RECOGNISING ACHIEVEMENT

UNIFYING CONCEPTS IN CHEMISTRY

Mark Scheme 2816/01
June 2003

1. (a) (i) $Br^-(aq)$ 1st order ✓
[$Br^-(aq)$] triples rate triples ✓

[2]

$H^+(aq)$ 2nd order ✓
[$H^+(aq)$] doubles rate quadruples ✓

[2]

$BrO_3^-(aq)$ 1st order ✓
[$BrO_3^-(aq)$] doubles rate doubles ✓

[2]

(ii) rate = $k[Br^-(aq)]\,[H^+(aq)]^2\,[BrO_3^-(aq)]$ ✓ (state symbols not needed)

[1]

(iii)

$$k = \frac{\text{rate}}{[Br^-(aq)]\,[H^+(aq)]^2\,[BrO_3^-(aq)]} = \frac{1.2 \times 10^{-3}}{0.1 \times 0.1^2 \times 0.1} ✓ =$$

rate constant, k:= 12 ✓ units: $dm^9\ mol^{-3}\ s^{-1}$ ✓

(0.0833 would score 1 mark)

[3]

(b) (i) slowest step✓

[1]

(ii) rate equation shows reaction is 1st order wrt HBr and 1st order wrt O_2 ✓
which corresponds to molecules in step 1 ✓

[2]

(iii) $4HBr + O_2 \longrightarrow 2Br_2 + 2H_2O$ ✓

[1]

[Total: 14]

2. (a) decrease temperature ✓ exothermic direction ✓
increase pressure ✓ favours side with fewer molecules✓

[4]

(b) (i) The contribution of a gas to the pressure in a gas mixture /
mole fraction x total pressure ✓

[1]

(ii)

$$K_p = \frac{p\,COCl_2(g)}{p\,CO(g) \times p\,Cl_2(g)}$$ ✓✓

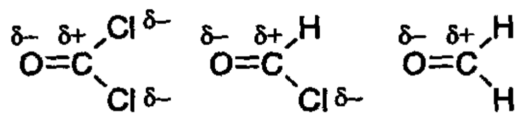
If any [ ] then only ✓ for K_p expression
If upside down with **no** concentration terms [ ], ✓ only

$$K_p = \frac{4.13 \times 10^{-5}}{2.5 \times 10^{-6} \times 2.5 \times 10^{-6}} = 6.6 \times 10^{6}$$ ✓ Pa^{-1}

If expression is upside down, then answer consequentially is 1.51×10^{-7}.

[3]

(c) (i)



A **B**

C=O dipole ✓; δ– on chlorines ✓

C=O dipole shown correctly on one structure without any contradiction scores 1 mark

[2]

(ii) **A** has 2 δ- / **A** has 2 electronegative atoms / **A** has more electronegative elements than **B** ✓

$COCl_2$ is symmetrical / **A** is **not** symmetrical ✓

dipoles cancel in $COCl_2$ ✓

3 marking points gives [2] max

(iii) $COCl_2 + 2H_2O \longrightarrow H_2CO_3 + 2HCl$ ✓✓

OR

$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$ ✓✓

OR

$COCl_2 + H_2O \longrightarrow O{=}COHCl + HCl$ ✓

[2]

[Total: 14]

3. (a) (i) $H_2 + Cl_2 \longrightarrow 2HCl$ ✓

[1]

(ii) $C_6H_{14} + Cl_2 \longrightarrow C_6H_{13}Cl + HCl$ ✓

[1]

(b) (i) moles HCl = 8 x 15 = 120 mol ✓

volume HCl(g) = 120 x 24 = 2880 (dm^3) ✓

[2]

(ii) solution must be diluted by 8.00/0.0200 = 400 times ✓

To 2.50 cm^3 of 8.00 mol dm^{-3} HCl✓ add sufficient water to make 1 dm^3 of solution.

[2]

(iii) pH= $-\log[H^+]$ ✓ = 1.70 ✓

[2]

(c) (i) Final pH is approx 11 / equivalence point <7 ✓

[1]

(ii) volume of NH_3(aq) that reacts is 15 cm^3 ✓

amount of HCl used = 0.0200 x 20.00/1000 = 4 x 10^{-4}

concentration of NH_3(aq) = 4 x 10^{-4} x 1000/15 = 0.0267 mol dm^{-3} ✓

[2]

(iii) chlorophenol red ✓

pH range coincides with pH change **during sharp rise** OR pH 4-7 /

coincides with equivalence point ✓

[2]

[Total: 13]

4. (a) A solution that minimises changes in pH (after addition of acid/alkali) ✓

equilibrium: $HCOOH \rightleftharpoons HCOO^- + H^+$

/ HCOOH and $HCOO^-$ / weak acid and its conjugate base ✓

HCOOH reacts with added alkali / $HCOOH + OH^- \longrightarrow H_2O + COO^-$/

added alkali reacts with H^+ / $H^+ + OH^- \longrightarrow H_2O$✓

$\longrightarrow HCOO^-$ / Equilibrium moves to right (to counteract change) ✓

$HCOO^-$ reacts with added acid or H^+ ✓

$\longrightarrow$ HCOOH / Equilibrium moves to left (to counteract change) ✓

[6]

qwc: communicates in terms of relevant equilibrium ✓ [1]

(b) For a buffer, $K_a = [H^+] \times [HCOO^-]/[HCOOH]$ ✓

$[H^+] = K_a \times [HCOOH]/[HCOO^-] = 1.6 \times 10^{-4} \times 1/2.5 = 6.4 \times 10^{-5}$ mol dm^{-3}✓

$pH = -\log[H^+] = -\log(6.4 \times 10^{-5}) = 4.19 / 4.2$ ✓

OR

$pH = pK_a - \log [HCOOH]/[HCOO^-]$ ✓

$pK_a = 3.8$ ✓

$pH = 3.8 + 0.4 = 4.2$ ✓

NOTES

3.19 worth ✓✓ (incorrect power of 10)

3.4 worth ✓✓ (use of $[HCOOH]/[HCOO^-]$)

[3]

[Total: 10]

5.

	Ca	:	C	:	O
=	31.3/40.1	:	18.7/12	:	50.0/16 ✓
=	0.78	:	1.56	:	3.125
=	1	:	2	:	4

Empirical formula of Y = CaC_2O_4 ✓

[2]

mass of Ca in kidney stone = 2 x 31.3/100 = 0.626 g ✓
moles of Ca in kidney stone = 0.626/40.1 = 0.0156 mol ✓
number of Ca^{2+} ions removed = $6.02 \times 10^{23} \times 0.0156 = 9.39 \times 10^{21}$ ions ✓
0.0156 mol Ca is 2 marks (molar mass 128.1 g mol^{-1})

OR

moles of Ca = 2/128.1 ✓ = 0.0156 mol ✓
number of Ca^{2+} ions removed = $6.02 \times 10^{23} \times 0.0156 = 9.39 \times 10^{21}$ ions ✓
For consequential marking of last point, must be evidence of ***moles*** *x L*

[3]

Molecular formula of **X** = $H_2C_2O_4$ ✓
Structural formula = $(COOH)_2$ ✓

[2]

Oxalic acid forms hydrogen bonds with water ✓
2 x O–H in structure / 2 x COOH groups / no hydrocarbon chain / diagram showing at least 2 H bonds with water per oxalic acid molecule ✓

[2]
[Total: 9]