## Equilibria

## Mark Scheme 10

| Level | International A Level |
| :--- | :--- |
| Subject | Chemistry |
| Exam Board | CIE |
| Topic | Equilibria |
| Sub-Topic |  |
| Paper Type | Theory |
| Booklet | Mark Scheme 10 |

Time Allowed:
Score:
Percentage:

Grade Boundaries:

| A* | A | B | C | D | E | U |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $>85 \%$ | $777.5 \%$ | $70 \%$ | $62.5 \%$ | $57.5 \%$ | $45 \%$ | $<45 \%$ |

(a) $\mathrm{N}_{2}+2 \mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}\left(\right.$ or via NO ) or $2 \mathrm{NO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$
(b) (i) catalytic converter and passing the exhaust gases over a catalyst/Pt/Rh
(ii) $\mathrm{NO}_{2}+2 \mathrm{CO} \rightarrow 1 / 2 \mathrm{~N}_{2}+2 \mathrm{CO}_{2}$ or similar Allow $2 \mathrm{NO}_{2}+\mathrm{CH}_{4} \rightarrow \mathrm{CO}_{2}+\mathrm{N}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
(c) No, it wouldn't be reduced. Because the reaction in (a) does not presuppose a particular fuel (owtte)
Allow formed from $\mathrm{N}_{2}$ and $\mathrm{O}_{2}$ in air during combustion
(d) (i) $\mathrm{SO}_{3}$ produces acid rain
(ii) $\mathrm{NO}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{NO}_{2}$
(iii) $\mathrm{K}_{\mathrm{p}}=\left(p_{\mathrm{NO}} \cdot p_{\mathrm{SO}_{3}}\right) /\left(p_{\mathrm{NO}_{2}} \cdot p_{\mathrm{SO}_{2}}\right)$
units: dimensionless/none (don't accept just a blank!)
(iv) $\mathrm{K}_{\mathrm{p}}=99.8^{2} / 0.2^{2}=2.5 \times 10^{5}$
(v) It will shift to the right (owtte) because the reaction is exothermic. NOT just Le Chatelier argument [1]
[Total: 11]
diag: $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}---\mathrm{OHCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ or $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}--\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ (i.e. H-bond from OH group to either OH or $\mathrm{NH}_{2}$ )
(b) propylamine is more basic than phenylamine
because lone pair on N is delocalised over ring in phenylamine (so less available for protonation)
or the propyl group is electron-donating, so the lone pair is more available
(c) $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{H}^{+} \longrightarrow \mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}$
or $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{HCl} \longrightarrow \mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+} \mathrm{C} t$
or $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+} \mathrm{OH}^{-}$ (reaction with any acceptable Bronsted acid accepted)
(d) ( X is $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CN}$
(ii) step 1 is KCN in ethanol, heat [HCN negates]
step 2 is $\mathrm{H}_{2}+\mathrm{Ni} / \mathrm{Pt}$ or $\mathrm{LiAlH}_{4}$ or Na in ethanol [NOT $\mathrm{NaBH}_{4}$ or $\mathrm{Sn} / \mathrm{HCl}$ ]
(1) $[3]$
(e) ethanolamine:
Na
or $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-} / \mathrm{H}^{+}$
or $\mathrm{MnO}_{4}^{-} / \mathrm{H}^{+}$
or $\mathrm{PCl}_{3} / \mathrm{PCl}_{5} / \mathrm{SOCl}_{2}$
(1) steamy fumes
phenylamine:
$\mathrm{Br}_{2}(\mathrm{aq})$
decolourises / white ppt formed
or $\mathrm{HNO}_{2} / \mathrm{H}^{+}$at $\mathrm{T}<10^{\circ} \mathrm{C}$, then phenol in NaOH
(1) coloured dye formed

3 (a (i) $\mathrm{Br}_{2}$ (ignore solvent, but do not credit $\mathrm{AlCl}_{3}$ or HCl or light) (1)
(ii) curly arrow from $\mathrm{C}=\mathrm{C}$ to Br (1) another one breaking $\mathrm{Br}-\mathrm{Br}$ bond. (1) correct intermediate cation and $\mathrm{Br}^{-}$produced (not $\mathrm{Br}^{\delta-}$ ) (1)
[max 3]
(b) $\mathbf{B}$ is $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ (1)

C is $\mathrm{NCCH}_{2} \mathrm{CH}_{2} \mathrm{CN}$ (1)
E is $\mathrm{ClCOCH} \mathrm{CH}_{2} \mathrm{COCl}(1)$
(Allow $\left(\mathrm{CH}_{2}\right)_{2}$ or $\mathrm{C}_{2} \mathrm{H}_{4}$. Allow correct atoms in any order on LHS but order must be correct on RHS)
(c) reaction II: heat, dilute $\mathrm{H}^{+}(\mathrm{aq})$ or $\mathrm{HCl}(\mathrm{aq})$ or $\mathrm{HCl}($ conc $)$ or $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$ (1)
reaction III: $\mathrm{H}_{2}+\mathrm{Ni}$ (or other named catalyst) or $\mathrm{LiAHH}_{4}$ or Na in ethanol (1)
(d) $\mathrm{NH}_{4}^{+}(1)$
(e) (i) $\left[-\mathrm{NHCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}-\mathrm{COCH}_{2} \mathrm{CH}_{2} \mathrm{CO}-\right]$ (1) (allow $\left(\mathrm{CH}_{2}\right)_{4}$ and $\left(\mathrm{CH}_{2}\right)_{2}$ ) (not dimer, needs bonds both ends)
(ii) $\mathrm{HCl}(1)$
(f) (i) $\left[\mathrm{H}^{+}\right]=10^{-\mathrm{pH}}=10^{-2.6}=2.51 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)(1)$
(ii) $\mathrm{Ka}=\left[\mathrm{H}^{+}\right]^{2} / \mathrm{c}=6.31 \times 10^{-5}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$ (allow ecf from (i)) (1)

4 (a (i) Partition coefficient (PC) is an equilibrium constant representing the distribution of a solute between two solvents.
or $\mathrm{PC}=$ ratio of the concentrations of the solute in the two solvents or $\mathrm{PC}=[\mathrm{X}]_{a} /[\mathrm{X}]_{b}$
(ii) If 0.4 g has been extracted, 0.1 g remain in the aqueous layer.
the concentration in the hexane layer $=\frac{0.4}{20}=0.02 \mathrm{~g} \mathrm{~cm}^{-3}$
the concentration in the aqueous layer $=\frac{0.1}{100}=0.001 \mathrm{~g} \mathrm{~cm}^{-3}$

$$
\begin{equation*}
K_{\mathrm{pc}}=0.02 / 0.001=\mathbf{2 0} \tag{1}
\end{equation*}
$$

(iii) $1^{\text {st }}$ extraction: hexane $x / 10 \mathrm{~g} \mathrm{~cm}^{-3}$ water $(0.50-x) / 100 \mathrm{~g} \mathrm{~cm}^{-3}$
$K_{\text {pc }}=\frac{\mathrm{x} / 10}{(0.5-\mathrm{x}) / 100}=20$
hence $\quad x / 10=(10-20 x) / 100$ $100 x=10(10-20 x)$ or $100 x=100-200 x$

$$
\begin{equation*}
x=0.33 \mathrm{~g} \tag{1}
\end{equation*}
$$

$2^{\text {nd }}$ extraction: hexane $y / 10 \mathrm{~g} \mathrm{~cm}^{-3} \quad$ water $(0.17-y) / 100 \mathrm{~g} \mathrm{~cm}^{-3}$
$K_{\mathrm{pc}}=\frac{\mathrm{y} / 10}{(0.17-\mathrm{y}) / 100}=20$
hence $y / 10=(3.4-20 y) / 100$

$$
100 y=10(3.4-20 y) \text { or } 100 y=34-200 y
$$

$$
\begin{equation*}
y=0.11 \mathrm{~g} \tag{1}
\end{equation*}
$$

 (correct answer = [3])
(b) berries are aqueous media

PCBs are insoluble/sparingly soluble in water or more fat-soluble
(ii) partition coefficient or [fat]/[water] is greater than 1
(c) (i) 4 (four)
(ii)

correct spot circled
correct spot squared
[in each case, more than one spot circled or squared negates the mark]

5 (a d-orbitals split into two / different levels light is absorbed electron is promoted from a lower to a higher level colour observed is the complement of the colour absorbed $\mathrm{E}=\mathrm{hf}$
any 3 points
(b) $\quad\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ is pale blue
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ is deep / dark blue or purple
(ii) because it has a larger absorbance peak or a larger $\varepsilon_{0}$ value
because $\lambda_{\text {max }}$ is in the visible region (hence more visible light is absorbed)
(iii) curve will have $\lambda_{\text {max }}$ between $>600 \mathrm{~nm}$ and 800 nm with maximum $\varepsilon_{0}$ in between the other two
(c) $\quad \mathrm{K}_{\mathrm{c}}=\left[\mathrm{CuCl}_{4}{ }^{2-}\right] /\left(\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{4}\right)$ units are $\mathrm{mol}^{-4} \mathrm{dm}^{12}$
(ii) $\left[\mathrm{CuCl}_{4}{ }^{2-}\right]\left[\mathrm{Cu}^{2+}\right]=\mathrm{K}_{\mathrm{c}}\left[\mathrm{Cl}^{-}\right]^{4}=672$ (no units)

