Experimental details will be reported elsewhere.

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G. Fodor
K. Nádor

Institute of Organic Chemistry,
University, Szeged. Sept. 28.

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Anion Affinity and Polarizing Power of Cations

It is suggested that the ionization potential, *I* (first for univalent cations, second for divalent cations, third for trivalent cations, and so on), be used as a relative measure of the power of a cation to attract an anion (its 'anion affinity'), and of its polarizing power. Its use thus may be demonstrated by some of the comparisons below. The general concept used here of the ability of cations to polarize and deform anions follows that discussed in the writings of Fajans[1,2] and of others, and the homopolar bonds referred to below are regarded as strongly polarized ionic bonds.

(1) *Univalent ions*

(*I* increases ⟶)

	Cs^+	Rb^+	K^+	Na^+	Li^+	Tl^+	Ag^+	Cu^+	Au^+
I (volts)	3·9	4·2	4·34	5·14	5·4	6·1	7·57	7·7	9·22
Radius (A.)	1·67	1·47	1·33	0·97	0·68	1·47	1·27	0·96	1·37

Radii are included, based mainly on those of Pauling[3], as revised, with additions, by Ahrens[4].

A progressive change in bond type (ionic → covalent) with a given partner (O^{2-}, S^{2-}, Cl^-, etc.) is usually apparent when going from left to right, with thallium frequently occupying an intermediate position. For some purposes of comparison, Li^+ should be omitted because of its small size.

(2) *Medium-sized* (0·6–0·8 *A.*) *divalent cations*

(*I* increases ⟶)

	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}	Pt^{2+}	Pd^{2+}	Cu^{2+}
I (volts)	15·03	15·64	16·24	17·4	17·95	18·2	19·3	19·9	20·3
Radius (A.)	0·66	0·80	0·74	0·73	0·74	0·69	0·80	0·80	0·72

With increase in anion affinity there is again a progressive change in chemical, crystal chemical and stereochemical properties, and in the ability to form stable complexes. Manganese and nickel frequently occupy positions intermediate between the two extremes, magnesium and platinum, palladium and copper.

The possibility that the coplanar stereochemistry of divalent copper, palladium, platinum (all partners except fluorine) and sometimes nickel could arise as a result of extreme deformation (polarization) of the partner suggests itself as a possible alternative to the concept of hybridization of bond orbitals as postulated by Pauling[5].

When arranged in order of increasing anion affinity, large (0·97–1·20 A.) divalent cations, Ba^{2+}, Ca^{2+}, Pb^{2+}, Cd^{2+} and Hg^{2+}, also show progressive changes of properties as above. These ions have the 8 : 4 (fluorite) structure with the rigid anion F^-, whereas the 6 : 3 (rutile) structure is common for divalent ions of the medium-sized group.

The greatest ionization potential of any divalent metal is that of Ag^{2+} (22·0 volts; radius 0·89 A.) and is a probable cause for the unusual properties of this ion and for the instability of all its compounds, AgF_2 included.

L. H. Ahrens

Department of Geology,
Massachusetts Institute of Technology,
Cambridge, Mass.
Sept. 25.

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Reaction Velocities and Activation Energies of some 'Instantaneous' Complex Ion Reactions

In connexion with an investigation of the slow time reactions in the chromic thiocyanate system in aqueous solution, one of us (J. B.) had the idea that it might be possible to estimate the energies of activation in 'instantaneous' complex ion reactions by investigating the reactions in alcoholic solutions at low temperatures. These expectations have been to a great extent fulfilled.

The introductory experiments were carried out in test-tubes at approximately − 75° C. in a bath of solid carbon dioxide and 96 per cent ethanol in an unsilvered litre Dewar flask, and at about − 100° C. in a bath of melting methanol (made by means of liquid air and kept in circulation by aeration). Various complex systems with strongly coloured complexes were examined visually in methanol solution, and the following new measurable reactions with times of half-completion varying from many hours to a few seconds in 0·05–0·001 molar solutions were discovered:

(1) Ferric ions reacted measurably with thiosulphate to form a stable violet complex, as also with phenols at − 75° C. The colour reaction with sulphosalicylic acid occurred several times faster than with salicylic acid, probably due to the electronegative influence of the sulphonic group.

(2) Nickel ions (Ni^{2+}) gave slow reactions with dimethylglyoxime, pyridine and ethylenediamine at − 75°, while Cu^{2+} reacted in a few seconds with ethylenediamine at − 100° C., but instantaneously with ammonia and pyridine.

(3) Thiocyanate ions gave delayed reactions with $PdCl_4^{--}$, $AuCl_4^-$, $PtCl_6^{--}$, Fe^{3+} at − 75° C. with rates increasing in the order mentioned, and at − 100° C. also with Co^{2+}. Cupric ions still reacted instantaneously at this temperature.

(4) Dithizone gave delayed reactions with mercuric, cobaltous and nickel ions at − 75° C. With ferrous ions it reacted almost instantaneously, and ferric ions immediately gave a green colour which after a short time changed into the usual red. At − 100° C., moreover, silver and lead ions gave somewhat delayed reactions, whereas cupric ions reacted instantaneously and manganese and zinc ions almost instantaneously.

These experiments support qualitatively the idea of a connexion between rates of complex formation and valency and electron configurations of the metals in the transition series : (i) for ions with the same electron configuration, for example, Fe^{3+}, Mn^{2+}, higher valency corresponds to lower rate and higher complexity ; (ii) in cases of equal valency, ions with half-completed and completed (or nearly completed) electron shells give a much higher rate of complex formation than the remainder of the ions in the transition series (compare, for example, Fe^{3+} with Cr^{3+}, Co^{3+}, and Mn^{2+}, Cu^{2+}, Zn^{2+} with Fe^{2+}, Co^{2+}, Ni^{2+}). This is contrary to the complex-affinity, which increases more or less evenly with the atomic number in the series Cr^{3+}, Fe^{3+}, Co^{3+}, and from Mn^{2+} to Cu^{2+}, before it falls[1,2] to Zn^{2+}.

Some few systems were more thoroughly examined, and the times necessary for reaching a certain degree of reaction determined at different temperatures. As the systems contain several coloured complexes, it was not always possible to determine true degrees of reaction; but the same degrees of reaction could be determined by comparison with an appropriate standard solution with smaller concentration of the metal salt than the reacting mixture. Colours were compared visually, and the constancy of the temperature during the reaction controlled to an accuracy of 0·25° C. by a copper–constantan thermocouple. Only in the chromic thiocyanate system were real velocity constants determined more exactly by other methods[3,4]. The activation energy E_A and frequency factor A in the Arrhenius equation $k = A.\exp(-E_A/RT)$ were calculated in the usual way by plotting ln k against $1/T$ (see table).

System	Ligand taken up	E_A (kcal./mol.)	log A (sec.$^{-1}$)	Solvent ionic strength	Temperature range
$Ni^{2}+$, py	∼ 1st	∼ 17	∼ 16	CH_3OH, $\mu \sim 0·1$	196–218° K.
$Co^{2}+$, SCN^-	∼ 4th	∼ 15	∼ 17	CH_3OH, $\mu \sim 0·05$	181–192° K.
$Fe^{3}+$, SCN^-	1st	∼ 12·7	∼ 14	CH_3OH, $\mu \sim 0·01$	190–199° K.
$Cr^{3}+$, SCN^-	1st	25·2 ± 0·2 25·2 ± 0·2	13·6 ± 0·2 13·3 ± 0·2	H_2O, $\mu \sim 0·1$ H_2O, 1 N $NaClO_4$	298–348° K. ,,
,,	6th	∼ 25	∼ 13	H_2O, μ var.	288–298° K.

The results suggest that most complex-reactions are instantaneous at room temperature due to a high value of the frequency factor rather than a low activation energy.

The experiments are being continued, and we hope in the near future to publish a paper in *Acta Chemica Scandinavica* dealing with the mechanism of complex formation.

Jannik Bjerrum
Knud Georg Poulsen

Chemistry Department A,
Danish University of Technology,
Copenhagen.
Oct. 9.

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Thermodynamics of Three-Component Systems

Although relations of the type

$$(\partial \ln a_1/\partial n_2)_{n_1,n_3} = (\partial \ln a_2/\partial n_1)_{n_2,n_3}, \qquad (1)$$

where a is activity, n is number of moles, and the suffixes denote the components, are by no means new[1], they have been little exploited. Further types such as

$$(\partial \ln a_1/\partial n_2)_{a_2,n_3} = (\partial \ln a_2/\partial n_1)_{a_1,n_3} \qquad (2)$$

and

$$(\partial \ln a_1/\partial \ln a_2)_{n_1,n_3} = -(\partial n_2/\partial n_1)_{a_2,n_3} \qquad (3)$$

do not seem to appear in the literature at all, though they are sometimes more convenient to use than equation (1). Despite their neglect, these cross-differentiation relations provide a versatile tool in the study of three-component and more complicated systems, as the brief survey in this communication will indicate. They can be generalized by replacing the ln$a$'s by any partial molal quantities. Perhaps the most important conclusion is that, from measurements of the solvent activity only, it is possible to calculate the activities of all the other components.

It is usually desirable, as a first stage, to convert the basic relations into mole ratio (molality) or mole fraction form. This has the effect of reducing from two to one the number of constancy conditions applying to each differential coefficient, since all the variables are now intensive. Equation (1), for example, can be written :

$$(\partial \ln a_1/\partial r_{23})_{r_{13}} = (\partial \ln a_2/\partial r_{13})_{r_{23}}, \qquad (4)$$

(where r_{ij} is n_i/n_j), or if component 3 is taken as solvent,

$$(\partial \ln a_1/\partial m_2)_{m_1} = (\partial \ln a_2/\partial m_1)_{m_2}, \qquad (5)$$

(where m is molality).

The next stage in most applications is to integrate the relations. Thus (4) integrated at constant r_{13} gives

$$\left\{ \ln(a_1/a_1{}^*) = \int_{r_{23}{}^*}^{r_{23}} (\partial \ln a_2/\partial r_{13})_{r_{23}}\, dr_{23} \right\}_{r_{13}} \qquad (6)$$

(asterisk denotes lower limit of integration). If a_2 has been measured as a function of composition, that is, of r_{13} and r_{23}, this equation gives the variation of a_1 with r_{23} at constant r_{13}. Sometimes, too, by a suitable choice of lower limit, $a_1{}^*$ becomes a known function, and a_1 is then known absolutely. There are two principal cases :

(1) If a_1 is defined by reference to an infinitely dilute solution in component 2, for example so that $a_1 \rightarrow r_{12}$ as $r_{23} \rightarrow \infty$ (supposing component 1 to be non-dissociating), then,

$$\left\{ \ln(a_1/r_{12}) = \int_{\infty}^{r_{23}} (\partial \ln a_2/\partial r_{13})_{r_{23}}\, dr_{23} \right\}_{r_{13}}, \qquad (7)$$

which gives a_1 absolutely. There is a similar equation for a_3 in terms of a_2. This is the result mentioned above, namely, the determination of a_1 and a_3 from measurements of a_2 only. Hitherto it has generally