PART A

GENERAL INTRODUCTION
AND
EXPERIMENTAL
Brief review on the electrochemical behaviour of the azo group at the dropping mercury electrode

Organic compounds containing the characteristic group \(-N\equiv N-\) are called azo compounds. The group \(-N\equiv N-\) may be linked to two aliphatic groups (R) or two aromatic groups or to aromatic group and an heterocyclic group as shown below.

\[
R-N\equiv N-R
\]

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array}
\]

The azo group may be an exocyclic one or it may be a part of the cyclic structure.
Electroreduction of azo compounds

Azo group undergoes electroreduction at the dropping mercury electrode (DME) irrespective of the nature of the moieties linked to it.

The azo compounds undergo electroreduction\(^1\,\,^3\) involving two or four electrons as shown below.

\[
\text{\( -N=N\)} \xrightarrow{2e^-,2H^+} \text{\( -NH-NH\)} ...
\]

\[
\text{\( -N=N\)} \xrightarrow{4e^-,4H^+} \text{\( -NH_2^+\)} \text{\( -NH_2\)} ...
\]

The earlier electrochemical investigations are mostly related to the electrolytic preparations. But the emphasis has slowly shifted from the preparative studies to the investigatory studies on the electrode reaction mechanism in the recent times.

The study of azo compounds is interesting and useful since this has application in the dye stuff industry and in chemical analysis. All these compounds have chemical carcinogenic nature.

Electrochemical studies in aqueous solution are susceptible to interference by the adsorption of the depolariser at the electrode-system interface. However the adsorption problems can be minimised to a larger extent by adding sufficient volume of an organic co-solvent to water. The electrochemical reductions in aprotic media involve single electron step with the formation of radical ions while such studies in aqueous solutions involve even number of electrons. Aromatic\(^1\,\,^2\) and heterocyclic\(^4\,\,^9\)
azo compounds in general exhibit two-electron reduction at the dropping mercury electrode.

\[
R_1\text{N=N--C} \quad 2e^-+2H^+ \quad R_1\text{NH--NH--Cl} \quad (3)
\]

\[
R_2\text{N=N--C--C--NR}_3 \quad 2e^-+2H^+ \quad R_3\text{NH--NH--C--C--NR}_3 \quad (4)
\]

Strong electron donating substituents such as -OH, -NH₂ present in the aromatic system or the basicity of the heterocyclic moiety cause four-electron reduction to the amines.

**Electrochemistry of the azo group in protolytic solvents**

Che-Man Chang has reviewed extensively the electrochemistry of the aromatic azo-hydrazo redox systems in aqueous solutions. Aromatic azo compounds generally undergo two-electron reduction at the dropping mercury electrode.

\[
X\text{N=N--C} \quad 2e^-+2H^+ \quad X\text{NH--NH--C--C--Y} \quad (5)
\]
The polarographic studies made on different azo compounds reveal that the polarographic behaviour is complex in nature\textsuperscript{13-17}. The behaviour depends critically on

(a) the pH of the solution\textsuperscript{18},

(b) the solvent composition\textsuperscript{19},

(c) the concentration of the compound\textsuperscript{14,20} and

(d) the presence of the surfactant\textsuperscript{15}.

The $E_{1/2} - \text{pH}$ relation of the reversible polarographic wave of the process represented in the equation (5) is given by the equation\textsuperscript{21}

$$E_{1/2} = \text{Constant} - \frac{0.059p}{n}\text{pH}$$ \hspace{1cm} (6)

where $p$ and $n$ denote the number of protons and the number of electrons respectively involved in the reduction process.

If $p = n = 2$, the half-wave potential is expected to change by -0.059V for every unit increase in the pH of the solution. Literature survey\textsuperscript{15,22,23} reveals that for many azo compounds, the slope of $E_{1/2}$-$\text{pH}$ plot differs considerably from this value of -0.059 V. $E_{1/2}$-$\text{pH}$ plots in many instances are even non-linear or consist of two linear portions. The reduction of the azo group is diffusion-controlled and the limiting current is proportional to the concentration of the compound at lower concentration\textsuperscript{13,22,24}. A deviation has been noticed in the linearity at higher concentrations of the substrate.
Factors affecting the reversibility of the reduction

The reversibility of the electrode reaction is very much influenced by

(a) the pH of the solution\textsuperscript{13-17,25} and

(b) the adsorptivity of the depolariser.

(a) Effect of pH

The reduction of the azo compounds is highly reversible at the extremes of the pH range 1.0-6.0\textsuperscript{12,14,16}. However, acids with slow dissociation rate in the buffer systems caused multistep irreversible polarographic waves. Thus, factors which affect the supply of protons at the electrode surface are found to cause unusual features in the polarograms. Delahay and co-workers\textsuperscript{26} observed similar phenomenon in the presence of acetic acid. Azobenzene-4-sulphonic and azobenzene-4',4'-disulphonic acids in buffer solutions containing ammonia or ethanolamine at the vicinity of the pH 9.0 however exhibited reversible waves. It is also observed that in many cases the pH of the solution decides the nature of the final product in the reduction. Hydrazobenzene obtained in the two-electron reduction of azobenzene, slowly rearranges to benzidine and diphenyl amine at the extremes of the pH range.
The rate of the rearrangement depends on the pH and is faster at low pH values. Slow rearrangement causes reversible reduction while rapid rearrangement causes irreversible reduction. In strongly acidic aqueous or alcoholic solutions, the end products of the reduction are benzidine (70%) and diphenylamine (30%).

(b) **Effect of adsorption on the electroreduction of the azo group**

The major disturbances encountered in the electrochemistry of azo-hydrazo systems are due to the adsorption of the azo compound or the hydrazo compound on the dropping mercury electrode. This is predominant in the solvents containing higher water content.

The rate of the electrode reaction in 30% methanol in the pH range 1.0-7.0 is very much determined by the adsorption kinetics of the azo-hydrazo species involved\textsuperscript{14}. Most strongly adsorbed surfactants were found to inhibit the electrode reaction altogether\textsuperscript{27,28}. 
Effect of the structure of the moiety on the electrochemical reduction of the azo group

The moieties linked to the azo group may behave as +R as well as -R groups depending on the electronic requirements of the reaction. The electronic effects of phenylazo groups are examined in two ways. In the first instance -N=N-C₆H₄- functions as the single system which transfers the effects of the variable phenyl group to the reaction site in the side chain. The efficiency of this transfer process is referred to as transmission coefficient \( \pi \). This is expressed as the ratio of the Hammett's reaction constants (\( \rho \)) for the phenylazo series and the phenyl series.

Phenylazo substituent behaves in most of its electrophilic substitution reactions as an electron withdrawing group with a \( \sigma_p \) value of +0.34. Further p-phenylazo substituent activates the aromatic system towards nucleophilic substitutions.

The results of polarographic reductions of the aromatic azo compounds reported in the literature are presented below. These are represented under two-heads namely two-electron reductions and four-electron reductions for convenience.

Two-electron reductions of aromatic azo compounds

Che-Man Chang comprehensively reviewed the different reports made on the electrochemistry of aromatic azo-hydrazo redox system in aqueous solutions. Some typical examples of two-electron reductions are presented in the Table 1.1.

The above reports reveal that azo group linked between two phenyl rings, undergoes in general two-electron reduction to hydrazo stage. The substituted
### TABLE 1.1

Some typical examples for two-electron reduction of azobenzenes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-Methyl azobenzene</td>
<td>20% EtOH</td>
<td>1.0-12.0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Azobenzene-4-carboxylic acid</td>
<td>20% EtOH</td>
<td>1.5-13.0</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>4-(Phenylazo)anisole</td>
<td>20% EtOH</td>
<td>1.5-13.0</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>4-(Phenylazo)acetophenone</td>
<td>20% EtOH</td>
<td>1.5-13.0</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>4-N,N'-Dimethylamino azobenzene-4'-sulphonic acid</td>
<td>H₂O</td>
<td>3.5-6.0</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>2-(4'-N,N-Dimethylamino-phenylazo)-benzoic acid</td>
<td>20% EtOH</td>
<td>9.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>4-(4'-Phenylazo sulphonic acid)-1-naphthol</td>
<td>H₂O</td>
<td>1.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>Azobenzene-4-sulphonic acid</td>
<td>H₂O</td>
<td>1.0-12.0</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>Azobenzene-4,4'-disulphonic acid</td>
<td>H₂O</td>
<td>1.0-12.0</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>Azobenzene</td>
<td>25-100%</td>
<td>0.0-12.4</td>
<td>19</td>
</tr>
<tr>
<td>11</td>
<td>4-N,N'-Dimethylamino azobenzene-4'-sulphonic acid</td>
<td>10% EtOH</td>
<td>3.5-9.8</td>
<td>23</td>
</tr>
<tr>
<td>12</td>
<td>4,4'-Diamino azobenzene</td>
<td>10% EtOH</td>
<td>3.5-9.8</td>
<td>23</td>
</tr>
</tbody>
</table>
azobenzenes as well as the parent compound show similar behaviour and a good correlation has been observed between the polarographic half-wave potential ($E_{1/2}$) and the Hammett substituent constant ($\sigma$) for meta and para substituents.

$$E_{1/2}(X) = E_{1/2}(H) + 0.136 \sigma_p(H)$$  \hspace{1cm} (8)

where

- $E_{1/2}(X)$ = half-wave potential of the substituted azobenzene
- $E_{1/2}(H)$ = half-wave potential of the azobenzene
- $\sigma_p(H)$ = Hammett substituent (para) constant.

The relationship was found valid for eight mono substituted azobenzenes in 20% ethanol at pH 0. But no linear relation was observed between the Hammett substituent constant (ortho) $\sigma_o$ and $E_{1/2}$ values probably due to steric factors.

The mechanism proposed for the two-electron reduction of the azo compounds at the dropping mercury electrode is presented in Scheme 1.1.

**Four-electron reduction of substituted azobenzene dyes**

Aromatic azo compounds generally undergo two-electron reduction at the dropping mercury electrode, but the compounds containing strongly electron donating groups such as -OH, -NH$_2$ etc. show four-electron reduction to the amine. Methyl orange$^{10}$, methyl red$^{10}$ and 4-hydroxy$^{3,32}$, 4-amino$^{10}$, 4-N,N-dimethyl-amino$^{10,22,23}$, 4-hydroxy-4'-sulphonic acid$^{10}$, 2,4-dihydroxy-4'-sulphonic acid$^{10}$ and 2,2',4-trihydroxy-4'-sulphonic acid derivatives$^{10}$ gave four-electron polarographic
Scheme 1.1*

\[
\begin{align*}
\text{Scheme 1.1*} \\
\text{Y} - \text{N} = \text{N} - \text{X} + \text{H}^+ & \iff \text{Y}^+ - \text{NH} = \text{N} - \text{X} \\
\text{Y} - \text{NH} = \text{N} - \text{X} \quad \text{Hg electrode} & \iff \text{Y}^+ - \text{NH} = \text{N} - \text{X} \\
\text{Y}^+ - \text{NH} = \text{N} - \text{X} (\text{ads}) + 2\text{e}^- & \iff \text{Y} - \text{NHN} \quad \text{Hg electrode} \\
\text{Y} - \text{NHN} (\text{ads}) + \text{H}^+ & \iff \text{Y} - \text{NH} = \text{N} - \text{X} \\
\text{Y} - \text{N} = \text{N} - \text{X} \quad \text{Hg electrode} & \iff \text{Y} - \text{N} = \text{N} - \text{X} \\
\text{Y} - \text{N} = \text{N} - \text{X} (\text{ads}) + 2\text{e}^- + 2\text{H}^+ & \iff \text{Y} - \text{NH} = \text{N} - \text{X} \\
\cdots \quad \cdots \\
\text{desorbed and/or further products} \\
\end{align*}
\]

* Taken from “The Chemistry of the hydrazo, azo and azoxy groups” - Part I, by S. Patai (John Wiley and Sons).
reduction waves. The end product is always the amine. Typical examples of four-electron reductions are presented in the Table 1.2.

The mechanism proposed for the four-electron reduction of the azo compounds at the dropping mercury electrode is presented in Scheme 1.2.

Reduction of heterocyclic azo compounds

Mailk et al.\textsuperscript{36} after studying the polarographic reduction of 3,5-dimethyl-1-thiocarbonyl-4-phenylazo pyrazole and its derivatives, reported that ortho substituted pyrazoles are reduced more easily than the corresponding p-substituted compounds. Goyal and Rajeev Jain\textsuperscript{37} reported that arylazo pyrimidinyl pyrazoles exhibit a single two-electron wave corresponding to the reduction of azo group. Rajeev Jain \textit{et al.}\textsuperscript{9} observed a single two electron transfer in the reduction of benzyl sulfonyl arylazo pyrazoles. Some typical examples of two-electron reductions are presented in Table 1.3.

The mechanism proposed for the two-electron reductions of the heterocyclic azo compounds at dropping mercury electrode is presented in Scheme 1.3.

Bannerjee \textit{et al.}\textsuperscript{52} reported that 3,5-dimethyl-4-(4'-sulphonamido benzeneazo) pyrazoles exhibit a four-electron irreversible double wave in acidic medium and a two-electron single wave in alkaline medium. They further proposed that the reduction in acidic medium does not involve the hydrazo-pyrazole as the intermediate. Fahmy, Abdel Aziz and Badran\textsuperscript{53} observed a well defined single polarographic wave for 5-arylazo-1-phenyl-2-thiohydantoin in a wide range of pH conditions in the entire pH range. A similar wave was reported for other compounds containing the
# TABLE 1.2

Some typical examples for four-electron reduction of azobenzene dyes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-N,N'-Dimethylamino azobenzene</td>
<td>20% EtOH</td>
<td>1.0-6.0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>4-(Phenylazo) aniline</td>
<td>20% EtOH</td>
<td>1.5-5.0</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>4-(N,N-Dimethylamino phenylazo)-4-sulphonic acid</td>
<td>H₂O</td>
<td>8.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>4-(4'-Phenylazo sulphonic acid)-resorcinol</td>
<td>H₂O</td>
<td>3.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>4-(4'-Phenylazo sulphonic acid)-1-naphthol</td>
<td>H₂O</td>
<td>1.5-6.0</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>2-(4'-Phenylazo sulphonic acid)-2-naphthol</td>
<td>H₂O</td>
<td>3.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>2-(2'-Hydroxy naphthylazo)benzene-4-sulphonic acid</td>
<td>H₂O</td>
<td>3.0-13.0</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>Benzeneazo-1-naphthol</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>1-(Benzeneazo-4-sulphonic acid)-2,4-dihydroxy naphthalene</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>2-(2', 4'-Dihydroxy naphthylazo)-1-phenol-5-sulphonic acid</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>11</td>
<td>2-(2', 4'-Dihydroxy naphthylazo)-1-phenol-4-sulphonic acid</td>
<td>50% EtOH</td>
<td>3.7-9.5</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>1-(4'-Hydroxy naphthylazo)-1-phenol-4-sulphonic acid</td>
<td>50% EtOH</td>
<td>9.5</td>
<td>13</td>
</tr>
<tr>
<td>13</td>
<td>Phenylazo phenol</td>
<td>50% EtOH</td>
<td>3.0-12.0</td>
<td>13</td>
</tr>
<tr>
<td>14</td>
<td>2-(4'-Bromo-2'-pyridylazo)-5-(N,N-dimethyl)aminophenol</td>
<td>50% EtOH</td>
<td>11.3-13.5</td>
<td>33</td>
</tr>
<tr>
<td>15</td>
<td>2-(3'-Hydroxy pyridylazo)-1-naphthalene</td>
<td>50% EtOH</td>
<td>11.3-13.5</td>
<td>33</td>
</tr>
<tr>
<td>16</td>
<td>4-Nitro azobenzene</td>
<td>50% EtOH</td>
<td>3.0-12.0</td>
<td>33</td>
</tr>
</tbody>
</table>
Table 1.2 (Cont.)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1-(Phenylazo)-3-pyridine</td>
<td>40% EtOH</td>
<td>3.0-12.0</td>
<td>33</td>
</tr>
<tr>
<td>18</td>
<td>2-(3'-Pyridyl azo)-phenol</td>
<td>40% EtOH</td>
<td>3.0-12.0</td>
<td>34</td>
</tr>
<tr>
<td>19</td>
<td>1-(2'-Hydroxy quinonylazo)-4-pyridine</td>
<td>40% EtOH</td>
<td>3.0-12.0</td>
<td>35</td>
</tr>
</tbody>
</table>
Scheme 1.2*

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N} &= \text{N} \rightarrow \text{N(C}_3\text{H}_2) \quad + \quad 2e^- + 2H^+ \quad \rightarrow \quad \text{C}_6\text{H}_5\text{N}^- \quad \text{NH} \rightarrow \quad \text{N(C}_3\text{H}_2) \\
\text{C}_6\text{H}_5\text{N}N\text{H} &\rightarrow \text{N(C}_3\text{H}_2) \quad + \quad H^+ \quad \rightarrow \quad \text{HN} \quad \rightarrow \quad \text{N} = \text{N} \quad \text{N(C}_3\text{H}_2) \quad + \quad \text{C}_6\text{H}_5\text{NH}_2 \\
\text{HN} = \text{N} \quad &\rightarrow \quad \text{N(C}_3\text{H}_2) \quad + \quad 2e^- + H^+ \quad \rightarrow \quad \text{H}_2\text{N} \quad \rightarrow \quad \text{N} \quad \text{N(C}_3\text{H}_2) \\
\text{HN} = \text{N} \quad &\rightarrow \quad \text{N(C}_3\text{H}_2) \quad + \quad \text{C}_6\text{H}_5\text{N}N\text{H} \quad \rightarrow \quad \text{N} \quad \text{N(C}_3\text{H}_2) \quad + \quad \text{C}_6\text{H}_5\text{NH}_2 \quad + \quad H^+ \\
\text{overall} &\rightarrow \quad \text{C}_6\text{H}_5\text{N} = \text{N} \rightarrow \text{N(C}_3\text{H}_2) \quad + \quad \text{H}_2\text{N} \quad \rightarrow \quad \text{N} \quad \text{N(C}_3\text{H}_2) \\
\text{C}_6\text{H}_5\text{N} &= \text{N} \rightarrow \text{N(C}_3\text{H}_2) \quad + \quad 4e^- + 4H^+ \quad \rightarrow \quad \text{C}_6\text{H}_5\text{NH}_2 \quad + \quad \text{H}_2\text{N} \quad \rightarrow \quad \text{N} \quad \text{N(C}_3\text{H}_2) \\
\end{align*}
\]

* Taken from "The Chemistry of the hydrazo, azo and azoxy groups" - Part I, by S. Patai (John Wiley and Sons).
TABLE 1.3
Some typical examples for two-electron reduction of heterocyclic azo compounds

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Thiocarbamoyl-3,5-diphenyl-4- (substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>1-Thiocarbamoyl-3,5-dimethyl-4- (substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Solochrome red ERS</td>
<td>H₂O</td>
<td>1.8-8.0</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>N'-Carbomoyl-3,5-dimethyl-4- (substituted benzeneazo)pyrazoles</td>
<td>90% DMF +10% EtOH</td>
<td>2.0-10.0</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>1-Phenyl-3,5-dimethyl-4- (substituted phenylazo)pyrazoles</td>
<td>90% DMF +10% EtOH</td>
<td>2.0-10.0</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>2-Amino-4-methyl-5- (substituted phenylazo)thiazoles</td>
<td>90% DMF +10% EtOH</td>
<td>2.0-10.0</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>N'-Benzyl sulfonyl-3,5-diphenyl-4- (substituted phenylazo)pyrazoles</td>
<td>20% EtOH</td>
<td>2.0-11.0</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>2-(Phenylazo)pyridine</td>
<td>50% EtOH</td>
<td>1.0-13.0</td>
<td>33</td>
</tr>
<tr>
<td>9</td>
<td>4-(2'-Pyridylazo)phenyl</td>
<td>50% EtOH</td>
<td>1.0-13.0</td>
<td>33</td>
</tr>
<tr>
<td>10</td>
<td>4-(2'-Pyridylazo)resorcinol</td>
<td>50% EtOH</td>
<td>1.0-13.0</td>
<td>33</td>
</tr>
<tr>
<td>11</td>
<td>4-(2'-Pyridylazo)-5-resorcinol</td>
<td>50% EtOH</td>
<td>1.0-13.0</td>
<td>33</td>
</tr>
<tr>
<td>12</td>
<td>2-(2'-Pyridylazo)-5-aminophenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>13</td>
<td>2-(2'-Pyridylazo)-5-(N,N-dimethyl)aminophenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>14</td>
<td>4-(3'-Pyridylazo)phenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>15</td>
<td>4-(3'-Pyridylazo)resorcinol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>16</td>
<td>1-(2'-Pyridylazo)-2-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>17</td>
<td>4-(2'-Pyridylazo)-1-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>18</td>
<td>4-(2'-Pyridylazo)-1-naphthyl amine</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>19</td>
<td>2-[(4'-Bromo-2'-pyridylazo)-5-(N,N-diethyl)] aminophenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>20</td>
<td>1-(3'-Pyridylazo)-2-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>21</td>
<td>1-(4'-Pyridylazo)-2-naphthol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
</tbody>
</table>
### Table 1.3 (Continued)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2-(2'-Quinolylazo)-4-(N,N-diethyl)aminophenol</td>
<td>50% EtOH</td>
<td>1.0-8.0</td>
<td>33</td>
</tr>
<tr>
<td>23</td>
<td>N'-(4', 6'-Dimethyl pyrimidinyl)-3,5-diphenyl (substituted phenylazo)-pyrazoles</td>
<td>DMF</td>
<td>2.0-10.0</td>
<td>37</td>
</tr>
<tr>
<td>24</td>
<td>3,5-Dimethyl-4-(substituted phenylazo)isoxazoles</td>
<td>50% DMF</td>
<td>2.0-10.0</td>
<td>38</td>
</tr>
<tr>
<td>25</td>
<td>N'-Benzoyl-3,5-dimethyl-4-(substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>39</td>
</tr>
<tr>
<td>26</td>
<td>N'-Benzoyl-3,5-diphenyl-4-(substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>40</td>
</tr>
<tr>
<td>27</td>
<td>N'-Benzoyl-3-methyl-5-phenyl-4-(substituted phenylazo)pyrazoles</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>41</td>
</tr>
<tr>
<td>28</td>
<td>2-Amino-4,6-dimethyl-5-(substituted phenylazo)pyrimidines</td>
<td>20% EtOH</td>
<td>2.0-10.0</td>
<td>42</td>
</tr>
<tr>
<td>29</td>
<td>4-[8'-Hydroxy quinolyl]azo]-benzene sulphonamide drugs</td>
<td>20% EtOH</td>
<td>3.3-11.2</td>
<td>43</td>
</tr>
<tr>
<td>30</td>
<td>N'-Phenylthiocarbomoyl-3,5-dimethyl-4-(substituted phenylazo)-pyrazoles</td>
<td>20% EtOH</td>
<td>2.0-12.0</td>
<td>44</td>
</tr>
<tr>
<td>31</td>
<td>1-Phenyl-3-amino-4-(4'-nitrobenzeneazo)pyrazolin-5-one</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>45</td>
</tr>
<tr>
<td>32</td>
<td>1-Phenyl-3-amino-(2'-substituted benzeneazo)pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>46</td>
</tr>
<tr>
<td>33</td>
<td>1-Phenyl-3-benzene sulphonamide-4-(4'-substituted aryl hydrazono)-pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>47</td>
</tr>
<tr>
<td>34</td>
<td>3-Amino-4-(4'-substituted benzeneazo)pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>48,49</td>
</tr>
<tr>
<td>35</td>
<td>N-(Benzene sulfonyl)-3-methyl-4-(4'-substituted benzeneazo)-pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>50</td>
</tr>
<tr>
<td>36</td>
<td>1-(4'-Hydroxy phenyl)-3-amino-4-(4'-substituted benzeneazo)-pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>51</td>
</tr>
</tbody>
</table>
Scheme 1.3

where \( R' = \)
The wave is different from the one observed with the compounds containing the hydrazone linkage. Darwish et al. reported that 5-arylazo-1-phenyl-4-thiohydantoin derivatives exhibit two waves. The reductive splitting of the azo linkage by a four-electron irreversible process is ascribed to the first wave. The second wave is ascribed to the reduction of -CO-NH-CO- group in the resulting molecule. 5-Arylazo-8-hydroxy quinoline exhibits two waves as reported by Issa et al. The first wave was attributed to the four-electron reduction of the azo group to the amine. Elnagdi et al. reported that coupling products of 4-hydroxycoumarins with aryl diazonium salt exist in the azo form from their polarographic studies.

These compounds give a single pH dependent irreversible four-electron wave in the pH range 2.0-11.0. Florence et al. observed that several differences occur between the electrode reactions of heterocyclic azo compounds and their benzene or naphthalene counterparts. The hydrazo derivatives of heterocyclic dyes are more stable towards disproportionation. Issa et al. reported that azo-azomethine compound in universal buffer solutions of pH 2.0-12.0, exhibit two waves of almost equal heights due to the reduction of the -N=N- and >C=N- centres respectively. The reduction corresponds to 8-electrons per molecule, 4-electrons for each -N=N- and >C=N- centre. Mary Suguna et al. reported that 2,4-dihydroxy-5-(4'-substituted benzeneazo)acetophenone in the pH range 8.1-10.1, containing 40% v/v dimethylformamide exhibit two waves in acidic medium and one wave in alkaline medium. The first wave is ascribed to the four-electron reduction of the azo group to the amine stage. p-Nitrophenyl diazoaryl sulphide exhibits two waves in 40%
ethanol-aqueous buffers (pH range 1.0 - 12.0). The first wave corresponds to the 4-electron reduction of the -N=N- group to form p-nitroaniline and the second wave to the 6-electron reduction of the nitroaniline to the diamine. Some typical examples of four-electron reductions are presented in Table 1.4.

The mechanism for the four-electron reduction of the azo group to the amine via hydrazo stage can be represented by the Scheme 1.4.

**Reduction of azo (-N=N-) group in the azomethine form (>C=N-NH-)**

*Four-electron reduction*

Azo compounds exhibit *cis-trans* isomerism\(^{71,72}\). Aromatic\(^{71,72}\) and heterocyclic\(^{73}\) azo compounds also exhibit azo-hydrazone tautomerism. Generally the phenyl hydrazones exist in the following structural forms and the hydrazone form is predominant in non-polar solvents or in pure liquids\(^{74,75}\), while ene hydrazone form (R-CH=CR\(_1\)-NHC\(_3\)H\(_3\)) is predominant in polar solvents.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{III} & \quad \text{IV}
\end{align*}
\]
### TABLE 1.4

Some typical examples of pyrazolin-5-ones involving four-electron reduction

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the compound</th>
<th>Solvent</th>
<th>pH range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-Amino-1-phenyl-4-phenylazo-pyrazolin-5-one</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>1-Phenyl-3-amino-4-(2'-nitro-benzeneazo) pyrazolin-5-one</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>1-Anilinomalonyl-3-methyl-4-(substituted benzeneazo)-5-pyrazolones</td>
<td>40% DMF</td>
<td>2.0-10.0</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>3-Amino-1-phenyl-4-(substituted benzeneazo) pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>N'-(2-Pyridine carbonyl)-3-methyl-4-(4'-substituted benzeneazo)-2-pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>N'-Benzoyl-3-methyl-4-(substituted benzeneazo)-2-pyrazolin-5-ones</td>
<td>40% DMF</td>
<td>2.1-10.1</td>
<td>70</td>
</tr>
</tbody>
</table>
Scheme 1.4

\[
\begin{align*}
\text{N=N=R} & \quad 2H^+ + 2e^- \quad \text{NH-NH-R} \\
\text{N=NH} & \quad + \\
\text{O} & \\
\end{align*}
\]

\[
\begin{align*}
\text{NH} &\quad 2H^+ + 2e^- \quad \text{NH}_2 \\
\text{O} & \\
\end{align*}
\]
The polarographic studies and the IR studies\textsuperscript{76} carried out on the phenyl hydrazones in aqueous methanol solutions\textsuperscript{59} showed the presence of all the three tautomeric forms. The hydrazo-azo tautomerism is strongly influenced by the nature of the solvent and is shifted towards the hydrazone form in polar solvents.

\begin{center}
\begin{tikzpicture}
\node (1) at (0,0) {IV};\node (2) at (2,0) {V};
\draw (0,0) -- (2,0) ;
\end{tikzpicture}
\end{center}

\textbf{In non-polar solvent} \hspace{1cm} \textbf{In polar solvent}

Ortho and para hydroxy-azo benzenes exhibit predominantly this tautomerism and the compounds exist largely in the hydrazone form in solutions and even in the solid state. The hydroxy-azo anthracenes exist in the hydrazone form\textsuperscript{72}, both in solution and the solid state. The azo group acts as a proton acceptor via hydrogen bond formation if hydroxyl group (\(\text{-OH}\))\textsuperscript{77,78} or amino group (\(\text{-NH}_2\))\textsuperscript{79} is present in the molecule in ortho and para positions. Generally hydroxy-azo aromatic compounds exist as intra-molecularly hydrogen bonded hydrazones in aqueous solutions and in methanol. An equilibrium exists between the azo and the hydrazone form.
The hydrazone tautomer (VII) is present predominantly in polar solvents. Huckel molecular orbital calculations support the above concept. The stability of the azo form or the hydrazone form depends on the following factors:

(a) the presence or absence of intra-molecular hydrogen bond.

(b) the electron withdrawing substituents and

(c) the large ring system bearing the oxygen atom.

The increase in OH—N bond strength shifts the equilibrium towards the hydrazone form. The decrease in the electron density on the proton accepting nitrogen atom increases the stability of the hydrazone form.

The azo-hydrazone tautomerism is also present in the number of aromatic azo heterocycles and the nature of the substituents present in the heterocyclic system plays a significant role on the azo-hydrazone tautomerism.

Hydrazone-azo tautomerism is also observed in benzeneazo heterocycles as in benzeneazo pyrazolin-5-ones. Further the azo-hydrazone tautomerism exists both in the solid state and in aqueous solution. However in the case of pyrazoles, the
tautomerism depends on the nature of the substituent present in the heterocyclic moiety.

(1) Pyrazoles (Structure VIII) with $R_2$ and $R_3$ as alkyl or phenyl groups do not exhibit azo-hydrazone tautomerism.

(2) On the other hand if $R_2$ and $R_3$ are -OH or =O group, they exhibit tautomerism.

Thus the nature of the substituent present in the heterocyclic moiety plays a significant role in the azo-hydrazone tautomerism. Polarography is generally employed as a tool to investigate this tautomerism since the reduction paths at the dropping mercury electrode differ for the two forms.

A brief account of the polarographic studies of the azo-heterocycles in the hydrazone form and undergoing 4-electron reduction cleavage to the amine is presented below.

5,5-Dimethylcyclohexane-2-benzothiozolyl hydrazone-1,3-diones in Britton-Robinson buffers in the pH range 2.0 - 12.0, undergo 4-electron reduction in a single wave. The following mechanism is suggested for the reduction process.
The reduction pattern of 2,3,4-pentane trione-3-phenyl hydrazone and some para substituted derivatives in the buffer solutions of pH 0.8 - 9.5, depends on the conversion of the hydrazone form to the azo form.

\[
\begin{align*}
\text{(A)} & \quad \text{Azo} \\
\text{(B)} & \quad \text{Hydrazone}
\end{align*}
\]

1-Ethyl mercapto-3-(4H) isoquinolones in alcoholic media, undergo four-electron reduction. The structure (B) is stable since it contains the conjugated double bond and this is further stabilised through hydrogen bonding between -OH group and the nitrogen attached to the aryl group.
\[
\text{I} \quad \text{H}^+ \quad \text{II} \quad \text{H}^+ \\
\text{NH}_2 \quad \text{E}_2 \quad \text{IV} \\
\text{IV} \quad \text{H}_3\text{O}^+ \quad \text{Hydrolysis} \\
\]

\[
\text{I} \quad \text{H}^+ + 2e^- + \text{H}^+ \rightarrow \text{II} + \text{H}_2\text{N}-\text{C}_6\text{H}_5 \\
\text{II} + 2e^- + 2\text{H}^+ \rightarrow \text{IV} \\
\text{IV} \quad \text{H}_3\text{O}^+ \rightarrow \text{Amid} + \text{HSC}_2\text{H}_5
\]
2-Naphthylhydrazone-5,5-dimethylcyclohexane-1,3-dione in buffered (pH 3.5-11.0) methanol-water mixture containing 60-80% v/v methanol exhibits a well-defined four-electron reduction in the entire pH range\textsuperscript{85}. The compound in the hydrazone form (A) undergoes reduction to the primary amine, consuming four-electrons.

It was reported by Ravindranath \textit{et al.}\textsuperscript{86} that 1-phenyl-3-amino-4-aryla-zopyrazolin-5-ones undergo reduction at mercury cathode in Britton-Robinson buffers (pH range 3.0 - 10.0) containing 40% v/v dimethylformamide according to the following mechanism.
The following mechanism for the polarographic reduction of 3-phenyl-2,3- 
diketopropionitrile-2-phenylhydrazine was however reported by Sammour et al. ⁸⁷
5-Arylazo-1-phenyl-2-thiohydantoin in 40% v/v ethanolic aqueous buffers resembles the compounds containing the hydrazone linkage and deviates from those containing the azo group in the electrochemical behaviour\textsuperscript{53}. 
Malik and Goyal reported that hydrazone tautomer plays a significant role in the four-electron reduction of 1-phenyl-2-substituted phenyl hydrazono-1,2,3-butanetrones in dimethylformamide.

\[ R_1 = -\text{CH}_3; \quad R_2 = -\text{C}_6\text{H}_5 \]
The hydrazone tautomer is prominent and involves four-electron reduction in the polarographic reduction of 4-aryl hydrazono-N'-hippuryl-3-methyl-2-pyrazolin-5-ones in Britton-Robinson buffer in the pH range 2.0 - 12.0.

\[
\begin{align*}
\text{R} & \quad \text{N} = \text{N} - \text{CH} - \text{C} - \text{CH}_3 \\
\text{O} & \quad \text{C} - \text{N} \\
\text{COCH}_2\text{NHCOC}_6\text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{N} = \text{N} - \text{C} - \text{C} - \text{CH}_3 \\
\text{O} & \quad \text{C} - \text{N} \\
\text{COCH}_2\text{NHCOC}_6\text{H}_5
\end{align*}
\]

\[
4\text{H}^+, 4\text{e}^-
\]

\[
\begin{align*}
\text{R} & \quad \text{NH}_2 \\
\text{H}_2\text{N} - \text{CH} - \text{C} - \text{CH}_3 \\
\text{O} & \quad \text{C} - \text{N} \\
\text{COCH}_2\text{NHCOC}_6\text{H}_5
\end{align*}
\]

The polarographic studies reveal that 3-arylazo-4-hydroxycoumarins exist in the hydrazone form. Therefore the following mechanism is suggested for the polarographic reduction.

\[
\begin{align*}
\text{OH} & \quad \text{N} = \text{N} - \text{C}_6\text{H}_5 \\
\text{N} & \quad \text{N} - \text{NH} - \text{C}_6\text{H}_5 \\
\text{O} & \quad \text{N} - \text{NH} - \text{C}_6\text{H}_5
\end{align*}
\]

\[
4\text{e}^-, 4\text{H}^+
\]

\[
\begin{align*}
\text{OH} & \quad \text{N} = \text{N} - \text{C}_6\text{H}_5 \\
\text{NH}_2 & \quad \text{H}_2\text{N} - \text{NH} - \text{C}_6\text{H}_5
\end{align*}
\]

Guanyl pyrazolin-5-ones in Britton-Robinson buffers of pH range 2.0-10.0 undergo four-electron diffusion-controlled, irreversible reduction in the hydrazone form.
The mechanism for the polarographic reduction of the aryl hydrazone of \( \alpha \)-cyano ketones has been proposed\(^9\) as

\[
\begin{align*}
\text{H}_3\text{C}_6-\text{N} &= \text{N}-\text{NH}-\text{N} = \text{C} \quad \text{R} \\
\text{R} &= -\text{C}_6\text{H}_5\text{CO}, -\text{CH}_3\text{CO}, -\text{CH}_3\text{C}=\text{NH} \\
\text{C}_6\text{H}_5-\text{NH}-\text{N} &= \text{C} \\
\text{C}_6\text{H}_5-\text{NH}-\text{N} &= \text{C} \\
\text{C}_6\text{H}_5-\text{NH}-\text{N} &= \text{C} \\
\text{OC}_2\text{H}_5
\end{align*}
\]

It is thus evident that the nature of the reduction of azo group is very much influenced by the structural features of the moiety to which the group is linked.
Basic principles of polarography

Polarography, a good and first electrochemical method of analysis, invented in 1922 by Jaroslav Heyrovsky, rests on the properties of current-potential curves obtained with a micro electrode usually, a dropping mercury electrode (DME). The current-potential relationships are used to determine the identity or concentration of a species reacting at the microelectrode.

By applying steadily increasing voltage of the polarographic cell, S-shaped current-potential pattern is obtained. When emf is applied to the cell, the species capable of undergoing electron transfer reaches the electrode surface by the process called general mass transfer. This takes place by three factors: migration, diffusion, and convection. Migration can be eliminated by using an indifferent electrolyte in excess which is called the supporting electrolyte. Diffusion of the species to the electrode is due to the concentration gradient produced at the electrode surface. The mass transfer by convection is due to the perturbation of the solution caused by stirring, by rotating or by vibrating the electrode or by causing periodic changes in the volume of the electrode as in the case of dropping mercury electrode (DME).

The important terms related to the polarograms are residual current, limiting current, diffusion current, half-wave potential, polarographic maxima.

Residual current

A small current which flows before the start of decomposition of the solution when a current-voltage curve is recorded is known as residual current. This is due to the changing current and to the impurities present if any.
Limiting current

It is the total current flowing through the polarographic cell when the electroactive species is almost reduced completely on the surface of the electrode.

Diffusion current

It is the current flowing through the polarographic cell when the electroactive species arrives at the electrode only by diffusion reduces/oxidises completely ($i_d$).

Half-wave potential

The potential corresponding to half the height of the wave is a quantity characteristic for each substance, thus enabling the analysis results to be evaluated quantitatively ($E_{1/2}$).

Polarographic maxima

Sometimes sharp and rounded maximum appears on the polarographic curves which is called polarographic maximum. These maxima are due to the streaming of the electrolyte close to the electrode surface. This can be suppressed by the addition of capillary-active substance such as gelatin, Triton x-100, agar and other colloids in suitable conditions.

The relationship between the maximum diffusion current and the concentration of the electroactive species is given by Ilkovic$^{93-96}$ as

$$i_d = 708 \, n \, C \, D^{1/2} \, m^{2/3} \, t^{1/6}$$  \hspace{1cm} (9)

and for mean diffusion current$^{95}$, the equation is

$$i_d = 607 \, n \, C \, D^{1/2} \, m^{2/3} \, t^{1/6}$$  \hspace{1cm} (10)
where

\[ i_d \text{ and } i_d' = \text{ diffusion current in } \mu\text{A} \]
\[ n = \text{ total number of electrons involved in the electrode process} \]
\[ C = \text{ concentration of the depolariser in mM} \]
\[ D = \text{ diffusion coefficient of the depolariser in } \text{cm}^2\text{s}^{-1}. \]
\[ m = \text{ rate of mercury flow in mg/sec} \]

and

\[ t = \text{ drop time in seconds.} \]

From the above equation, it can be understood that diffusion current is directly proportional to the square root of mercury column height (h) provided \( nD^{1/2}C \) is held constant. The plot of \( i_d \) vs \( h^{1/2} \) should be linear passing through origin which can be taken as a diagnostic criterion for the diffusion controlled nature of the process. Any deviation from this indicates the involvement of adsorption complications.

Heyrovsky and Ilkovic\(^9\) first derived an equation applicable to current-voltage curves for a reversible reaction such as

\[ A + ne^- \rightleftharpoons B \]

as

\[ E = E_{1/2} - \frac{0.05915}{n} \log \frac{i}{i_d - i} \text{ at } 25^\circ\text{C} \]  \( \ldots (11) \)
where

\[ E = \text{potential applied to the dropping mercury electrode in volts} \]

\[ E_{1/2} = \text{half-wave potential of the depolariser in volts} \]

\[ = E^\circ + \frac{RT}{nF} \ln \frac{f_A D_B^{1/2}}{f_B D_A^{1/2}} \]

\[(f_A \text{ and } f_B, D_A \text{ and } D_B \text{ are activity coefficients and diffusion coefficients pertaining to } A \text{ and } B \text{ respectively}).\]

\[ i = \text{cathodic current in } \mu\text{A at the applied potential} \]

\[ i_d = \text{cathodic diffusion current in } \mu\text{A} \]

\[ n = \text{number of electrons involved in the charge transfer process.} \]

Equation (11) is often referred to as the Heyrovsky-Ilkovic equation. The plot of \( E \) vs \( \log \frac{i}{i_d - i} \) should be linear with slope \( 0.05915/n \) for a reversible process\(^{98}\). If the process involves rapid charge transfer it is taken to be reversible, Tomes' criterion\(^{98,99}\) for a reversible process is given by

\[ E_{1/4} - E_{3/4} = \frac{0.0564}{n} V \]

\[ \ldots (12) \]

where \( E_{1/4} \) and \( E_{3/4} \) are potentials when \( i = i_d/4 \) and \( 3i_d/4 \) respectively.

In the case of an irreversible process, the equation is given\(^{100,101}\) by

\[ E = E_{1/2} - \frac{0.0542}{\alpha n_a} \log \left( \frac{i}{i_d - i} \right) \]

\[ \ldots (13) \]
with \[ E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n_a} \log \left( \frac{1.349K^*_{f,h} \tau^{1/2}}{D^{1/2}} \right) \] \hspace{1cm} (14)

where

\[ \alpha = \text{transfer coefficient} \]

\[ n_a = \text{number of electrons involved in the rate determining step} \]

\[ K^*_{f,h} = \text{heterogeneous forward rate constant in cm/sec.} \]

and all other terms have their usual significance. The \( \alpha n_a \) value for an irreversible process can be calculated using the equation

\[ E_{1/4} - E_{3/4} = \frac{0.05172}{\alpha n_a} \]

\hspace{1cm} (15)

Equation (14) reveals that the half-wave potentials are drop time dependent for an irreversible process.

Explicitly\(^{102}\) \( \alpha n_a \) can be either from equation (16) or from the plot of \( E_{dne} \) vs \[ \log \left( \frac{i}{i_d - i} \right) - 0.546 \log t \] which has a slope of -54.2/\( \alpha n_a \) mv\(^{12}\).

\[ \frac{d E_{1/2}}{d (\log t)} = \frac{0.02957}{\alpha n_a} \]

\hspace{1cm} (16)

The number of protons (P) involved in the rate determining step of the reaction is given by\(^{102}\)

\[ \frac{\Delta E_{1/2}}{\Delta pH} = -\frac{0.059}{\alpha n_a} \cdot P \]

\hspace{1cm} (17)
Adsorption waves\textsuperscript{103-107} are usually observed when the electroactive species or the product of the electrode reaction is adsorbed at the DME surface. At very low concentrations of the depolariser, only a single wave is observed that behaves like a diffusion controlled wave. At higher concentration at which the adsorbed material forms a monolayer on the electrode surface, the polarographic wave shows two steps. If the electroactive species is adsorbed, an adsorption post wave is observed. If the product is adsorbed, an absorption pre wave is observed. These two types of adsorption waves reach a limiting height corresponding to the formation of the complete surface coverage of the electrode. The total polarographic wave height increases with bulk concentration as predicted by Ilkovic equation. Due to the convection of the electroactive species currents become very much larger than pure diffusion currents, giving rise to two types of maxima. Maxima of the first kind\textsuperscript{108-110} are usually acute and appear at the beginning of a wave in relatively dilute solution. Maxima of second kind\textsuperscript{111,112} are obtained with concentrated solutions and at high flow rates of mercury. They are usually rounded and return gradually to the limiting plateau.

Apart from the diffusion current obtained in the polarography, there are other types of currents called kinetic currents\textsuperscript{113-117} and catalytic currents\textsuperscript{118-122}. Kinetic current is a polarographic current that is limited by the rate of a chemical reaction that precedes the electrode reaction proper. If the diffusion current is found to be more than the expected current, it is called catalytic current provided $i_d$ does not vary with the mercury column height (h).
Criteria of reversibility

1. $E_{dme} \text{ vs } \log \left( \frac{i}{i_d - i} \right)$ plots are linear and the value of 'n' will be an integer (1, 2 or 3).

2. The half-wave potential of the oxidised and reduced forms of the depolariser are identical.

3. A mixture of the oxidised and the reduced forms of the depolariser will yield a single combined cathodic-anodic wave.

4. The half-wave potential will not change with the concentration of the depolariser.

5. The half-wave potential agrees well with potentiometrically determined standard potential or the formal potential.

6. The half-wave potential is nearly independent of temperature.

Criteria of irreversibility

1. The value of 'n' calculated from the slope of semi-logarithmic analysis plot will not be an integer.

2. The half-wave potential shifts towards more negative values with increase in the pH of the medium.

3. The half-wave potential shifts to more negative values with increase in the concentration of the depolariser. 


4. The heterogeneous forward rate constant \((K^{\circ}_{f,h})\) of the electrode process calculated from the Meites-Israel equation\(^{124}\) (equation 18) is less than \(10^{-4}\).

\[
E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n_s} \log 1.349. \quad K^{\circ}_{f,h} - \frac{0.05915}{\alpha n_s} \log D^{1/2} \quad \ldots \quad (18)
\]

5. The \(\Delta G^*\) values computed from the relation

\[
K^{\circ}_{f,h} = \frac{KT}{h} \nu_a \exp \left( -\frac{\Delta G^*}{RT} \right) \quad \ldots \quad (19)
\]

increases with increase in pH.

**Kinetic parameters of the irreversible electrode reaction**

The heterogeneous rate constant, \(K^{\circ}_{f,h}\) (cm sec\(^{-1}\)) value is evaluated from the equations proposed by Meites-Israel, Oldham-Parry and Gaur-Bhargava for the totally irreversible waves at 25°C.

The equation proposed by Meites-Israel\(^{124}\) for the calculation of \(K^{\circ}_{f,h}\) is

\[
E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n_s} \log \frac{1.349K^{\circ}_{f,h} D^{1/2}}{D^{1/2}} \quad \ldots \quad (20)
\]

In the above equation \(E_{1/2}\) is referred to the SCE (Standard calomel electrode) and the currents are those at the end of the drops.

where

\[
K^{\circ}_{f,h} = \quad \text{heterogeneous formal rate constant for the forward reaction (cm/sec)}.
\]
The value of $\alpha_n$ is generally deduced from the slope $(0.05915/\alpha_n)$ of the linear plot, $-E_{dme}$ vs $\log \left( \frac{i}{i_d - i} \right)$. The intercept of the plot gives the value of $E_{1/2}$ from which the value of $K^o_{th}$ can be obtained.

Oldham-Parry\textsuperscript{25} deduced the following relationship

$$E_{1/2} - E_{dme} = \frac{0.0592}{\alpha_n} \log \frac{2(3 - X)}{5(1 - X)} \quad \ldots \quad (21)$$

where $X = \left( \frac{i}{i_d} \right)$ i.e., the ratio of the current at any potential along the polarogram to the limiting diffusion current.

The plot of $\log \frac{2(3 - X)}{5(1 - X)}$ vs $-E_{dme}$ is a straight line with a slope of 0.0592/$\alpha_n$ volt s\textsuperscript{-1} at 25°C and the intercept $E_{1/2}$. The half-wave potential is in turn used to calculate $K^o_{th}$ by the following equation.

$$E_{1/2} = E_T + \frac{0.0592}{\alpha_n} \log \frac{1.35 K^o_{th} t^{1/2}}{D^{1/2}} \quad \ldots \quad (22)$$

where $K^o_{th}$ is the formal rate constant at some convenient reference potential of $E_T$.

Recently, Gaur and Bhargava\textsuperscript{126} considered that the diffusion to the electrode surface is spherical and not a linear process as assumed earlier and they extended the Koutecky's\textsuperscript{100} treatment and deduced the following equation for an irreversible wave.

$$E_{dme} = E_{1/2} - \frac{0.0569}{\alpha_n} \log \left( \frac{i}{i_d - i} \right) \text{ at } 25°C \quad \ldots \quad (23)$$
The diffusion coefficient \(D\) value required for the calculation of \(K^o_{f,h}\) is calculated from Stoke-Einstein\(^{127}\) equation.

\[
D = \frac{3.38 \times 10^{-5}}{\frac{V_m}{\eta}} \text{ at } 30^\circ \text{C}
\]  \quad \text{... (25)}

where

\(\eta\) = viscosity of the solution

\(V_m\) = apparent molar volume

The activation free energy change \((\Delta G^*)\) is obtained from the relation

\[
K^o_{f,h} = \frac{K}{h} \nu_o \exp \left(\frac{-\Delta G^*}{RT}\right)
\]  \quad \text{... (19)}

where

\(K\) = Boltzmann constant (erg. deg\(^{-1}\) molecule\(^{-1}\))

\(h\) = Planck's constant (erg. sec)

\(\nu_o\) = mean distance between the depolarised ions in bulk solution (cm) and is generally equal to \(2 \times 10^{-8}\) cm.

\(\Delta G^*\) = activation free energy change (cal. mole\(^{-1}\))

\(R\) = gas constant (cal.)

\(T\) = absolute temperature (K).

\[
\text{with } E_{1/2} = -0.2412 + \frac{0.0569}{\alpha n_i} \log \frac{K^o_{f,h}^{1/2}}{1.128D^{1/2}} \quad \text{... (24)}
\]
Effect of temperature

The temperature coefficient of the diffusion current is calculated from the following equation

\[
\text{Temperature coefficient} = \frac{2.303}{\Delta T} \log \frac{i_2}{i_1}
\] ...

(26)

where

\(i_1\) = diffusion current at lower temperature (\(\mu\)A)

\(i_2\) = diffusion current at higher temperature (\(\mu\)A)

\(\Delta T\) = temperature difference

Thermodynamic parameters

The thermodynamic parameters - enthalpy of activation (\(\Delta H^*p\)), heat of activation at constant volume (\(\Delta H^*v\)) and the entropy of activation (\(\Delta S^*\)) are calculated as follows:

Enthalpy of activation (\(\Delta H^*p\)) is calculated by substituting the value of the slope of the plot (log \(K^*_{th}\) vs 1/T) in the Van't Hoff's equation\(^{128}\).

\[
\Delta H^*p = -2.303 \times R \times \text{slope}
\] ...

(27)

Heat of activation at constant volume (\(\Delta H^*v\)) is evaluated from the relation

\[
\Delta H^*p = \Delta H^*v + RT
\] ...

(28)
Activation free energy change ($\Delta G^*$) is determined by the following relation

$$K_{f,h}^{\circ} = \frac{KT}{h} \nu_0 \exp \left( \frac{-\Delta G^*}{RT} \right)$$

... (19)

Entropy of activation ($\Delta S^*$) is calculated using Helmholtz equation.

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T}$$

... (29)

Evaluation of number of electrons

Millicoulometric method

The millicoulometer described by the De Vries and Kroon\textsuperscript{129} consisting of a mercury pool cathode was used to determine the number of electrons.

$$n_2 = n_1 \frac{(\Delta i_d \text{Cad})(i_d \text{Sub})}{(i_d \text{Cad})(\Delta i_d \text{Sub})} \cdot \frac{C_1 V_1}{C_2 V_2}$$

... (30)

where

$$i_d = \text{diffusion current (\mu A)}$$

$$\Delta i_d = \text{change in the diffusion current (\mu A) of polarograms obtained, when the experimental solution is subjected to polarography.}$$

$$n_1 = \text{number of electrons involved in the reduction of cadmium ions and}$$

$$n_2 = \text{number of electrons involved in the reduction of substrate.}$$
Cyclic voltammetry

Cyclic voltammetry is a modern electrochemical technique which provides convenient means to study the electron transfer processes in solution\(^{130-132}\). This technique has several advantages over polarography in the study of electrochemical reductions especially with respect to the identification of the intermediate species having low half-lives. In cyclic voltammetry, a stationary electrode is used in unstirred solutions and the d.c. potentials are applied to the electrode in the form of isosceles triangular waves. The experiments are carried out in unstirred solutions to eliminate convection currents as far as possible.

The most common indicator electrodes used are planar platinum electrode, platinum wire electrode, hanging mercury drop electrode (HMDE) and carbon paste electrode.

In cyclic voltammetry, the potential applied to an electrode is changed linearly with time in a repetitive manner. The technique is measured as a function of potential or time. The current is usually referred to as the linear potential - sweep method, if only a single cathodic or anodic sweep is performed. In both the cases, the experiment is conducted in unstirred solutions, where convection is eliminated as far as possible. The basic feature of a voltammogram (i.e., a plot of current vs potential during cyclic voltammetry) is the appearance of a current peak at a potential characteristic of the electrode reaction that is taking place. The position and shape of a given peak depends on several factors such as sweep rate, electrode material, composition of the solution and the concentration of reactants.
The fundamental equations for cyclic voltammetry have been developed by Delahay\textsuperscript{133}, Shain\textsuperscript{134} and others\textsuperscript{135-139} for the electrode process represented by the equation

$$O + ne^- \xrightarrow{K_{th}} \frac{K_{th}}{K_{b,h}} R$$

where

$$K_{f,h} = \text{rate constant of forward reaction}$$

$$K_{b,h} = \text{rate constant of backward reaction}$$

The current at the cathodic peak potential (if the reduced form R is initially absent) is proportional to the square root of the sweep rate and is given by the equation

$$i_p = 0.447 \frac{(nf)^{2/3}}{(RT)^{1/2}} A D^{1/2} C_o \nu^{1/2}$$

where

$$i_p = \text{peak current in } \mu\text{A}$$

$$n = \text{number of electrons involved in the reduction process}$$

$$A = \text{area of the electrode in cm}^2$$

$$D = \text{diffusion coefficient of the electroactive species in cm}^2 \text{sec}^{-1}$$

$$C_o = \text{bulk concentration in mM}$$

$$\nu = \text{scan rate in volt sec}^{-1}$$
The equation (32) may be rearranged and written as

\[ \frac{i_p}{v^{1/2}C_0} = k' \]  

... (33)

where \( k' \) comprises of all the constants of the equation (32).

Some important aspects of cyclic voltammetry are briefly described under the headings reversible and irreversible charge transfer.

(1) **Reversible charge transfer**

In the case of reversible reactions (Fig. 1.1A), the rate of charge transfer is very much greater than the potential scan rate and the current form is diffusion controlled. The potential of the peak (\( E_p \)) is related to the polarographic half-wave potential (\( E_{1/2} \)) by the equation

\[ E_p = E_{1/2} - 1.1 \frac{RT}{nF} \]  

... (34)

The potential of separation (\( \Delta E_p \)) between the anodic and cathodic peaks is given by the following equation at 25°C.

\[ \Delta E_p = E_{pa} - E_{pc} = \frac{60}{n} \text{ mV} \]  

... (35)

It follows from the equation (35) that the difference between the peak potentials decreases with an increase in the number of electrons 'n' exchanged in the primary reduction process. Furthermore, the ratio of cathodic to anodic peak currents, \( i_{pc}/i_{pa} \) is equal to one for a reversible charge transfer in the absence of coupled chemical reactions.
Fig. 1.1. Typical cyclic voltammograms
(A) Reversible Process (B) Irreversible Process
(2) Irreversible charge transfer

The form of cyclic voltammogram in the case of irreversible processes is identical to that of the reversible one (Fig. 1.1B) with the exception that both the peak width and the peak separations are much greater than what the equation predicts for the reversible one. The deviation is due to the fact that a slow charge transfer takes place. The deviation increases with increase in scan rate. The dependence of peak separation on the scan rate can be used to determine the rate constant of the charge transfer. The transient current \( i_p \) is given by the equation

\[
i_p = 0.495 \, n \left( \frac{\alpha n_a}{RT} \right)^{1/2} F^{3/2} A D^{1/2} C_v^{1/2} \]

where

\[
\alpha = \text{transfer coefficient} \\
n_a = \text{number of electrons in the rate determining step}
\]

The above equation can also be written as

\[
i_p = 3.01 \times 10^5 \, n \left( \alpha n_a \right)^{1/2} A D^{1/2} C_v^{1/2} \]

The peak current is proportional to \( v^{1/2} \). The peak potential varies with sweep rate in irreversible charge transfer process.

Cyclic voltammetry serves as a useful tool for establishing the reversibility or irreversibility of the electrode process. If \( E_{pa} \) and \( E_{pc} \) are the potentials corresponding to the anodic and cathodic peak currents and \( E_{pa/2} \) and \( E_{pc/2} \) are the potentials
corresponding to the half-wave currents (Fig. 1.1A), \( E_{pa} - E_{pc} \) and \( E_{pa/2} - E_{pc/2} \) will each be equal to \( 0.056/n \) v for a reversible process.

Further

\[
E_{pc/2} = E_{pa} = E_o + \frac{0.028}{n} V
\]

... (38)

and

\[
E_{pa/2} = E_{pc} = E_o - \frac{0.028}{n} V
\]

... (39)

The absence of any measurable anodic peak current upon scan reversal past the peak potential is an indication of totally irreversible process\(^1\)\(^3\)\(^5\). Equation for such process is given by

\[
E_{p/2} - E_p = \frac{0.048}{\alpha n_a} V
\]

... (40)

The values of \( \alpha n_a \) can be evaluated using equation (40). The forward rate constant, \( K_{rh}^f \) in all the irreversible processes can be calculated using the following equation\(^1\)\(^4\)\(^0\),\(^1\)\(^4\)\(^1\).

\[
E_p = -1.14 \frac{RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \left( \frac{K_{rh}^f}{D^{1/2}} \right) - \frac{RT}{2\alpha n_a F} \ln (\alpha n_a v)
\]

... (41)

where all the terms have their usual significance.

Appearance of a relatively diminished anodic peak at normal scan rates and its increase at higher scan rates and decrease at lower scan rates respectively suggests the association of a chemical reaction subsequent to electron transfer.
Nicholson-Shain\textsuperscript{134} presented a great deal of data concerning the effects of coupled chemical reactions on the shapes of cyclic voltammograms. They proposed eight types of mechanisms for the electrode processes which are summarised as follows.

Case I: Reversible charge transfer

\[ O + ne^- \rightleftharpoons R \]  \hspace{1cm} (Electrode reaction) \hspace{1cm} (42)

\[ R \xrightarrow{K_1} \text{Products (Chemical reaction)} \] \hspace{1cm} (43)

Case II: Irreversible charge transfer

\[ O + ne^- \xrightarrow{K} R \]

Case III: Chemical reaction preceding a reversible charge transfer

\[ Z \xrightarrow{K_f} K_b \xrightarrow{K_b} O \]

\[ O + ne^- \rightleftharpoons R \]

Case IV: Chemical reaction preceding an irreversible charge transfer

\[ Z \xrightarrow{K_f} K_b \xrightarrow{K_b} O \]

\[ O + ne^- \rightarrow R \]
Case V: Reversible charge transfer followed by a reversible chemical reaction

\[ O + n\text{e}^- \rightleftharpoons R \]

\[ R \rightleftharpoons Z \]

Case VI: Reversible charge transfer followed by an irreversible chemical reaction

\[ O + n\text{e}^- \rightleftharpoons R \]

\[ R \xrightarrow{K_f} Z \]

Case VII: Catalytic reaction with reversible charge transfer

\[ O + n\text{e}^- \rightleftharpoons R \]

\[ R + Z \xrightarrow{K_f} O \]

Case VIII: Catalytic reaction with irreversible charge transfer

\[ O + n\text{e}^- \xrightarrow{K} R \]

\[ R + Z \xrightarrow{K_f} O \]

The parameters which are to be measured at each of a number of scan rates for obtaining insight into the electrode process include

(1) the ratio of anodic to cathodic peak currents \( \frac{i_{pa}}{i_{pc}} \),

(2) the cathodic current function \( \frac{i_{pc}}{\nu^{1/2}} \) and
the change in cathodic half-peak potential per ten fold change in scan rate, 
\[ \frac{\Delta E_{pc}}{2} / \log u. \]

Certain criteria have been arrived at involving the above parameters from the studies on various types of compounds.

1. The current function and half-peak potential are independent of scan rate for reversible processes.

2. The peak current ratio is equal to unity and independent of scan rate for reversible processes and

3. the \( E_{pc/2} \) value shifts cathodically approximately by \( 30/n \) mV for each ten-fold increase in the scan rate for an irreversible process and this fact enables the calculation of \( n \).

The variation of current function \( (i_{pc}/v^{1/2}) \) and the variation of \( \Delta E_{pc/2} / \Delta \log v \) with the scan rate is illustrated in the Figs. 1.2 and 1.3 for all the eight cases suggested by Nicholson and Shain.

Cyclic voltammetry is an important electrochemical technique by which a convenient study on the adsorption phenomena is made in detail. Adsorption controlled waves are frequently symmetrical about \( i_p \) unlike normal waves and \( i_{pc}/\nu^{1/2} \) increases rapidly with increase in scan rate. Wopschall and Shain\textsuperscript{142,143} have studied the nature of the effects of adsorption processes with the help of cyclic voltammetric responses. If the product or reactant is strongly adsorbed, a separate adsorption peak will occur prior to or after the normal peak\textsuperscript{143-145} respectively.
Fig. 1.2. Plots of the cathodic current function \( \frac{i_{pc}}{v^{1/2}} \), as a function of scan rate for various electrode processes.

Fig. 1.3. Plots of the change in cathodic half-peak potential, \( \frac{\Delta E_{pc2}}{\Delta \log v} \), as a function of scan rate for various electrode processes.
Cyclic voltammetry has several applications in organic electrochemistry. Kemula and Kublik have also employed this technique for understanding the significance of charge transfer coefficients\textsuperscript{146}, ECE mechanisms\textsuperscript{147}, multistep charge transfer processes\textsuperscript{148} etc. Jayarama Reddy \textit{et al.}\textsuperscript{149,150} have used this technique for their studies on the electrochemical oxidations and reductions of several organic and inorganic systems. A good account of the use of cyclic voltammetry by a good number of organic electrochemists is given by Baizer\textsuperscript{151}. 
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<td>Gaur, J.N. and Bhargava, S.K.</td>
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