ s^{-1}}{(0.24)^2(0.24) \ mol^3 \ dm^{-9}} = 1.59 \times 10^{-2} \ mol^{-2} \ dm^6 \ s^{-1}$

Calculate rate for new experiment

For the experiment $[A] = [B] = 0.20 \text{ mol } \text{dm}^{-3}$ Rate of formation $= 1.59 \times 10^{-2} \text{ mol}^{-2} \text{ dm}^{6} \text{ s}^{-1} ([0.20]^{2}[0.20]) \text{ mol}^{3} \text{ dm}^{-9}$ $= 1.27 \times 10^{-4} \text{ mol } \text{dm}^{-3} \text{ s}^{-1}$

Problem of the Day 3

To determine the amount of ascorbic acid (vitamin C) in 500 cm³ of fruit juice purchased, a student reacts the ascorbic acid contained in the juice with an excess of iodine and back-titrates the excess iodine with thiosulphate solution. The student reacts 25 cm³ of orange juice with 30 cm³ of 0.080 moldm⁻³ of iodine. At the end of the reaction, the excess iodine required 20 cm³ of 0.20 moldm⁻³ of Na₂S₂O₃. Determine the mass of ascorbic acid present in the fruit juice purchased. [C = 12 g/mol; O = 16 g/mol; H = 1.0 g/mol].

The equation of reactions are as follows:

$$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2H^- + 2I^-$$

 $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

SOLUTION

Number of moles of $S_2O_3^{2-} = 0.020 \times 0.2 = 0.0040$ mol

From equation of reaction, number of moles of $I_2 = 0.0040/2 = 0.0020$ mol

Moles of I_2 added = $0.080 \times 0.030 = 0.0024$ mol

Hence moles of I_2 which reacted = moles of $C_6H_8O_6 = 0.0024 - 0.0020 = 0.00040$ mol

Moles of $C_6H_8O_6$ in 500 cm³ of juice = $500 \times 0.00040/25 = 0.0080$ mol

Mass of ascorbic acid, $C_6H_8O_6 = 0.0080 \times 176 = 1.408 = 1.41$ g

Problem of the Day 4

The decay constant of a radioactive isotope is $1.155 \times 10^{-3} \text{ s}^{-1}$.

- a) How long will it take 19.2 mg of the isotope to decay to 0.15 mg
- b) Given an initial 25.6 mg sample of the radionuclide, what amount of radionuclide will decay after 3600 seconds.

[Take ln 2 as 0.693]

SOLUTION

Half-life = $0.693/1.155 \times 10^{-3} = 600 \text{ s} = 10 \text{ minutes}$

19.2 mg to 0.15 mg occurs in 7 half-lives.

Hence time taken = 7×10 minutes = **70** minutes = **4200** seconds

3600 seconds = 60 minutes = 6 half-lives

After 6 half-lives amount of original 25.6 mg remaining will be **0.40 mg**.

Amount decayed after 3600s = 25.6 - 0.40 = 25.2 mg

Problem of the Day 5

A 0.864 g sample containing silver was dissolved in 400 cm³ of water and reacted with 30.0 cm³ of 0.500 moldm⁻³ of potassium iodide solution. The resulting precipitate was carefully washed, dried to a constant mass, and weighed to obtain a mass of 0.470 g. Determine the percentage composition by mass of silver in the sample.

Given that, 200 mg of silver is required to make a coin, how many coins can be made from the sample given?

[K = 39.0 g/mol; I = 127 g/mol; Ag = 108 g/mol]

SOLUTION

Precipitate = AgI

Equation of reaction = $Ag^+ + I^- \rightarrow AgI(s)$

Mass of AgI = 0.470 g

Molar mass of AgI = 235 g/mol

Moles of AgI = 0.470/235 = 0.00200 mol

Mass of Ag = $0.00200 \times 108 = 0.216$ g

Percentage of silver in sample = $0.216/0.860 \times 100 = 25.0\%$

Sample contains 216 mg of silver. Hence only one coin can be made from sample.

A hydrocarbon has the molecular formular C_5H_{10} . Give the names of all possible structures of the hydrocarbon.

SOLUTION

- 1) 1-pentene
- 2) 2-pentene
- 3) 2-methyl-1-butene
- 4) 2-methyl-2-butene
- 5) 3-methyl-1-butene
- 6) Cyclopentane
- 7) Methyl cyclobutane
- 8) 1,1-dimethylcylopropane
- 9) 1,2-dimethylcylopropane

ROUND 3

PROBLEM OF THE DAY C1

A hydrocarbon Q is made up of 85.7% carbon and 14.3% hydrogen. At 127° C and 80.0kPa 0.510dm³ of the hydrocarbon burns in excess oxygen to give 2.04dm³ of CO₂ and 2.04dm³ of water vapour. Calculate the molecular formula of the hydrocarbon from the data given. The Ideal Gas constant is 8.31JK⁻¹mol⁻¹.

C = 12.0; H = 1.00

Ans:

С	Н
85.7/12.0	14.3/1.00
7.14	14.3
1	2
Hence empirical formula =	CH ₂ ;
Assume Molecular formula =	n(CH ₂) where n is an integer
$Q_{(g)} \longrightarrow nCO_{2(g)}$	+ $nH_2O_{(g)}$
Volumes in the combustion: 0.510	$dm^3 Q; 2.01dm^3 CO_{2(g)}; 2.01dm^3 H_2O_{(g)}.$

Ratio of volumes in the combustion 1:4:4

Applying Gay-Lussac's Law, the stoichiometric ratios in the combustion should be 1:4:4

Hence 1 mol Q burns to give 4 mol $CO_{2(g)}$ and 4 mol $H_2O_{(g)}$

Hence Molecular formula of Q C_4H_8 .

[Note Full marks not to be awarded if the deduction is not fully shown.]

ROUND 3

PROBLEM OF THE DAY C2

The balanced equation for the gas-phase decomposition of compound A to B and C is as follows:

 $2A_{(g)} \quad \rightleftharpoons \quad 2B_{(g)} \quad + \quad C_{(g)}.$

The equilibrium constant K_c of the reaction at 250°C is $1.08*10^{-11}$.

- a) Write down the expression for the equilibrium constant K_c of the reaction.
- b) Calculate the equilibrium concentration of $A_{(g)}$, $B_{(g)}$ and $C_{(g)}$ of the reaction if the initial concentration of $A_{(g)}$ is 0.100moldm⁻³.
- c) State a reasonable assumption made in the calculation.
- d) Predict the effect of an increase in the total pressure on the equilibrium process.

Ans:	a)	Kc	=	[B] ² [C]/[A]	2				
	b)		$2A_{(g)}$	⇒		2B _(g)		+	C _(g) .
	Initial	conc.	0.100			0.00			0.00
	At equ	uil.	(0.100) – 2x)		2x			x
	Kc	=	$(2x)^{2}($	x)/(0.100 - 2	$(x)^2 =$	4x ³ /(0	0.100 -	$(2x)^{2}$.	
		\approx	4x ³ /(0	$(.100)^2$	=	1.08*	10-11		
	4x ³	=	1.08*	10 ⁻¹³ ;	x ³	=	27.0*	⁻¹⁵	
	X	=	3.00*	10 ⁻⁵ moldm ⁻³ .					
Hence	e conc o	of A	=	0.100 or 1.	00*10-1	[OR	0.099	94 or 9.	99*10 ⁻²] moldm ⁻³ .
3.	Conc	of B	=	6.00*10 ⁻⁵ m	noldm ⁻³ ;	Conc	of C	=	3.00*10 ⁻⁵ moldm ⁻

- c) <u>The assumption</u>: The amount of A that decomposes at equilibrium is small and negligible compared with the initial concentration.
- d) Increase in pressure will favour the reverse reaction OR less of A will be formed at higher pressure <u>but the equilibrium constant K_c will not change</u>.

ROUND 3

PROBLEM OF THE DAY C3

You are provided with about 10.0 g of neutral, solid organic compound X. The compound is contaminated with an organic acid. You are also informed that X is insoluble in cold ethanol but moderately soluble in hot ethanol. It is very soluble in cold ethyl ethanoate . It is insoluble in cold water but sparingly soluble in hot water.

- a) Describe in detail how you would remove the organic acid compound from X and get X ready for recrystallisation.
- b) State the solvent that would be most suitable for the re-crystallisation of X.

Ans: a) 1) The solid is <u>transferred</u> into a $200 - 400 \text{ cm}^3$ <u>beaker</u>.

- 2) About 50 to 100 cm^3 of <u>ethyl ethanoate</u> is added to the solid X to <u>dissolve</u> it.
- The solution of X is transferred into a <u>separating funnel</u> and about 50 cm³ of <u>dilute</u> <u>NaOH solution</u> is added. Two layers are observed.
- 4) The funnel is stoppered and <u>shaken</u> intermittently for about two minutes.
- 5) The funnel is clamped long enough for the two layers to separate.
- The stopper is removed, the tap of the funnel is opened, and the <u>lower (aqueous) layer</u> is run down.
- 7) The extraction is <u>repeated a few (up to three)</u> more times.
- The ethyl ethanoate solution of X is <u>washed</u> twice with de-ionised water using the separating funnel.
- 9) The washing is repeated until the water tests <u>neutral</u> to litmus.
- The solution of X is transferred into a conical flask and about 5g of anhydrous Na₂SO₄ or MgSO₄ is added to <u>dry</u> the solution.
- 11) After about 30 minutes the solution is filtered into a beaker and heated/boiled to remove the solvent(The solvent may be removed by distillation)
- b) Solvent for re-crystallisation is ETHANOL

ROUND 3

PROBLEM OF THE DAY C4

An entrepreneur in Ghana decides to set up a factory by using the large limestone deposits close to her hometown to manufacture aqueous suspension of slaked lime which can be used as white paint. The limestone will be subjected to three processes to obtain the intended product as follows:

- 1. The limestone is heated in a kiln to give lime or calcium oxide and CO₂ gas.
- 2. The lime is treated with a measured amount of water to convert it into solid slaked lime.
- 3. The slaked lime is then suspended or partially dissolved in excess water to obtain the paint.

Consider the following enthalpies of formation all in kJmol⁻¹ and deduce if the heat to be generated from the three steps can be used to operate the factory on a sustainable basis: CaCO_{3(s)} -1206; CaO_(s) -635; Ca(OH)_{2(s)} -986; Ca²⁺_(aq) -543; CO_{2(g)} -

 $OH^{-}_{(aq)}$ -230.

394;

H₂O₍₁₎ -286;

Ans: Step 1:
$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$
.
 $\Delta H_1(reaction) = (-635 + -394) - (-1206) =$
 $+177kJ$.
Step 2: $CaO_{(s)} + H_2O_{(1)} \rightarrow Ca(OH)_{2(s)}$
 $\Delta H_2(reaction) = -986 - (-635 + -286) = -$
 $65.0kJ$.
Step 3: $Ca(OH)_{2(s)} + excess water \rightarrow Ca^{2+}_{(aq)}$
 $+2OH^{-}_{(aq)}$.
 $\Delta H_3(reaction) = [-543 + 2(-230)] - [-986] = -$
 $17.0kJ$

Sum of the three enthalpies of reaction = +177 - 65.0 - 17.0 = +95.0kJ

<u>Hence</u> the three reactions will not generate any heat to sustain the three processes. Rather external heat will be needed to keep the factory running.

[Note: If the conclusion is not based on the ΔH 's of the three processes no marks should be awarded for the conclusion.]

ROUND 3

PROBLEM OF THE DAY C2

2,2,4-Trimethylpentane burns smoothly in internal combustion engines and for this reason assigned octane rating of 100. Its enthalpy of combustion can be calculated by i) Hess's Law and ii) use of bond energies. Determine the enthalpy of combustion by the two methods and comment on the relative values obtained. You may use the following enthalpies of formation and bond energies all in kJmol⁻¹:

2,2,4-Trimethylpentane -225; CO_{2(g)} -394; H₂O_(g) -242; C=O 745; C-C 350; C-H 415; O-H 464; O₂ 498.

Ans: 2,2,4-Trimethylpentane = C_8H_{18} . C_8H_{18} + 25/2O₂ \rightarrow 8CO_{2(g)} + 9H₂O_(g) <u>Enthalpy of combustion by Hess's Law</u>: $\Delta H(\text{combustion})$ = (-394*8 + -242*9) - (-225) = -5105 or -5.11*10³kJmol⁻¹.

Enthalpy of combustion using bond energies:

Bonds broken	=	7C-C +	18C-	H + 12.	502	
Energy required	=	350*7 + 415	*18 + 4	98*12.5	=	16145kJ
Bonds formed	=	16C=O	+	18O-H		
Energy given out	=	-745*16	+	-464*18	=	-20,272kJ
$\Delta H'$ (combustion)	=	16,145 - 20,2	272	= -4,1	127 or	-
4.13*10 ³ kJmol ⁻¹ .						

Enthalpy of combustion by Hess's Law is larger than the Enthalpy of combustion using bond energies.

The former is more accurate because it is obtained using enthalpies of formation which are experimental values whereas bond energies are approximate (or theoretical) values.

ROUND 3

PROBLEM OF THE DAY C1

A metal Q forms an oxide when 10.4g of it reacts with 7.48dm³ of oxygen gas at 27.0°C and 100kPa.

Determine the formula of the oxide and the percent oxygen by mass in the oxide. Atomic mass of Q is 52.0. The Ideal Gas constant is 8.31JK⁻¹mol⁻¹.

Ans:	Moles of Q made to react with oxy	=	10.4/52	.0	=	0.200.	
7.48dı	Moles of oxygen gas, n reacting, m^3 ; $T = 300K$.	=	PV/RT; $P = 10$		00kPa;	V =	
		=	100*7	.48/8.31*	*300	=	0.300
	Moles of oxygen atoms	=	0.600				
	Hence formula	=	QO ₃				
	%O by mass in QO ₃	=	[48.0/	(48.0+52))]*100)	
		=	48.0				

ROUND 3

PROBLEM OF THE DAY C4

Calculate the concentrations of HCO_3^- , OH^- , CO_3^{2-} , and H_2CO_3 in a 0.100moldm⁻³ solution of Na₂CO₃. You should state any assumption(s) made to enable you calculate the values. For the purpose of these calculations the first and second dissociation constants of H_2CO_3 may be taken as $5.00*10^{-7}$ and $5.00*10^{-11}$ respectively. The value of K_w is $1.00*10^{-14}$. Where necessary an answer may be left as a surd.

Ans: CO_3^{2-} is the conjugate base of HCO_3^{--} :

CO_{3}^{2-}	+	H_2O	⇒	HCO ₃ -	+	OH⁻;	K _{b2}	= ?
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$$K_{b2} = K_w/K_{a2} = 1.00*10^{-14}/5.00*10^{-11} = 2.00*10^{-4}$$
$$K_{b2} = [HCO_3^-][OH^-]/[CO_3^{2-}] = [HCO_3^-]^2/[CO_3^{2-}] \text{ since}$$
$$[HCO_3^-] = [OH^-]$$

<u>First assumption</u>: The amount of CO_3^{2-} reacting is negligible compared with its original concentration, hence $[CO_3^{2-}] = 1.00*10^{-1} \text{ moldm}^{-3}$

Hence K_{b2} = 2.00*10⁻⁴ = [HCO₃⁻]²/1.00*10⁻¹ [HCO₃⁻] = (2.00*10⁻⁵)^{1/2} moldm⁻³ [OH⁻] = (2.00*10⁻⁵)^{1/2} moldm⁻³

 HCO_3^- as a conjugate base of H_2CO_3 $K_{b1} = K_w/K_{a1}$

 $K_{b1} = K_w/K_{a1} = 1.00^{*}10^{-14}/5.00^{*}10^{-7} = 2.00^{*}10^{-8}$

 HCO_3^- + $H_2O \rightleftharpoons H_2CO_3$ + OH^- ;

$$2.00*10^{-8}$$
 = [H₂CO₃][OH⁻]/[HCO₃⁻]

<u>Second assumption</u>: Since it is one equilibrium solution [HCO₃⁻] = [OH⁻]

 $[H_2CO_3] = 2.00*10^{-8} \text{ moldm}^{-3}$ Summary $[HCO_3^{-1}] = (2.00*10^{-5})^{\frac{1}{2}} \text{ moldm}^{-3}$ $[OH^{-1}] = (2.00*10^{-5})^{\frac{1}{2}} \text{ moldm}^{-3}$ $[CO_3^{2-1}] = 1.00*10^{-1} \text{ moldm}^{-3}$ $[H_2CO_3] = 2.00*10^{-8} \text{ moldm}^{-3}$

ROUND 3

PROBLEM OF THE DAY C3

Gaseous compounds A and B react to give product compound C according to the following equation:

 $A(g) + B(g) \rightarrow 2C(g)$

1. Use the following kinetic data to determine the Rate Law for the reaction

Experiment	Initial concent	tration in moldm ⁻³	Initial Rate
	A	В	(moldm ⁻³ s ⁻¹)
1	0.100	0.100	2.40*10 ⁻²
2	0.200	0.100	9.60*10 ⁻²
3	0.300	0.100	2.16*10 ⁻¹

4	0.300	0.200	4.32*10 ⁻¹
5	0.300	0.300	6.48*10 ⁻¹

- 2. Use the results to determine the rate constant k, for the reaction and give the units.
- 3. Predict the initial rate of the reaction if the initial concentrations of A and B were 0.400 and 0.500 moldm⁻³ respectively.
- Ans: 1) Rate Law: Consider the results of Expts. 1 and 2; When concentration of A is doubled while that of B remains constant the initial rate increases by a factor of 4. Hence the reaction is 2nd order with respect to A. Consider Expts. 3 and 4. It can be deduced that the reaction is 1st order with respect to B.

Hence The Rate Law: Rate $= k[A]^2[B]$.

2) Use any set of experimental results to calculate k. e.g. Experiment 1

 $2.40^{*}10^{-2} = k(1.00^{*}10^{-1})^{2}(1.00^{*}10^{-1}) = k(1.00^{*}10^{-3})$

 $k = 2.40*10^1 \, dm^6 mol^{-2}s^{-1}$

3) Using Expt. 1, when the concentration of A is increased from 0.100 to 0.400 moldm⁻³ the rate increases by a factor of 16. When the concentration of B is increased from 0.100 to 0.500 moldm⁻³ the rate increases by a factor of 5. Hence the total expected increase = $5 \times 16 = 80$ The expected rate = $80.0*2.40*10^{-2}$ = $192*10^{-2}$ = $1.92 \text{ moldm}^{-3}\text{s}^{-1}$

[Note: Accept any mathematical method giving the right answer]