cadmium and lead in aqueous and dioxane–water mixed solvents containing 3 mol dm^{-3} LiClO$_4$ as a constant ionic medium at 25 °C [1–4].

It has generally been found that the composition of the hydrolytic species and the formation constant *β_{pq} for the reaction $q\text{M}^{z+} + p\text{H}_2\text{O} = \text{M}_q(\text{OH})_p^{(qz-p)^+} + p\text{H}^+$ were little affected by the solvent composition up to 0.5 mole fraction (*ca.* 88% w/w) of dioxane in the medium. Free energy changes of transfer, $\Delta G_{pq}^t = -RT[\ln\{\beta_{pq}(\text{mix})/\beta_{pq}(\text{aq})\}]$ for the reaction: $q\text{M}^{z+} + p\text{OH}^- = \text{M}_q(\text{OH})_p^{(qz-p)^+}$ ($\beta_{pq} = [\text{M}_q(\text{OH})_p^{(qz-p)^+}]/[\text{M}^+]^q[\text{OH}^-]^p = \text{*}\beta_{pq}/\text{K}_i^p$; K_i denotes the autoprotolysis constant of the solvent) were strongly dependent on the composition and charges of the complexes. However, the values $(1/p)\Delta G_{pq}^t$ were approximately independent of the complexes examined at a given concentration of dioxane. Since the free energy change of transfer can be expressed as $(1/p)\Delta G_{pq}^t = (q/p)((1/q)\Delta g_{pq} - \Delta g_\text{M}) - \Delta g_\text{OH}$ (Δg_i stands for the partial molar free energy change of transfer of species i) and the contribution of Δg_OH to $(1/p)\Delta G_{pq}^t$ is the same in all the cases, the results obtained indicated that the values, $(1/q)\Delta g_{pq} - \Delta g_\text{M}$, depend only on p/q ($= z - z'$ where z' represents the formal charge per metal ion of the complex).

Enthalpy changes for the hydrolytic reactions of some divalent metal ions and the autoprotolysis reaction of the solvents were determined by use of a fully automatic on-line-controlled system developed in our laboratory [5] and the enthalpy and entropy changes of transfer of the reaction, ΔH_{pq}^t and ΔS_{pq}^t, respectively, were evaluated. The value, $(1/p)\Delta H_{pq}^t = (q/p)((1/p)\Delta h_{pq} - \Delta h_\text{M}) - \Delta h_\text{OH}$, strongly depended on metals, where Δh_i denotes the partial molar enthalpy change of transfer of species i. For a given metal ion, $(1/p)\Delta H_{pq}^t$ became more negative (or less positive) with an increase in z' in the complex, and at a given z' the value was practically independent of the composition of the complexes. The results obtained indicated that the value of $(1/q)\Delta h_{pq} - \Delta h_\text{m}$ depends on both p/q and Δh_M.

For a strongly solvated metal ion (*i.e.*, $(1/p)\Delta H_{pq}^t$ may be largely negative for such a ion), the ion may have a large ordering effect for the solvent molecules even in the secondary solvation shell of the ion, and thus, $(1/p)\Delta S_{pq}^t$ may become less positive. Therefore, the effect due to $(1/p)\Delta H_{pq}^t$ on $(1/p)\Delta G_{pq}^t$ may be compensated by the effect due to $(1/p)\Delta S_{pq}^t$ and thus, the $(1/p)\Delta G_{pq}^t$ value becomes practically independent of metal ions.

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On the Ag(II, I) and Co(III, II) Standard Redox Potentials
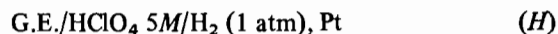
R. ZINGALES

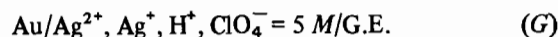*Istituto di Chimica Generale, Via Archirafi 28, 90123 Palermo, Italy*

Investigating the solution chemistry of transition metal ions in high oxidation states, at low temperature (−5 °C) and in strongly acidic medium (5 *M* HClO$_4$), our first success was, the evaluation of the standard redox potential of the Ag(II, I) pair. This is the e.m.f. of the hypothetic cell:

$$\text{Au/Ag}^{2+}, \text{Ag}^+, \text{H}^+, \text{ClO}_4^- = 5\,M/\text{H}_2\,(1\text{ atm}), \text{Pt} \quad (R)$$
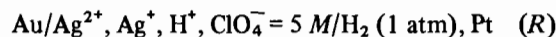
at −5 °C, with $[\text{Ag}^{2+}] = [\text{Ag}^+]$, $C_{\text{HClO}_4} \to 5M$, and E = O for the half cell: Pt, H$_2$ (1 atm)/H$^+$ ($a = 1$). Owing to the experimental impossibility of building such a cell, and thanks to the good working of the glass electrode in such conditions [1], we measured the e.m.f.s of the cells without junction:
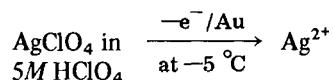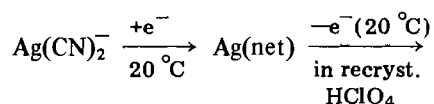
$$\text{G.E./HClO}_4\ 5M/\text{H}_2\ (1\text{ atm}), \text{Pt} \quad (H)$$

and

$$\text{Au/Ag}^{2+}, \text{Ag}^+, \text{H}^+, \text{ClO}_4^- = 5\,M/\text{G.E.} \quad (G)$$

whose combination and rearrangement leads to:

$$E_R - K \log [\text{Ag}^{2+}]/[\text{Ag}^+] + K \log[\text{H}^+] =$$
$$= E^\circ_{\text{Ag}^{2+}/\text{Ag}^+} + K \log F = E^\circ \quad (1)$$

where F is the activity coefficients ratio and all concentrations are expressed in molality. All the terms on the left side of eqn. (*1*) are directly measurable, while we call standard redox potential of the Ag(II,I) pair, at −5 °C and in 5 *M* HClO$_4$ (6.5 *M*), the sum of the right side terms.

The method of preparation of Ag^{2+} solutions can be summarized as follows:

$$Ag(CN)_2^- \xrightarrow[20\,°C]{+e^-} Ag(net) \xrightarrow[\substack{\text{in recryst.}\\ HClO_4}]{-e^-(20\,°C)}$$

$$AgClO_4 \text{ in } \atop 5M\,HClO_4 \xrightarrow[\text{at}\,-5\,°C]{-e^-/Au} Ag^{2+}$$

Once a Ag^{2+} solution was obtained, e.m.f. measurements of cell (G) were carried out at -5 °C, after successive additions of a cold $Ce(ClO_4)_3$ in $5\,M$ $HClO_4$ solution. The collected data enabled us to build a Gran diagram from which to draw the Ag^{2+} concentration at each point of the titration and, by eqn. (1), a set of $E°$ values for each titration. The mean value, derived from 5 titrations at different Ag^{2+} initial concentration, Ag total concentration, and varying the $[Ag^{2+}]/[Ag^+]$ ratio over a wide range, is 1977.5 ± 1.4 mV for $E°$, the standard redox potential of the $Ag(II, I)$ pair at -5 °C and in $5\,M\,(6.5\,M)$ $HClO_4$.

Likewise, adding to the Ag^{2+} solution, at -5 °C, successive amounts of a cold $Co(ClO_4)_2$ in $5\,M$ $HClO_4$ solution, we generated Co^{3+} by the reaction: $Ag^{2+} + Co^{2+} \rightarrow Ag^+ + Co^{3+}$. After the equivalent point, the cell (G) becomes:

$$Au/Co^{3+}, Co^{2+}, Ag^+, H^+, ClO_4^- = 5\,M/G.E. \qquad (G')$$
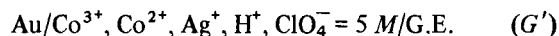
for which, from $E_{R'} = E_{G'} + E_H$, holds equation (2):

$$E_{R'} - K \log [Co^{3+}]/[Co^{2+}] + K \log[H^+] =$$

$$E°_{Co^{3+}/Co^{2+}} + K \log F' = E° \qquad (2)$$

where $E°$ is the standard redox potential of the Co-(III, II) pair at -5 °C in $5\,M\,(6.5\,M)\,HClO_4$. Preliminary titrations at -5 °C using cell (G') gave, by eqn. (2), $E° = 1.84$ V.

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Dipolar Effects in Electrolytes

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The specific solvation of the anion by hydrogen bonding accounts for the lower reactivity in metha-nol. The different behaviour of the halogens with respect to the sulphonates found in the other solvents can be explained in terms of (i) extent of bond-breaking and bond-making in the transition state (ii) assistance to the leaving group by the solvent.

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Acidity Function in Organic Solvents (Acetonitrile, Phenol, Acetone and Their Mixtures)

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Acidity function (A.F.) measured by protonation equilibria of indicators of the nitroanilines family, is under investigation for H_2SO_4 (CF_3SO_3H) solution $(10^{-4} \div 10^{-1}\,M)$ in organic solvents. The chosen systems are known to be much more acidic than the aqueous ones [1, 2] but no general A.F. has been described like the well known Hammett function for the aqueous system. Some results are reported for the solvent system Phenol–Acetone with a water content variable from 0.5 to 4%. Table I shows the pK_a^S of the two indicators, o-nitroaniline and p-nitro-aniline, determined by the extrapolation method in the system S (65% Phenol–35% Acetone) at variable amount of water. The reported pK_a^S values are higher than those in the water ideal state (pK_a^W), in agree-ment with the greater protonating ability of the system compound with the aqueous state. The varia-tion of the pK_a values with water concentration points out that water should be considered a strong base in the Phenol–Acetone solvent system.

It is not possible to derive an acidity function using the ideal solution in water as standard state, since there are specific effects probably due to the low dielectric constant of the medium. As it is known [1, 2] it is possible to define an 'operational' acidity function H_0^S using an ideal solution in the solvent itself, as reference state. Assuming as reference state the solvent system 65% Phenol/35% Acetone with 0.5% water, it is possible to obtain consistent data of the acidity function H_0^S. Fig. 1 shows the conti-nuous curves obtained at different water content. The