COORDINATION AND REDOX PROPERTIES IN SOLUTION

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ABSTRACT

A primitive description of the functional electron cloud is given and is used to account for the mutual influence between coordinating and redox properties. Rules are given for the change in redox properties by coordination and vice versa. It is further shown that the redox potential in a donor solvent is determined by its donor number and an empirical approach is suggested to obtain the electromotive series for any solvent of given donor number. The donor number is also considered important for the ionization of a covalent substrate. Finally a new classification is suggested for charge-transfer complexes.

THE PRIMITIVE DESCRIPTION OF THE FUNCTIONAL ELECTRON CLOUD

In a primitive way, a characteristic 'electron cloud' may be ascribed to each atom, ion or molecule. Even in the state of highest stability of the entity, the ground state, the electronic arrangement is usually far from 'ideal' as is evidenced by the tendency to undergo chemical reactions. In the primitive description of the 'functional electron cloud', the 'non-ideality' of the cloud is considered responsible for its tendency to change; the actual function will depend also on the properties of the reactant.

The functional cloud may deviate from the ideal by being either too 'dilute' or too 'dense' compared with that of the reacting molecule. An entity with a 'dilute' electron cloud will tend to gain electrons or to achieve an appropriate share of them and will thus function as an acceptor of electrons. A system with 'dense' electron cloud will function as a donor of electrons, as it will try to make electrons available. Thus the description emphasizes the actual function of a molecule or ion towards a given reactant and so takes into account amphoteric properties.

It has been said that a dense cloud system will function as a donor and a dilute cloud system will function as an acceptor of electrons. Each of these functions may involve either the interaction of an electron pair or the complete exchange of an electron between the reacting species.

The interactions of an electron pair donor (EPD or Lewis base) with an electron pair acceptor (EPA or Lewis acid) lead to the formation of a coordinate bond. If an electron is given up completely, the system is regarded as a reducing agent or an electron donor, ED. The oxidizing agent is characterized by accepting the electron and is thus considered the electron acceptor,

EA. It is unfortunate that the terms 'electron donor' and 'electron acceptor' are frequently used to indicate the sharing of an electron pair, synonymous to the terms 'Lewis base' and 'Lewis acid' respectively. For the sake of clarity, these shall be termed 'electron pair donor' (EPD) and 'electron pair acceptor' (EPA) respectively.

In a broad sense, an entity functions as a donor (either EPD or ED) when it is capable of making its functional electron cloud more dilute by reacting with a substrate the electron cloud of which is becoming more dense. Likewise an entity functions as an acceptor (either EPA or EA) when it tends to make its functional electron cloud more dense by reacting with a substrate prepared to dilute its own functional electron cloud. Thus in both types of reactions, namely the formation of a covalent bond and the electron transfer between a reducing and an oxidizing agent, changes in the functional electron clouds are involved within all the reacting entities. It is therefore expected that coordination will have an influence on the redox properties of a system and vice versa. Indeed, it has been pointed out by Ussanovich that a clear borderline cannot be drawn between coordinating reactions and redox reactions[1].

Because of the lack of thermodynamic data it is tempting to define molecular properties which in a crude way at least may be useful to account for donor and acceptor properties.

For the reducing and oxidizing properties molecular properties are available, namely the ionization potential and the electron affinity. It has recently been suggested that the $-\Delta H_{EPD} \cdot SbCl_5$ values for a given EPD may be considered as a measure of the electron pair donor properties, at least as long as π-donor properties and soft–soft interactions are excluded; this has been termed the 'donor number'[2, 3]. It would be useful to have an analogous quantity for the electron pair acceptor properties, which may be termed 'acceptor number', but this has not been defined yet. In the borderline regions the reactant may behave simultaneously as a coordinating agent and as a redox agent. The overall change in the electronic density of the substrate may be accounted for by linear combination of the molecular properties for both the coordinating and the redox properties.

Table 1

	Type	Characteristic
Donor	Electron pair donor (EPD) Electron donor (EP) (Reducing agent)	Donor number (DN) Ionization potential (I)
Acceptor	Electron pair acceptor (EPA) Electron acceptor (EA) (Oxidizing agent)	Acceptor number (AN) (to be defined) Electron affinity (E)

It is apparent that such values cannot be considered as molecular properties in the strict sense, since the terms 'donor' and 'acceptor' indicate a function which is exhibited only by the molecule or ion towards a given substrate.

IONIZATION

It has recently been demonstrated that the heterolytic fission of a covalent bond is essentially a chemical phenomenon, being the result of the shift of electrons between the bonded atoms. In a medium of low dielectric constant, essentially associated ions are produced and only their separation is in accord with the electrostatic theory and is a function of the dielectric constant[4-8]. It has therefore been suggested that a distinction be made between:

1. the formation of associated ions as a chemical phenomenon, and
2. the dissociation of associated ions as an electrostatic phenomenon[4-8].

We shall now be concerned only with the formation of associated ions from a covalent substrate. The electron shift can be achieved in five ways.

1. Reaction of EPD with the substrate

$$EPD + \underset{\text{substrate}}{M - X} = (EPD \rightarrow M \overset{\frown}{-} X) \rightarrow [(EPD)M]^+ + X^-$$
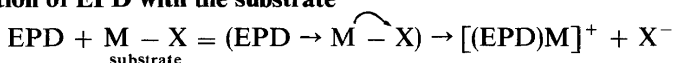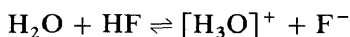
By nucleophilic attack of EPD at M of the covalent bond M—X an electron is moved from M to X. In this way the coordinating properties of M and X are also changed. M is yielding the cation, M^+, which has a more dilute electron cloud than M. Hence its electron pair acceptor properties are increased and stabilization of the cation by coordination with EPD is achieved. On the other hand, X gains an electron and in this way its electron pair donor properties are increased in X^-. The anion has a tendency to react with EPA and it is solvated by solvent molecules, as long as these are capable of acting as an EPA, such as water, which forms hydrogen bonds. Thus the cation is stabilized by coordination (and solvation) and the anion, if possible, by solvation.

Examples are

$$(n + m)H_2O + HF \rightleftharpoons [H_2O)_nH]^+ + [(OH_2)_mF]^-$$

usually represented as

$$H_2O + HF \rightleftharpoons [H_3O]^+ + F^-$$

or

$$2\,DMSO + B_2H_6 \rightleftharpoons [BH_2(DMSO)_2]^+ + [BH_4]^- \quad \text{(ref. 9)}$$

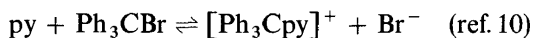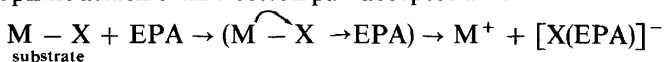$$py + Ph_3CBr \rightleftharpoons [Ph_3Cpy]^+ + Br^- \quad \text{(ref. 10)}$$
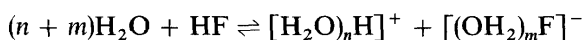
Figure 1 shows that the conductivities for the systems EPD–$(CH_3)_3SnI$ in nitrobenzene. Here the ionization is increased by increasing the DN or the EPD[4, 5].

2. Reaction of EPA with the substrate

By electrophilic attack of an electron pair acceptor at X:

$$\underset{\text{substrate}}{M - X} + EPA \rightarrow (M \overset{\frown}{-} X \rightarrow EPA) \rightarrow M^+ + [X(EPA)]^-$$

Stabilization of the anion is achieved by coordination (and solvation). The cation M^+ is again a stronger EPA than M in MX and in this way may be
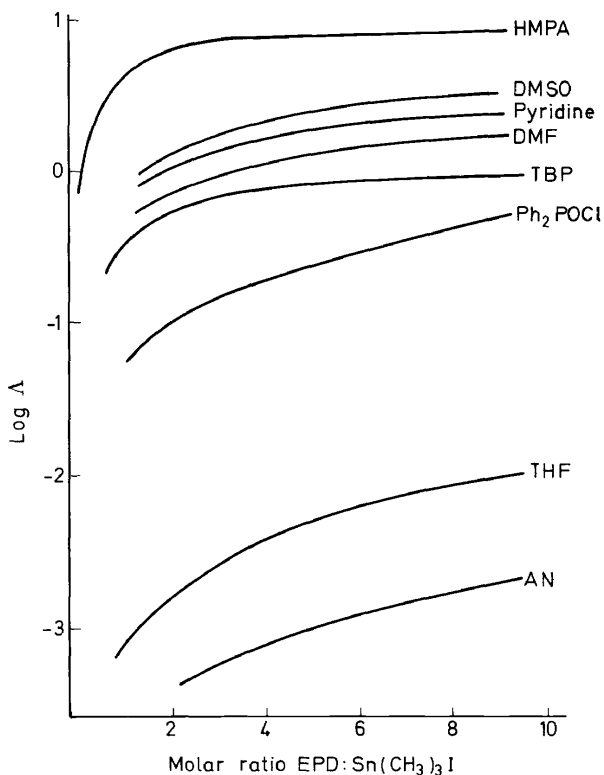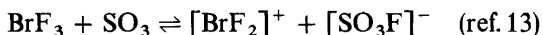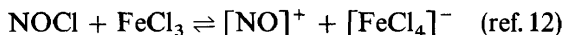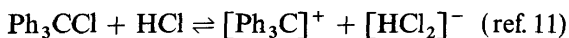
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Molar ratio EPD: Sn(CH₃)₃ I

Figure 1

stabilized by molecules exhibiting a donor function. Examples are:

$$Ph_3CCl + HCl \rightleftharpoons [Ph_3C]^+ + [HCl_2]^- \quad \text{(ref. 11)}$$

$$NOCl + FeCl_3 \rightleftharpoons [NO]^+ + [FeCl_4]^- \quad \text{(ref. 12)}$$

$$BrF_3 + SO_3 \rightleftharpoons [BrF_2]^+ + [SO_3F]^- \quad \text{(ref. 13)}$$

3. Reaction of ED with the substrate

Reaction of the substrate with an electron donor (reducing agent) may lead to complete electron transfer and thus to changes in the oxidation numbers in the system. It has been shown by Addison[14] that liquid sodium is an ionizing solvent which will ionize only species which undergo a redox reaction:

$$4\,Na + H_2O \rightleftharpoons 4\,Na^+ + 2\,H^- + O^{2-}$$

$$Na + \tfrac{1}{2}Cl_2 \rightleftharpoons Na^+ + Cl^-$$
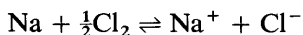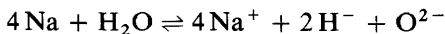
The sodium ions are believed to be solvated by sodium atoms.

4. Reaction of EA with the substrate

The reaction of the substrate with an electron acceptor (oxidizing agent) may also lead to complete electron transfer and thus to changes in the

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oxidation numbers in the system. The pure liquid halogens are known to react with numerous metals and the formation of ions has been shown to take place in liquid iodine[15]:

$$\underset{\text{substrate EA}}{K + \tfrac{3}{2}I_2} \rightleftharpoons K^+ + I_3^-$$
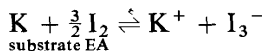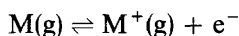
Here the anion is stabilized by coordination with the solvent molecules which act as EPA.
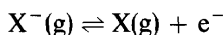
5. Combined actions

For example, (1) and (2) are involved in the self-ionization of water or liquid ammonia and (1) and (3) in the ionization of sodium in liquid ammonia.

REDOX POTENTIALS

For the standard potential of a redox system such as

$$M(g) \rightleftharpoons M^+(g) + e^-$$

or

$$X^-(g) \rightleftharpoons X(g) + e^-$$

the ionization potential of M and the electron affinity of M^+ or X are of importance.

In a coordinating medium, such as water, solvated species are involved and hence solvation is reflected in the redox potential of the system. The conventional electromotive series is valid for aqueous solutions only. An individual electromotive series exists for each medium.

By addition of a complexing agent a further change in redox potentials is observed. It is a well-established fact that the polarographic halfwave potential for a given redox couple is shifted to more negative potential values (according to the European convention) by complexing M^+ by EPD[16]. This shift in $E_{\frac{1}{2}}$ is a function of the increase in stability of M^+ by complex formation and stability constants for various complex species have been determined from the shifts in $E_{\frac{1}{2}}$[16].

The change in potential occurs since by coordination of an EPD both the ionization potential of M and the electron affinity of M^+ are decreased. In other words it is the further increase in electron density at M^+ due to coordination by EPD which makes the ion more reluctant to accept an electron.

It has been suggested that the donor number is an approximate measure for the solvation enthalpy of a given metal ion in different electron pair donor solvents[17, 18]. Popov and co-workers have shown that the plot of the ^{23}Na chemical shift of $NaClO_4$ or $NaBF_4$ in different solvents versus DN gives a straight line[19] (the only exception is water). Thus increased donor number of a coordinated donor causes an increase in the functional electron cloud of the metal ion.

In this way the desire of the metal ion to act as an oxidizing agent by accepting an electron is decreased (decrease in electron affinity). At the same time the ionization potential of the reducing agent is decreased and both

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effects lead to the observed shift of the redox potential towards more nega-
tive potential values. Apart from the application to the determination of
stability constants of complex species in a given medium, a relationship is
expected between the halfwave potential of a redox couple and the donor
properties of the donor solvent[17].

If the halfwave potentials of a certain redox couple in different EPD-
solvents is plotted versus the donor number, a characteristic curve is obtained,
which also allows the interpolation of the halfwave potential in solvent
of given donor number[18, 20].

The relation between the free enthalpy ΔG^0 for the redox reaction

$$M_{(s)} \rightleftharpoons M_{sv}^{z+} + ze^-$$
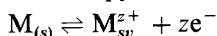
and the standard electrode potential, E^0, is represented by the equation

$$\Delta G^0 = -zFE^0$$

For the estimation of E^0 of a metal ion in solution a Born–Haber cycle may
be considered, as a result of which the formation of the solvated ion from the
metal in its reference state is due to the following steps[17]:

1. Sublimation of the metal,
2. Ionization of the gaseous metal atom,
3. Solvation of the gaseous metal ion.

For a given metal ion the ΔG terms for (1) and (2) are constant and hence
the value of E^0 in various solvents is determined only by the free energies of
solvation[17]. For metals, which are soluble in mercury, such as the alkali and
alkaline earth metals, the polarographic halfwave potential is a function of:

1. The standard electrode potential of the metal in the complex,
2. The solubility of the metal in mercury,
3. The free energy of amalgamation.

(2) and (3) are independent of the nature of the solvent. Thus for a reversible
reduction the halfwave potential is a measure of the interaction of the metal
ion with solvent molecules according to the reaction:

$$M_{sv}^{z+} + ze^- \rightleftharpoons M(Hg) + \text{solvent}$$

To compare the halfwave potentials of a given metal–metal ion complex
in different solvent, measurements versus a defined reference electrode,
such as the aqueous saturated calomel electrode must be available[21] and the
differences of liquid–liquid junction potentials must be eliminated. The
latter can be achieved with reasonable approximation by applying the method
of the reference ion, as suggested by Pleskov[22], assuming that the solvation
enthalpy of the reference ion is practically constant in solvents of different
donor number. A suitable reference ion is bisdiphenylchromium(I)[23], which
may be added to the solution under investigation. From such measurements
the difference in $E_{\frac{1}{2}}$ between the reference ion and the depolarizer ion can
be determined directly.

The donor number appears to be an approximate measure of the donor
properties of a neutral EPD, such as an EPD-solvent and it is thus related to
$E_{\frac{1}{2}}$. The difference in halfwave potential for a metal ion in two different donor
solvents is due to the difference in energy required to break down or to change
the structure of the solvate shell.

The following figures show the $E_{\frac{1}{2}}$/DN plots for various redox couples[18, 20]. The alkali metal ions give nearly the same values of $E_{\frac{1}{2}}$ in the strong coordinating solvents TMP, DMF, DMA and DMSO, but the lithium ion, which is reduced at more negative potential values shows a slightly different curve in the $E_{\frac{1}{2}}$/DN plot (*Figure 2*). The curves for the alkaline earth metal
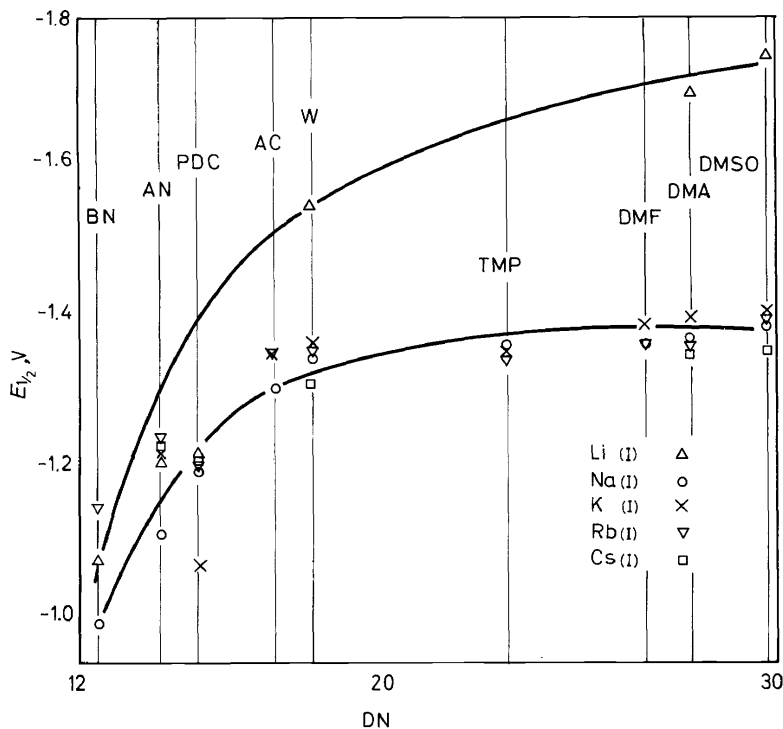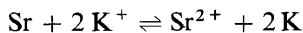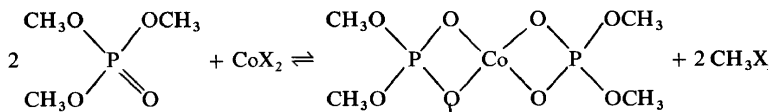

Figure 2

ions are similar to those of Li^+, but are found to lie at more positive potential values in the series $Li^+ < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (*Figure 3*). The curves for K^+ and Sr^{2+} show an intersection at $DN \approx 16$ and in a solvent of $DN > 16$, Sr^{2+} is reduced at more negative $E_{\frac{1}{2}}$ than K^+, thus indicating the occurrence of the reaction

$$Sr + 2 K^+ \rightleftharpoons Sr^{2+} + 2 K$$

in solutions of DMF, DMA or DMSO. Between the curves for Sr^{2+} and Ba^{2+} analogous curves are found for Yb^{2+}, Eu^{2+} and Sm^{2+} (*Figure 4*).

Nearly straight lines are found in the $E_{\frac{1}{2}}$/DN plot for Zn^{2+} and Co^{2+} while for Cd^{2+}, Tl^+ and Ni^{2+} the curves have a slightly different shape (*Figures 5* and *6*). Several ions give in TMP and H_2O potential values which are not expected from the interpolation of data in other solvents. With TMP $E_{\frac{1}{2}}$ is more negative than expected for Mn^{2+}, Co^{2+} and Ni^{2+} (*Figure 6*)

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and this is due to chelate formation [24] the stability of which is reflected in $E_{\frac{1}{2}}$:

$$2 \quad \begin{array}{c} CH_3O \\ \\ CH_3O \end{array} \hspace{-4pt} \diagup\hspace{-6pt}\underset{\displaystyle O}{\overset{\displaystyle OCH_3}{P}} \quad + CoX_2 \rightleftharpoons \quad \begin{array}{c} CH_3O \\ \\ CH_3O \end{array} \hspace{-4pt}P\hspace{-4pt} \begin{array}{c} O \\ \\ O \end{array} Co \begin{array}{c} O \\ \\ O \end{array} P\hspace{-4pt} \begin{array}{c} OCH_3 \\ \\ OCH_3 \end{array} \quad + 2\,CH_3X$$

Similar deviations are expected for Ti^{3+}, V^{3+} and other ions undergoing such reactions. The deviations for various hydrated metal ions in water (*Figures 5* and *6*) may be regarded as due to an entropy effect.
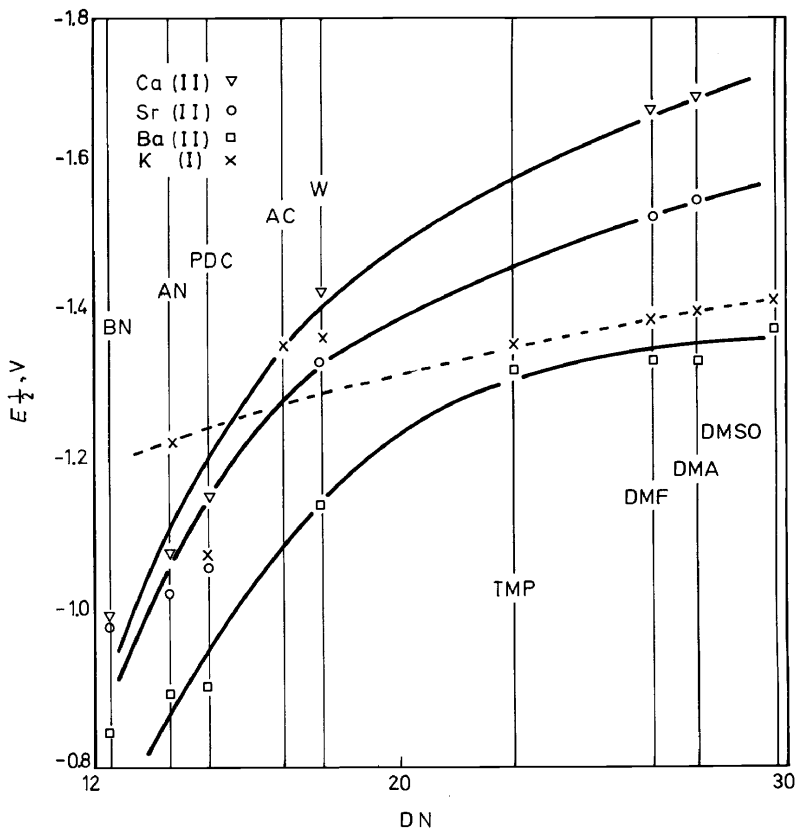

Figure 3

HMPA shows relatively weak interactions with certain metal ions such as Co^{2+} and this appears to be due to steric hindrance[25]. In such cases it may be expected that $E_{\frac{1}{2}}$ would have more positive values than determined from extrapolation of the curve in the $E_{\frac{1}{2}}/DN$ plot.

Nearly straight lines are obtained in the $E_{\frac{1}{2}}/DN$ plots for Sm^{3+}—Sm^{2+}, Eu^{3+}—Eu^{2+} and Yb^{3+}—Yb^{2+} (*Figure 7*) and it has been shown that addition of a complexing ligand causes further shifts towards negative poten-
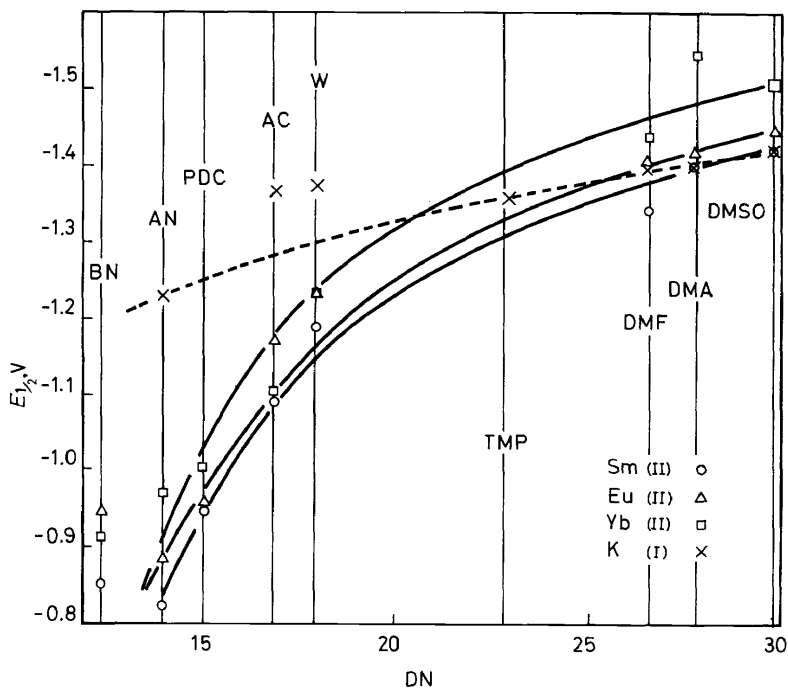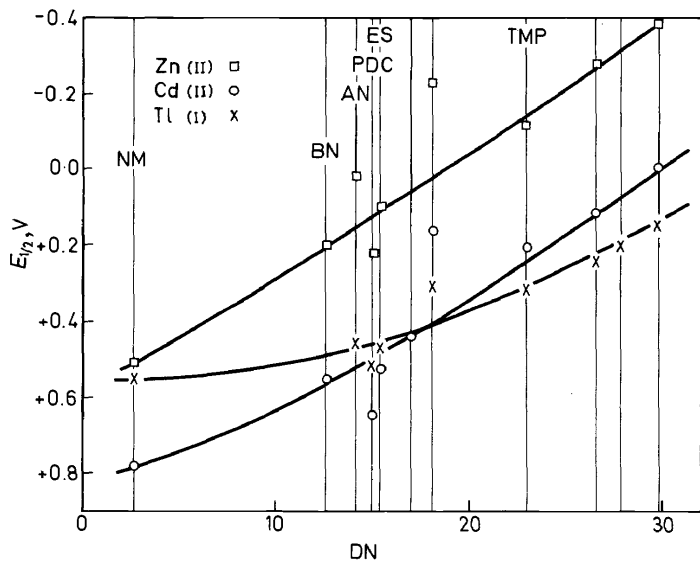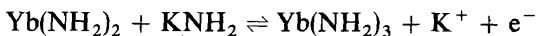
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Figure 4

Figure 5

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tial values, the magnitude of which at given concentration of the competitive ligand is a function of its donor number[26] (*Figure 8*). Thus in liquid ammonia the following reaction is found to take place[27]:

$$Yb(NH_2)_2 + KNH_2 \rightleftharpoons Yb(NH_2)_3 + K^+ + e^-$$

The extension of these considerations to complexing of a reducing agent by an electron pair acceptor leads to the conclusion that in this way the
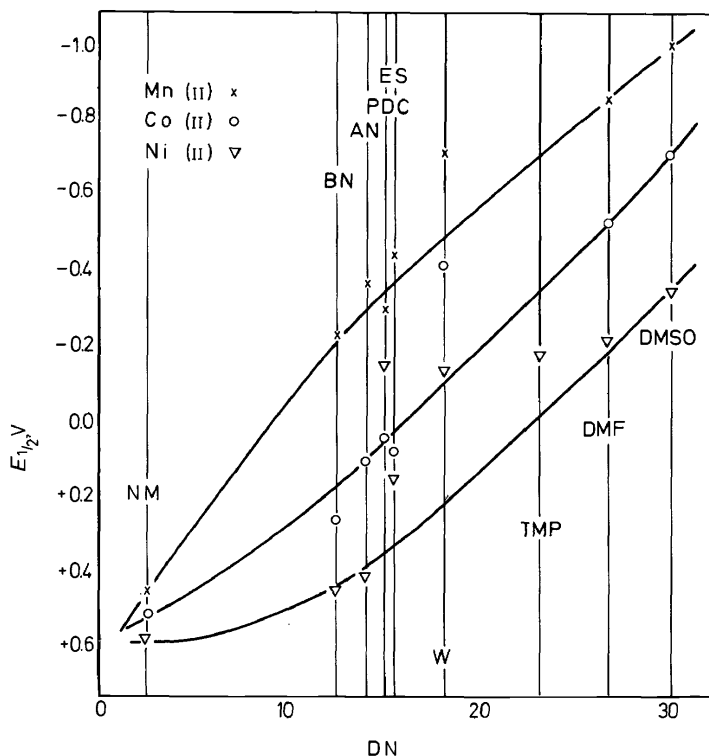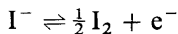

Figure 6

electron cloud of the reducing agent is diluted and hence its ionization potential is increased[28]. This should be reflected in a decrease of reducing properties and in a shift of the redox potential to more positive values. For example, it would be expected that the halfwave potential of the anodic wave for the reaction:

$$I^- \rightleftharpoons \tfrac{1}{2} I_2 + e^-:$$

should be shifted to more positive values by interaction of the iodide ions with an EPA (Lewis acid), such as boron(III) iodide or mercury(II) iodide[28].

Thus the rule that increased complex stability is accompanied by a shift of $E_{\frac{1}{2}}$ to more negative values is valid only as long as an electron pair donor acts as coordinating agent. The reverse effect is expected when coordination by an electron pair acceptor takes place.

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Consequently reduction or oxidation of a given entity should lead to changes in donor number and acceptor number. Since in the course of the oxidizing action of an oxidizing agent its electron cloud is increased, the donor number of the EPD is expected to be lower in its oxidized state. The iodide ion is a better EPD than iodine, because of its higher negative charge.
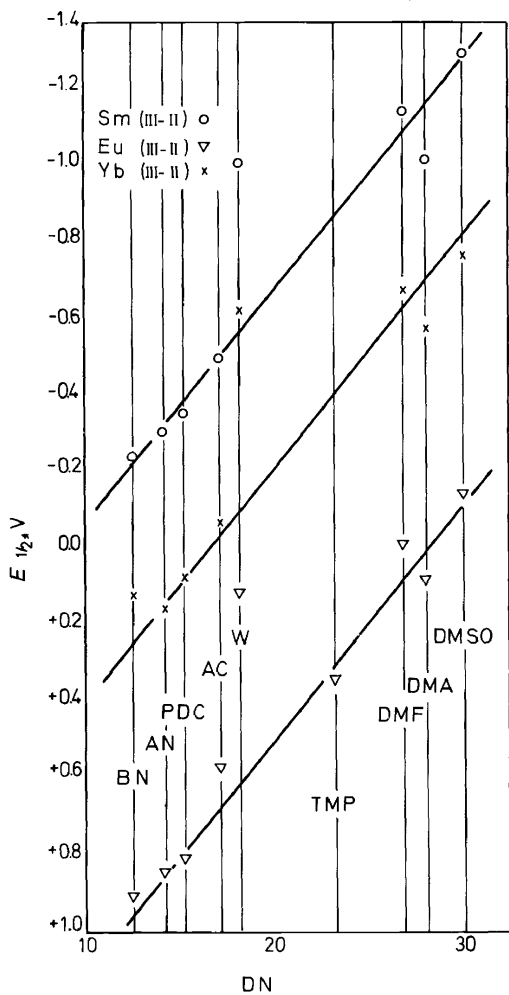

Figure 7

By analogy, the EPA properties are increased by increased positive charge, as in this way the electron cloud is diluted and the tendency to accept an electron pair is enhanced. Thus the sodium atom is a poor EPA, but sodium ion is a good EPA. Likewise the electron pair acceptor properties of various redox couples are in accord with this rule; for example: $Eu^{3+} > Eu^{2+}$, $Sn^{4+} > Sn^{2+}$, $Fe^{3+} > Fe^{2+}$.
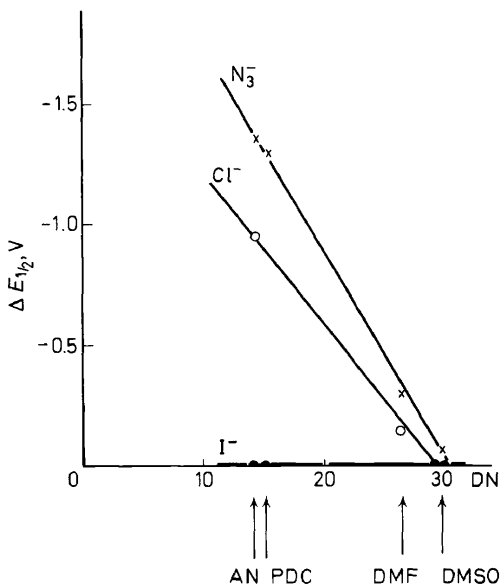
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Figure 8

The mutual influence between coordination and redox properties may be formalized in general by the following rules:

1. The reducing properties are increased by coordination of an EPD and they are decreased by coordination of an EPA.

2. The oxidizing properties are decreased by coordination of an EPD and they are increased by coordination of an EPA.

3. The electron pair donor properties are increased by increase in negative charge and they are decreased by increase in positive charge.

4. The electron pair acceptor properties are increased by increase in positive charge and they are decreased by increase in negative charge.

CHARGE-TRANSFER COMPLEXES

A charge-transfer complex may be considered as a result of an attempted ionization process or redox reaction which has been prevented from completion. Since the present description appears useful in relating ionization and redox phenomena to donor and acceptor interactions, it should be desirable to include charge-transfer complexes.

A survey of the literature[29] reveals that attempts to use molecular properties of the reactants in order to account for charge-transfer complexes were not always successful. Briegleb[29] considers the ionization potential of a donor and the electron affinity of the acceptor as decisive factors, although in many cases no relationship was found between these quantities and thermodynamic and thermochemical data. In some cases better relationships were found by replacing the ionization potential by the Lewis basicity[29, 30]. Recently it has been shown unambiguously that in the formation of EPD–ICF$_3$ complexes the donor number of EPD is related to both

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the enthalpy of interaction and to the chemical shift into the ^{19}F n.m.r. spectrum[31].

It is therefore apparent that the predominant molecular property to be considered will depend on the mode of the D–A interaction and the following classification of charge-transfer complexes is suggested[28]:

1. Charge-transfer complexes obtained by the interaction of an electron pair donor and an electron pair acceptor: EPD–EPA type

This class comprises all charge-transfer complexes whose formation does not involve any obvious change in the oxidation numbers within the system. Thus for a given acceptor the extent of complex formation is expected to be related to the donor properties of the EPD. It has been mentioned that this is true for the systems EPD–ICF$_3$, but no data are available for most other systems in this class.

It is useful to retain the following distinctions between different modes of EPD–EPA interactions:

1. π–π (naphthalene–trinitrobenzene)
2. n–π (ether–tetracyanoethylene)
3. σ-π(cyclohexane–tetracyanoethylene)
4. π–σ (benzene–iodine monochloride)
5. n–σ (pyridine–iodine monochloride)

The donor number, as defined, will be restricted to n–EPD functions, but it may be expected that systematic measurements by various techniques will lead to molecular properties indicating π-donor and π-acceptor properties as well as σ-donor and σ-acceptor properties.

2. Charge-transfer complexes formed by the interaction of an electron pair donor and an electron acceptor with electron pair acceptor properties: EPD–(EA + EPA) type

1. n–π (methanol–sulphur dioxide)
2. π–σ (benzene–iodine)
3. n–σ (pyridine–iodine)
4. σ–σ (cyclohexane–iodine)

In such reactions a change in oxidation number within the system is apparent, e.g.:

$$py + I_2 \rightarrow pyI^+ \ldots I^-$$
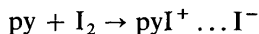
For a given acceptor again the donor number of EPD should be decisive for the interaction with an n-donor. Data are available for the formation constants of amine–iodine complexes and the linear relationship between $\log K$ and pK_b includes most of the bases[30]. Indices for π-donor and σ-donor properties should be used for the respective reactions.

For a given donor the acceptor properties might be properly represented by a suitable linear combination of the electron affinity and the acceptor number (the latter depending on the type of acceptor function).

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3. Charge-transfer complexes formed by the interaction of an electron donor and an electron acceptor with electron pair acceptor properties: ED–(EPA + EA) type

Because of the low ionization potential of the alkali metals electron transfer cyanoethylene, lithium-tetracyanochinondimethane and sodium–naptha-complexes, but ionization is usually also taking place. Examples are[29]: sodium–quinone, sodium–trinitrobenzene, sodium–chloranil, sodium–tetra-cyanoethylene, lithium-tetracyanochinondimethane and sodium–naptha-lene.

It is expected that for a given acceptor a relationship will exist between thermodynamic data and the ionization potential. For a given donor the acceptor properties may be expressed by the electron affinity of the acceptor and a linear combination of electron affinity and acceptor number is expected to represent the acceptor properties more accurately.

BACK DONATION

The phenomenon of back donation is in a qualitative way in full agreement with the present description[28]: when an n-electron pair donor such as the carbon monoxide molecule reacts with a weak electron pair acceptor, such as a suitable transition metal atom or ion, the acceptor number of CO is increased and at the same time the donor number of M is increased. Thus the functions of M and CO are reversed in that M behaves as an EPD and CO as an EPA.

CONCLUSION

I have tried to show the importance of donor and acceptor functions for both ionization and redox phenomena. Rules are given for the mutual influence between coordinating and redox properties and a new classification of charge-transfer complexes is suggested. The considerations given suggest numerous experiments and, it is hoped, may also inspire further theoretical developments.

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