

Sample Question Paper - 11
Chemistry (043)
Class- XII, Session: 2021-22
TERM II

Time allowed : 2 hours

Maximum marks : 35

General Instructions :

Read the following instructions carefully.

1. There are 12 questions in this question paper with internal choice.
2. SECTION A - Q. No. 1 to 3 are very short answer questions carrying 2 marks each.
3. SECTION B - Q. No. 4 to 11 are short answer questions carrying 3 marks each.
4. SECTION C - Q. No. 12 is case based question carrying 5 marks.
5. All questions are compulsory.
6. Use of log tables and calculators is not allowed.

SECTION - A

1. Limiting molar conductivity for some ions are $\text{Na}^+ - 50.1$, $\text{Cl}^- - 76.3$, $\text{H}^+ - 349.6$, $\text{CH}_3\text{COO}^- - 40.9$, $\text{Ca}^{2+} - 19.0$.
What will be the limiting molar conductivities of CaCl_2 , CH_3COONa and NaCl ?
2. Account for the following :
 - (i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN .
 - (ii) There are two $-\text{NH}_2$ groups in semicarbazide ($\text{H}_2\text{NNHCONH}_2$). However, only one is involved in the formation of semicarbazone.
3. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

SECTION - B

4.

$E^\circ_{(\text{M}^{2+}/\text{M})}$	Cr	Mn	Fe	Co	Ni	Cu
	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

From the given data of E° values, answer the following questions :

- (i) Why is $E^\circ_{(\text{Cu}^{2+}/\text{Cu})}$ value exceptionally positive?
 - (ii) Why is $E^\circ_{(\text{Mn}^{2+}/\text{Mn})}$ value highly negative as compared to other elements?
 - (iii) Which is a stronger reducing agent Cr^{2+} or Fe^{2+} ? Give reason.
5. (i) Write the structures of compounds A, B and C in each of the following reactions :
- (a) $\text{C}_6\text{H}_5\text{Br} \xrightarrow{\text{Mg/dry ether}} \text{A} \xrightarrow[\text{(b) H}_3\text{O}^+]{\text{(a) CO}_2(\text{g})} \text{B} \xrightarrow{\text{PCl}_5} \text{C}$
- (b) $\text{CH}_3\text{CN} \xrightarrow[\text{(b) H}_3\text{O}^+]{\text{(a) SnCl}_2/\text{HCl}} \text{A} \xrightarrow{\text{dil. NaOH}} \text{B} \xrightarrow{\Delta} \text{C}$
- (ii) Do the following conversion in not more than two steps: Benzoic acid to benzaldehyde



OR

- (a) Write the chemical reaction involved in Wolff-Kishner reduction.
- (b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.
 $\text{C}_6\text{H}_5\text{COCH}_3$, CH_3-CHO , CH_3COCH_3
- (c) A and B are two functional isomers of compound $\text{C}_3\text{H}_6\text{O}$. On heating with NaOH and I_2 , isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.
6. Ranju is using normal water for washing clothes. She observed that her clothes were not getting very clean although she is using more amount of soaps or detergents. Her friend Swarna advised Ranju washing clothes in warm water. Ranju was surprised to see that washing of clothes with soaps or detergents is easier in luke warm water than cold water.
- Now answer the following questions:
- (i) What are the processes involved in washing of clothes?
- (ii) Why washing of clothes using soap or detergent is easier in warm water?
7. From the data given below, calculate the order of reaction.

S.No.	[A](M)	[B](M)	Rate (M s^{-1})
1.	1.0	0.20	0.10
2.	2.0	0.20	0.20
3.	2.0	0.40	0.80

OR

For the first order thermal decomposition reaction, the following data were obtained :



Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant.

(Given : $\log 2 = 0.301$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

8. (a) What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when
- (i) $\Delta_o > P$ (ii) $\Delta_o < P$
- (b) Write two limitations of crystal field theory.

OR

- (a) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green and becomes violet when ethane-1,2-diamine is added to it. Identify the observation.
- (b) Write IUPAC name of $[\text{Ag}(\text{NH}_3)_2] [\text{Ag}(\text{CN})_2]$.
9. A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potential of copper and zinc are 0.34 V and -0.76 V respectively.
- (i) What will be the cell reaction?
- (ii) What will be the standard electromotive force of the cell?
- (iii) Which electrode will be positive?



OR

A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.

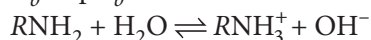
(Given : $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$)

10. (a) How would you account for the following :
- (i) The oxidising power of oxoanions are in the order
 $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$
 - (ii) The third ionization enthalpy of manganese ($Z = 25$) is exceptionally high.
- (b) Name a transition element which does not exhibit variable oxidation states.
11. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula $\text{C}_4\text{H}_8\text{O}$. Isomers (A) and (C) give positive Tollens' test whereas isomer (B) does not give Tollens' test but gives positive iodoform test. Isomers (A) and (B) on reduction with $\text{Zn}(\text{Hg})/\text{conc. HCl}$ give the same product (D).
- (a) Write the structures of (A), (B), (C) and (D).
 - (b) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN?

SECTION - C

12. Read the passage given below and answer the questions that follow:

Amines are basic in nature. The basic strength of amines can be expressed by their dissociation constant, K_b or $\text{p}K_b$.



$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} \text{ and } \text{p}K_b = -\log K_b$$

Greater the K_b value or smaller the $\text{p}K_b$ value, more is the basic strength of amine. Aryl amines such as aniline are less basic than aliphatic amines due to the involvement of lone pair of electrons on N-atom with the resonance in benzene. Electron-donating groups such as $-\text{CH}_3$, $-\text{OCH}_3$, etc. increase the basicity while electron-withdrawing substitutes such as $-\text{NO}_2$, $-\text{CN}$, halogens, etc. decrease the basicity of amines. The effect of these substituents is more at p -than at m -positions.

- (a) Which has the lowest $\text{p}K_b$ value between aniline and N,N -dimethylaniline? Explain.
- (b) Arrange the following in the decreasing order of basicity : Aniline, o -toluidine, m -toluidine
- (c) Why are amines less acidic than alcohols of comparable molecular masses?
- (d) Arrange the following compounds in increasing order of solubility in water : $\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$

OR

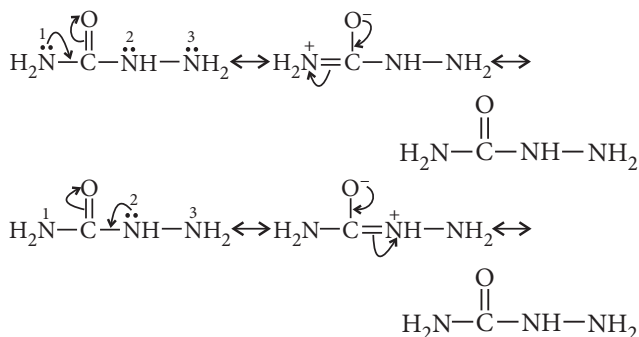
Aniline is a weaker base than cyclohexylamine. Explain.



$$\begin{aligned}
 1. \quad \Lambda_m^\circ \text{CaCl}_2 &= \lambda_{\text{Ca}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ \\
 &= 119.0 + 2 \times 76.3 = 271.6 \text{ S cm}^2 \text{ mol}^{-1} \\
 \Lambda_m^\circ \text{CH}_3\text{COONa} &= \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{Na}^+}^\circ \\
 &= 40.9 + 50.1 = 91 \text{ S cm}^2 \text{ mol}^{-1} \\
 \Lambda_m^\circ \text{NaCl} &= \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \\
 &= 50.1 + 76.3 = 126.4 \text{ S cm}^2 \text{ mol}^{-1}
 \end{aligned}$$

2. (i) It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3 there are two electron releasing methyl groups attached to the carbonyl carbon that hinders the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO , there is only one methyl group attached to carbonyl carbon.

(ii) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.



Lone pairs of N-1 and N-2 are involved in conjugation with >C=O group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

$$\begin{aligned}
 3. \quad \text{For first order reaction, } t &= \frac{2.303}{k} \log \frac{[R_0]}{[R_t]} \\
 \text{For 99\% completion of reaction} \\
 t = t_{0.99}, [R]_0 &= 1, [R]_t = (1 - 0.99) = 0.01 = 10^{-2} \\
 t_{0.99} &= \frac{2.303}{k} \log \frac{1}{10^{-2}} = \frac{2.303}{k} \log 10^2 = \frac{2.303}{k} \times 2 \quad \dots(i)
 \end{aligned}$$

$$\begin{aligned}
 \text{For 90\% completion of reaction} \\
 t = t_{0.90}, [R]_0 &= 1, [R]_t = (1 - 0.9) = 0.1 = 10^{-1} \\
 t_{0.90} &= \frac{2.303}{k} \log \frac{1}{10^{-1}} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} \quad \dots(ii)
 \end{aligned}$$

Comparing equations (i) and (ii),

$$t_{0.99} = 2 \times t_{0.90}$$

4. (i) Electrode potential (E°) value is the sum of three factors :

(a) Enthalpy of atomisation $\Delta_a H$ for $\text{Cu}_{(s)} \rightarrow \text{Cu}_{(g)}$

(b) Ionisation enthalpy $\Delta_i H$ for $\text{Cu}_{(g)} \rightarrow \text{Cu}_{(g)}^{2+}$

(c) Hydration enthalpy $\Delta_{hyd} H$ for $\text{Cu}_{(g)}^{2+} \rightarrow \text{Cu}_{(aq)}^{2+}$

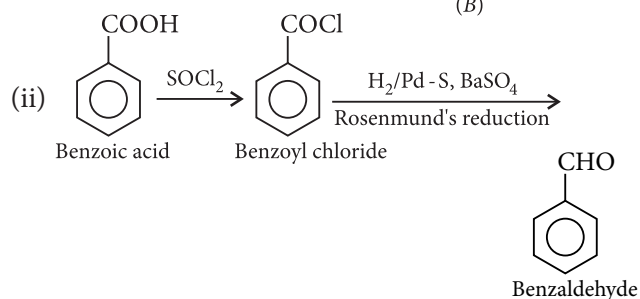
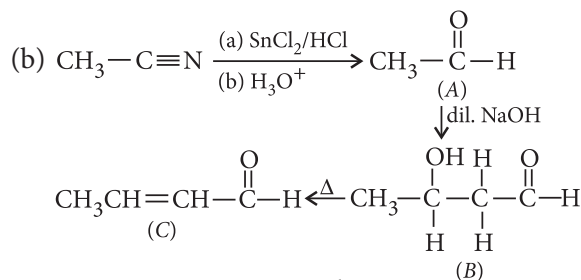
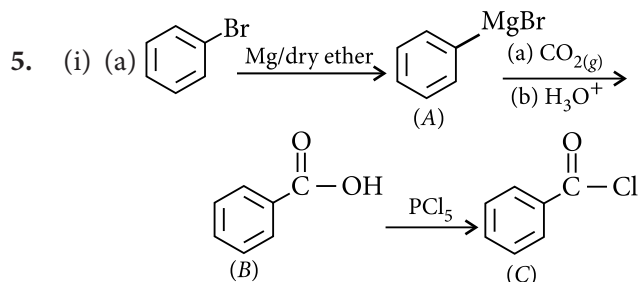
In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration.

This is why $E_{M^{2+}/M}^\circ$ for Cu is positive.

(ii) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence, $E_{\text{Mn}^{2+}/\text{Mn}}^\circ$ is more negative.

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+} .

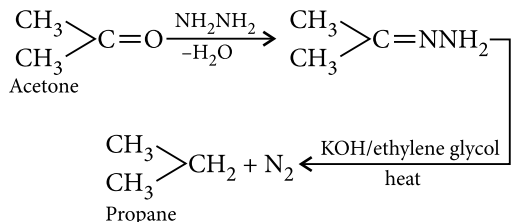
$E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^\circ$ is negative (-0.41 V) whereas $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ$ is positive ($+0.77 \text{ V}$). Thus Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+} . Hence, Cr^{2+} is stronger reducing agent than Fe^{2+} .



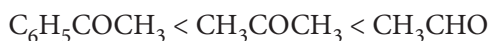
OR

(a) Wolff-Kishner reduction : The carbonyl group (>C=O) of aldehydes and ketones is reduced to >CH_2 group on treatment with hydrazine followed

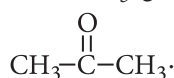
by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol, e.g.,



(b) Increasing order of reactivity towards nucleophilic addition reaction :



(c) Formula of compounds A and B is $\text{C}_3\text{H}_6\text{O}$. B forms yellow precipitate of iodoform. Hence, B must contain $-\text{COCH}_3$ group. Therefore, compound 'B' must be



A does not give iodoform test and it is functional isomer of B thus, it may be $\text{CH}_3\text{CH}_2\text{CHO}$.

6. (i) Washing of clothes involves micelle formation and emulsification.

(ii) Washing of clothes is due to micelle formation. Micelles are formed at a certain minimum temperature known as Kraft's temperature. This temperature is more readily achieved in warm water as compared to cold water.

7. Let rate of reaction $r = k[A]^a[B]^b$

From the data

$$r_1 = 0.10 \text{ M s}^{-1} = k(1.0 \text{ M})^a (0.20 \text{ M})^b \quad \dots \text{ (i)}$$

$$r_2 = 0.20 \text{ M s}^{-1} = k(2.0 \text{ M})^a (0.20 \text{ M})^b \quad \dots \text{ (ii)}$$

$$r_3 = 0.80 \text{ M s}^{-1} = k(2.0 \text{ M})^a (0.40 \text{ M})^b \quad \dots \text{ (iii)}$$

Dividing eqn. (i) by eqn. (ii)

$$\frac{r_1}{r_2} = \frac{0.10 \text{ M s}^{-1}}{0.20 \text{ M s}^{-1}} = \frac{k(1.0 \text{ M})^a (0.20 \text{ M})^b}{k(2.0 \text{ M})^a (0.20 \text{ M})^b}$$

$$\text{or, } \frac{1}{2} = \left(\frac{1}{2}\right)^a \text{ or } a = 1$$

Dividing eqn. (ii) by eqn. (iii)

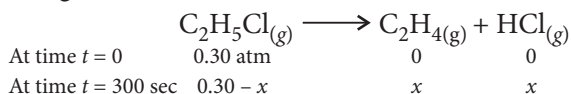
$$\frac{r_2}{r_3} = \frac{0.20 \text{ M s}^{-1}}{0.80 \text{ M s}^{-1}} = \frac{k(2.0)^a (0.20)^b}{k(2.0)^a (0.40)^b} \Rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^b$$

$$b = 2$$

Hence, order of reaction = $1 + 2 = 3$

OR

The given reaction is



$$\text{Total pressure} = 0.30 - x + x + x = 0.50$$

$$\text{or } 0.30 + x = 0.50$$

$$\therefore x = 0.50 - 0.30 = 0.20$$

$$\therefore \text{Initial pressure, } P_0 = 0.30 \text{ atm}$$

$$\text{Pressure of } \text{C}_2\text{H}_5\text{Cl} \text{ after 300 sec,}$$

$$P_t = 0.30 - 0.20 = 0.10 \text{ atm}$$

Using formula for first order reaction,

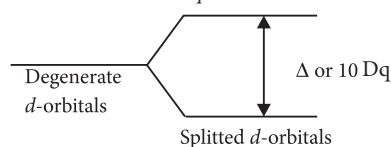
$$k = \frac{2.303}{t} \log \left(\frac{P_0}{P_t} \right)$$

$$k = \frac{2.303}{300} \log \left(\frac{0.30}{0.10} \right)$$

$$k = \frac{2.303}{300} \log 3 = \frac{2.303 \times 0.4771}{300} = 3.66 \times 10^{-3} \text{ sec}^{-1}$$

8. (a) The difference of energy between two splitted levels of d -orbitals is called crystal field splitting energy. It is denoted by Δ or 10 Dq .

For octahedral, it is denoted as Δ_o , for tetrahedral it is Δ_t and for square planar Δ_{sp} .



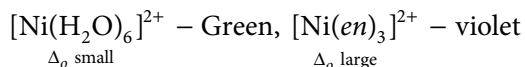
(i) When $\Delta_o > P$, $t_{2g}^4 e_g^0$ (ii) When $\Delta_o < P$, $t_{2g}^3 e_g^1$

(b) (i) It assumes ligand to be point charges.

(ii) It does not take into account the covalent character of bonding between the ligand and the central atom.

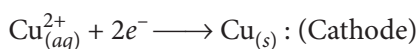
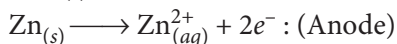
OR

(a) Ethane-1,2-diamine is stronger ligand than H_2O . When H_2O molecule is replaced by ethane-1,2-diamine (*en*) the crystal field splitting energy (Δ) increases. Complex absorbs light of higher frequency for $d-d$ transition. This is why colour of complex changes from green to violet.

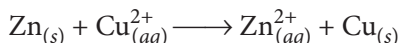


(b) Diammine silver (I) dicynidoarzenate (I)

9. (i) The cell reactions are :



Net reaction :



$$(ii) E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

(iii) Copper electrode will be positive on which reduction takes place.

OR

The given cell may be represented as



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{or } 0.422 \text{ V} = 0.46 \text{ V} - \frac{0.0591}{2} \log \frac{0.1}{[\text{Ag}^+]^2}$$

$$-0.038 \text{ V} = -0.0295 \log \frac{0.1}{[\text{Ag}^+]^2}$$

$$\text{or } \log \frac{0.1}{[\text{Ag}^+]^2} = \frac{-0.038}{-0.0295} = 1.288$$

$$\text{or } \frac{0.1}{[\text{Ag}^+]^2} = \text{antilog } 1.288 = 19.41$$

$$\therefore [\text{Ag}^+]^2 = \frac{0.1}{19.41} = 5.1519 \times 10^{-3}$$

$$[\text{Ag}^+] = 7.1 \times 10^{-2} \text{ M}$$

10. (a) (i) Change in $\text{Cr}_2\text{O}_7^{2-}$ to Cr(III) is 3 and in MnO_4^- to Mn(II) is 5.

Change in oxidation state is large and the stability of reduced products in $\text{V(III)} < \text{Cr(III)} < \text{Mn(II)}$. This is why oxidising power of $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$.

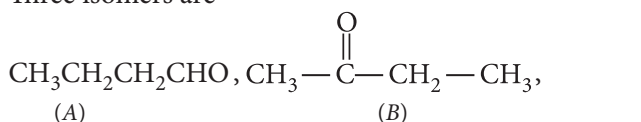
(ii) Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled $3d$ -orbitals $[\text{Mn}^{2+} (Z = 25) = 3d^5]$.

(b) Scandium ($Z = 21$) does not exhibit variable oxidation states.

11. (a) As (A) and (C) give positive Tollens' test thus these two should be aldehyde while (B) should be a ketone (does not give Tollens' test) with $-\text{C}(=\text{O})-\text{CH}_3$

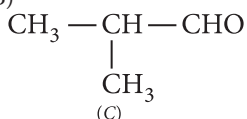
group (as it gives positive iodoform test).

Three isomers are

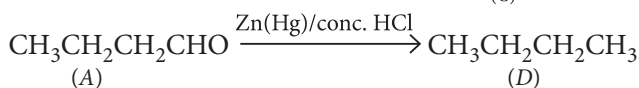


(A)

(B)

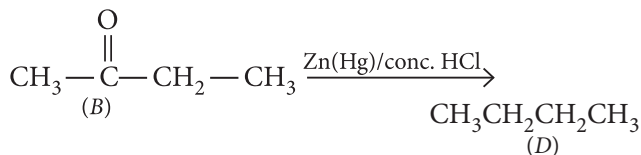


(C)



(A)

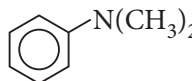
(D)



(B)

(D)

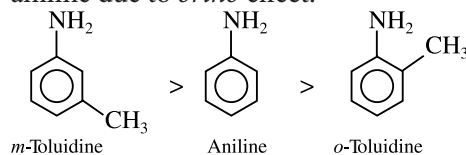
(b) Out of (A), (B) and (C) isomers, (B) is least reactive towards addition of HCN .

12. (a)  or *N,N*-dimethyl aniline is

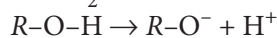
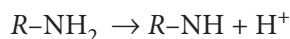
the stronger base than aniline due to $+I$ -effect of two methyl groups. Hence, it has lowest pK_b value.

(b) In general, electron donating ($+R$) group which when present on benzene ring ($-\text{NH}_2$, $-\text{OR}$, $-\text{R}$, etc.) at the para position increases the basicity of aniline.

Ortho substituted anilines are weaker bases than aniline due to *ortho* effect.



(c) In alcohols, the hydrogen atom is attached to more electronegative oxygen atom whereas nitrogen of amines is less electronegative. After the loss of H^+ ion, the negative charge is more easily accommodated on oxygen than in case of nitrogen in amines. Hence, amines have lesser tendency to lose H^+ ions, so they are less acidic than alcohols.



1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

OR

Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $-\ddot{\text{N}}\text{H}_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of $-\text{NH}_2$ group. So, cyclohexylamine is a stronger base.

