

It may be questioned whether the chloro complex formation, implied by physico-chemical methods, apply to association in the second co-ordination sphere (analogous to  $\text{Co}(\text{NH}_3)_6^{++}, \text{I}^-$ ) or to substitutions of water in the first co-ordination sphere. The old statement that changes of the absorption spectra occur only in the latter case<sup>13</sup> has been highly justified for d<sup>n</sup>-transitions in the recent years. The present author believes that the first co-ordination sphere of the aquo ions of trivalent lanthanides and actinides is not changed to a large extent in solutions, containing less than 4 M HCl, while in concentrated HCl actual complexes are formed with one or more chloride ions bound directly to the central ion. J. Bjerrum<sup>14</sup> investigated the case of Cu(II) and the strongly increasing chloride activity of strong HCl. The mass-action law on concentration units is very far from being valid; this is probably caused by the strong tendency towards dehydration of the aquo ions in strong HCl of low H<sub>2</sub>O-activity<sup>15</sup>. It is interesting that Katzin effect<sup>16</sup>, *i. e.* that complexes with anions are much more readily formed in anhydrous alcohols than in aqueous solutions or in alcohols with 10 % water content, can be described a similar dehydration effect: the spectral changes of Ce(III) in above 10 M aqueous HCl are reproduced by 0.002 M CeCl<sub>3</sub> alone in absolute ethanol<sup>12</sup>, but not of Ce(ClO<sub>4</sub>)<sub>3</sub>. Thus, water (and amines) have an extraordinarily large tendency to occupy the whole of the first co-ordination sphere (rather independently of the dielectric constant of the solvent), thus displacing anions to form second-sphere associates or leading to complete ionic dissociation.

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## The Hump of Ionization Potentials at Half-Filled Shells and the Influence of Spin-Pairing Energy on Standard Oxidation Potentials

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Recently, many properties of chemical complexes have been related to atomic spectroscopy<sup>1</sup>. Especially, the ligand field stabilization of partly filled d-shells has been evaluated<sup>2</sup> in terms of the parameter  $\Delta$  (also called  $(E_1 - E_2)$  or  $10 Dq$ ), determined from the absorption spectra.

The standard oxidation potentials<sup>3</sup> (with the opposite sign of that used by Latimer) express the ionization potentials in aqueous solutions when corrected for the energy necessary for the reaction  $\frac{1}{2}\text{H}_2 \rightarrow \text{H}_{\text{aq}}^+ + e^-$ . Since the latter energy probably is between 4.5 and 5 eV, the ionization potentials in solution are much lower, 4–7 eV, than for the gaseous ions known from atomic spectroscopy<sup>4</sup>. The divalent and trivalent hexaaquo ions of the first transition group represent the only case where the redox potentials are known for systems having several different numbers of d-electrons. In Table I, these potentials<sup>3</sup> are corrected for the influence of ligand field stabilization<sup>2</sup> (1 eV = 8 067

Table 1.

Ionization Process	V(II)→(III)	Cr(II)→(III)	Mn(II)→(III)	Fe(II)→(III)	Co(II)→(III)
Standard oxidation potential	-0.25 V	-0.41 V	+1.5 V	+0.77 V	+1.84 V
$\Delta$ of divalent ion	12 600 K	13 900 K	7 800 K	10 400 K	9 700 K
Stabilization of divalent ion	15 100 K	8 300 K	0 K	4 200 K	7 800 K
$\Delta$ of trivalent ion	18 600 K	17 400 K	21 000 K	13 700 K	18 600 K
Stabilization of trivalent ion	14 900 K	20 900 K	12 600 K	0 K	44 600 K
Ligand field correction	-200 K	+12 600 K	+12600 K	-4 200 K	-200 K
Corrected potential	-0.27 V	+1.10 V	+3.0 V	+0.25 V	+1.82 V

K (= cm<sup>-1</sup>). In the case of tetragonally distorted d<sup>4</sup>-systems<sup>2</sup>, viz. Cr(II) and Mn(III), the stabilization is assumed to be expressed by the increased value of  $\Delta$ . In the case of the diamagnetic d<sup>8</sup>-system Co(III), it is necessary to correct for the large energy  $5B + 8C$  in atomic term differences<sup>5</sup>, necessary to obtain the large stabilization  $-2.4\Delta$  of the magnetically anomalous groundstate.

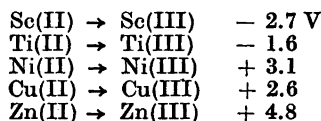
The last row in the table demonstrates that the oxidation potentials, when corrected for the ligand field stabilization, regularly increase 1.5 V per unit of atomic number,  $Z$ , except between manganese and iron, where a hump  $\sim 4$  V occurs. This hump can be ascribed to the special stability of half-filled shells with the maximum value of the total spin  $S$ . Actually, the ionization potentials of neutral Al, Si, P, S, Cl, A demonstrates a similar hump  $\sim 3.4$  eV at p<sup>\*</sup> besides the regular increase  $\sim 2.6$  eV per unit of  $Z$  (cf. Koefoed<sup>6</sup>). Orgel<sup>7</sup> and Griffith<sup>8</sup> have recently discussed the spin-pairing energy necessary for formation of magnetically anomalous complexes (cf. Co(III) in the table). For a given d<sup>n</sup>-electron configuration, the energy necessary in average<sup>9</sup> (of all the terms with the same  $S$ ) to decrease  $S$  by one unit is  $S \left( \frac{35}{6} B + \frac{7}{3} C \right) \sim S \times 14\,000$  K. The theoretical comparison of spin-pairing energies in different electron configurations is not as easy; the hump seen from the Table suggests that the ionization process necessitates 32 000 K less energy, when it increases  $S$  by a half unit rather than to decrease it. Actually, this value is comparable to the 37 000 K spin-pairing energy of Co(III) from  $S = 2$  to  $S = 0$ .

The ionization potentials<sup>4</sup> of the gaseous divalent d<sup>n</sup>-ions are in eV for Sc 24.75, Ti 28.14, V 29.7, Cr 30.95, Mn 33.69, Fe 30.64, Co 33.49, Ni 36.16, Cu 36.83 and for Zn 39.70, corresponding to an increase

of 2.2 eV for each unit of  $Z$ , and a d<sup>5</sup>-hump = 4.8 eV. The small irregularities can be explained, if it is assumed that ions with

$F$ -groundstates are stabilized  $\frac{3}{10} \cdot 15 B \sim 4\,000$  K, relative to ions with  $D$ - or  $S$ -groundstates. Thus, the corrected Cr(II): Cr(III) oxidation potential is also somewhat too low, because the transition is from <sup>5</sup>D to <sup>4</sup>F. Since the similar increase is 1.5 eV per unit of  $Z$  for the hexaquo ions, it can be concluded that the aquation stabilization increases 0.7 eV more for the trivalent than for the divalent ions per unit of  $Z$ , corresponding to smaller ionic radii and larger electric potentials near the trivalent ions.

By extrapolation from the table it can be shown that the standard redox potentials would be:



assuming  $\Delta = 12\,000$  K for the divalent and 20 000 K for the trivalent ions, and no formation of magnetically anomalous complexes. Thus, Ti(II) is probably a stronger reducing agent than reported<sup>4</sup> ( $-0.37$  V), and Sc(II) should disproportionate to the metal and Sc(III) in aqueous solution.

Since the d<sup>5</sup>-hump has no direct influence on the relative stability of different complexes of the same central ion (as has the competition between  $\Delta$  and the spin-pairing energy in Co(III) complexes), it is not surprising that the <sup>6</sup>S-states of d<sup>5</sup> (or <sup>6</sup>S of f<sup>7</sup>) exhibit smaller complex formation constants than their neighbours, due to the absence of ligand field stabilization. However, if the integrals of electrostatic interaction between the d-electrons,

forming a part of the d<sup>5</sup>-hump energy differences, actually decrease in anion complexes, compared to complexes of neutral ligands<sup>10</sup>, it cannot be excluded that this effect will produce a slight decrease of ligand field stabilization in the complexes with stronger partial covalent bonding.

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## Identification and Semiquantitative Determination of Phenyl Thiohydantoin

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In an earlier paper<sup>1</sup>, one of us described a paper chromatographic procedure for identification of the phenyl thiohydantoin (PTH) derivatives of natural amino acids. The procedure has now been improved in a way, that permits a semiquantitative determination based on the strong ultraviolet absorption of the PTH. This called for a method of locating the PTH's on the paper without destroying them and also for a low background absorption. For the first purpose a low pressure mercury lamp and a fluorescent screen with excitation in the appropriate ultraviolet region and emis-

Table 1.

PTH-amino acid	$R_F$ -value in solvent		
	<i>D</i>	<i>E</i>	<i>F</i>
Glycine	0.09	0.63	0.62
Alanine	0.18	0.77	0.78
Valine	0.53	0.87	0.89
Isoleucine	0.65	0.92	0.91
Leucine	0.67	0.92	0.92
Serine	0	0.47	0.14
Threonine	0	0.55	0.34
Proline	0.83	0.90	0.89
Hydroxyproline	—	—	0.54
Methionine	0.45	0.89	0.88
Cysteic acid *	0	0	0
Phenylalanine	0.57	0.90	0.91
Tyrosine	0	0.75	0.41
Tryptophan	0.12	0.86	0.82
Aspartic acid	0	0.38	0.16
Glutamic acid	0	0.56	0.27
Asparagine	0	0.31	0.08
Glutamine	0	0.41	0.15
Histidine	0	0.22	0
Arginine	0	0.11	0
$\epsilon$ -PTC-lysine	0.05	0.85	0.81

\* PTH-cysteic acid may be identified by paper electrophoresis.

sion in the visible were used\*. In order to cut out the visible light from the mercury lamp a dye emitting in the visible red was used and observations were made through red glasses. The PTH's then appear on the paper as black spots on a red background. The lower limit of sensitivity is approx. 1  $\mu$ g of PTH in a spot\*\*. For a semiquantitative determination at least 5  $\mu$ g in each spot is required. After location of the spot the area is cut out, the material extracted from the paper and its absorption measured. The yield varies between 75 and 105 %, the lower figure usually being obtained for the PTH's with highest  $R_F$ -values.

The solvents were chosen so that after drying the paper they did not leave material absorbing in the critical UV region around 270 m $\mu$ .

\* Related procedures have been described for the location of steroids<sup>2</sup> and nucleic acid material<sup>3</sup> on paper chromatograms.

\*\* For identification purposes the iodine-azide reaction<sup>1</sup> should afterwards be applied.