eral argument is that the metal layer on a charcoal such as Darco cannot be continuous since a monatomic layer covering the reported surface of this charcoal would require more metal (30% of the weight of the carrier) than corresponds to high efficiency. Further, since too high a carrier–metal ratio results in *less* active catalysts, it must be possible for the metal to be spread too thin. It, therefore, seems likely that active surfaces are supported by several layers of underlying metal.

(8) Curve C resembles some of those shown in the earlier Maxted papers, in which he proposed the existence of two types of active sites. An alternative interpretation is offered in ref 2, p 38.

(9) (a) E. B. Maxted and H. C. Evans, *J. Chem. Soc.*, 1004 (1937); (b) *ibid.*, 455 (1937); (c) *ibid.*, 2071 (1938).

(10) In various instances (e.g., G. B. Elion, private communication), protective benzyl groups elsewhere in the molecule were removed poorly by the Pd/C hydrogenation employed to convert N_3 to $NH_2 + N_2$. The author is of the opinion that poisoning through sulfur analogues present in commercial benzyl chloride is probably responsible. The shape of nucleosides, with ring systems at a sharp angle to each other, also presents a possibility for self-poisoning, should the nitrogen-containing heterocycle be adsorbed preferentially.

(11) In low concentration the poison does not attain the catalyst surface immediately. Without such a period of equilibration, the reduction data resemble those often observed in preparative reductions with poison present: the initial rate is almost normal and diminishes after 1 or 2 min to a low or zero level.

(12) As mentioned in the previous communication, a true C_s lim cannot exist in the presence of serious concentrations of inhibitor. However, deviations from constancy do not become notable during the first 10–20% of reaction.

(13) E. B. Maxted and M. S. Biggs, *J. Chem. Soc.*, 3844 (1957), reported on the toxicity of ammonia, butylamine, cyclohexylamine, and dicyclohexylamine in the reduction of cyclohexene over platinum. To avoid inhibition by solvent anions, they employed cyclohexane as solvent. This, in turn, raises questions as to the influence of the solvent on the activity of the poisons. (All were considerably more toxic than in the present study, but there was about a twofold variation among the first three with dicyclohexylamine much less toxic. Maxted suggested that this might be a case of hindrance, ignoring solubility effects.) In the present study it had been planned to examine ammonia, pyrrolidine, piperidine, and morpholine, whose activities should not vary much because of solubility. This plan was abandoned when it was found impossible to deal with the stronger bases under comparable conditions.

(14) Regarding N_3^- as a nucleophile, its adsorbed condition has some resemblance to hydrazoic acid.

(15) Rhodium has been especially recommended for the reduction of nitriles. Cf. M. Freifelder, *J. Am. Chem. Soc.*, **82,** 3286 (1960).

(16) While this phenomenon does not appear to have been observed previously with noble metals, preparative dethiation with Raney nickel is, of course, a familiar process.

(17) E.g., the occurrence of β-naphthol as a by-product in the reduction of octalone. Cf. R. L. Augustine, D. C. Migliorini, R. F. Fusante, C. S. Sudano, and M. J. Sisbarro, *J. Org. Chem.*, **34,** 1075 (1969).

(18) Maxted's ratio was 2.5:1 relating to the reduction of crotonic acid. From Table V we see that 2×10^{-7} mol of BuSH permitted 40% activity vs. nitrobenzene, whereas 10^{-7} of Bu_2S permitted 33%. Against acetophenone at 33% activity, the ratio is 3.7:1.

(19) R. Baltzly, *J. Org. Chem.*, following paper in this issue.

(20) Maxted preferred not to work with supported catalysts since he feared that adsorption of poison on the carrier would complicate the situation unduly. Consideration of the data of this table in light of the fact that in the acetophenone reductions ten times as much carrier was used as well as ten times as much metal shows that adsorption on the carrier cannot be significant. Comparing lines 1 and 4 of Table V (Bu_2S poisoning), if the carrier per se in the former case held 10% of the adsorbed poison, the carrier per se in the latter case should have held two-thirds. This seems unlikely.

Studies on Catalytic Hydrogenation. III. Poisoning and Promotion by Cations[1]

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Received June 3, 1975

The toxicities of zinc, cadmium, and manganese as bivalent cations earlier reported as equipotent poisons toward platinum have been examined with platinum, palladium, and rhodium on carbon and against a variety of substrates. Zinc and manganese are essentially nontoxic toward palladium and rhodium and, in fact, act as promoters in the palladium-catalyzed hydrogenolysis of benzyl alcohol. The observed promotion and certain variations in toxicity from substrate to substrate are interpreted as due to complex formation between cation and substrate and preferential adsorption of the complex in certain situations.

Maxted and Marsden[3,4] investigated the toxic action of a number of metallic cations in the reduction of crotonic acid in alcohol by Willstätter platinum. It was desired to reexamine a representative group of these against metallized charcoals, and zinc, cadmium, and manganese were selected for study. Of the 12 metallic elements identified by Maxted and Marsden as toxic, these have certain advantages. They are unlikely to be reduced to the metals under the conditions (as are Cu^{2+}, Ag^{+}, and Hg^{2+} or perhaps Pb^{2+} and Sn^{2+}). They were among the most toxic agents of this type, and their solutions are stable (whereas Fe^{2+} tends to pass to Fe^{3+}). It was anticipated that by using substrates having varying adsorption tendencies, further variation in the toxicities might be revealed, taking into account the arguments of the preceding communications of this series as to reaction kinetics and toxicity.

Since the variation in behavior far exceeded anticipation, it may be in point to outline the chronological course of this investigation. At the start of the program platinized charcoal was studied and the necessary conditions and techniques were worked out with it, using nitrobenzene and acetophenone as substrates. Toxicity studies were interspersed with standard runs as was convenient. The troublesome substrate, cyclohexene, was taken up later after which palladized charcoal was examined and finally (though somewhat incompletely) rhodium on charcoal.

The first data on cationic poisons that became available were, therefore, those of the left half of Table II followed by those of the first section of Table III. While poisoning by nucleophiles (the subject of the preceding communication) showed few unanticipated peculiarities of major importance, the nitrobenzene reductions exhibited far greater variation between Maxted's equitoxic ions than had been felt to be possible. The data with cyclohexene, when obtained, did, however, display the sort of behavior anticipated.

When the study of palladized charcoal was begun, there was special interest in the hydrogenation of benzyl alcohol (taken as an example of debenzylation for which this catalyst is especially preferred). When poisoning by zinc was studied, it was found that increasing concentrations of zinc ion had at first little effect on the reduction rate, but eventually produced a clear *increase* in rate. The prospect then presented itself that some or all of the anomalous results might be the result of concurrent poisoning and promotion.

Major interest in promotion arose from the work of Carothers and Adams[5] and of Faillebin.[6] Carothers and Adams studied promotion in the reduction of aldehydes by Adams'

Table I. Inhibition by Cations of Reductions of Nonpolar Substrates

	Substrate cyclohexene in 90% MeOH, 0.023 M $HClO_4$, C_s in = 0.6						Substrate benzene 5 mg of Rh/C (E) neutral in 85% MeOH, C_s in = 2.05	
	3% Pt/C, 1 mg Pt		3% Pd/C, 0.5 mg Pd		1% Rh/C, 0.1 mg Rh[a]			
Cation	$C_{i½}$	α_i/α_s	$C_{i½}$	α_i/α_s	$C_{i½}$	α_i/α_s	$C_{i½}$	α_i/α_s
Zn^{2+}	1.6×10^{-6}	3.75×10^5	$>8 \times 10^{-3}$	$<10^{-2}$	$(2 \times 10^{-4}$	$3 \times 10^3)$	1.5×10^{-4}	1.4×10^4
Mn^{2+}	$\sim 5 \times 10^{-5}$	1.2×10^4	$>6 \times 10^{-3}$	$<10^2$	$(1.5 \times 10^{-3}$	$4 \times 10^2)$	$>10^{-2}$[b]	$<2 \times 10^2$
Cd^{2+}	2×10^{-6}	3×10^5	3×10^{-6}	2×10^5	$(2 \times 10^{-6}$	$3 \times 10^5)$	7×10^{-5}	2.9×10^4
Fe^{2+}			$\sim 5 \times 10^{-5}$	1.2×10^4				

[a] Tentative values obtained with substrate samples giving control rates $^2/_3$–$^3/_4$ of standard. [b] 25% inhibited at 10^{-2}.

catalyst, Faillebin by Willstätter platinum. In their work, Carothers and Adams examined the effect of a number of metallic salts among which those of iron were preferred. Promotion was also observed with Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, and chromium. All of these except the last are on Maxted's list of poisons.[7] These authors reported further that their promoters acted as poisons as their concentration was raised beyond the optimum for aldehyde reduction. They also observed that with higher than optimal amounts of iron (but not obstructive quantities) reduction to toluene was extensive. This amounts to promotion of the hydrogenolysis of benzyl alcohol by concentrations of Fe^{2+} higher than optimal for benzaldehyde reduction.

Maxted and Akhtar[8] reexamined the problem of promotion and found Sn^{2+} to be even more effective than Fe^{2+} as a promoter. They also observed promotion in the reduction of acetone and of ethyl cinnamate. Of these, the former was unreduced in the absence of promoter; with the latter, promotion increased an already considerable reduction rate. (It is doubtful if this sort of effect could have been observed with the apparatus employed by Carothers and Adams.)

Tin salts, while poisons in the Maxted studies, were relatively weak and chromium is perhaps not toxic. The possibility arises, therefore, that the promotion phenomena may not be intimately connected with catalyst poisoning.

Experimental Section

The methods used have been described in the earlier communications of this series. Zinc and manganous chlorides were CP commercial materials. They were weighed out and made up to M/10 concentrations, further dilutions being made into methanol. Cadmium was available as the carbonate which was converted to the chloride after weighing. Iron was made up as ferrous sulfate. All the poisoning runs were made under acid conditions except those with Rh/C on benzene and acetophenone, which were neutral. The appropriate standard rates (cf. first communication) were taken as the basis for comparison. The amounts of chloride introduced with the poison were too small to influence the rate significantly.[9]

Results and Discussion

The poisoning data are shown in Tables I–IV. The first of these gives results with cyclohexene and benzene. Since promotion or other interaction between substrate and poison should be minimal in these situations, these data are believed to be indicative of the inherent tendencies of the cations to be adsorbed on the three catalysts. The calculated ratios α_i/α_s are also given for comparison. While none of the data of this table can be supported by crossover experiments, those conducted with $CdCl_2$ against nitrobenzene and acetophenone showed the bulk of the inhibitor to be in solution and that the true and apparent half-inhibitory concentrations were not far apart.

With platinized charcoal, cadmium and zinc are adsorbed about equally while manganous ion is bound less strongly. Using a less strongly adsorbed substrate below its C_s lim, this difference might not be apparent. Zinc is weakly adsorbed on rhodium and not appreciably on palladium, while manganous ion is minimally toxic to both these catalysts. Cadmium is highly toxic to all three catalysts; in fact, the α_i/α_s values are remarkably constant. Ferrous ion was moderately toxic toward palladized charcoal (it was examined mainly with respect to benzaldehyde and benzyl alcohol reductions, for which Pt/C and Rh/C are ineffective).

Table II. Inhibition of Nitrobenzene Reductions by Cations

	C_s in = 0.39 Pt/C, 1 mg Pt		$HClO_4$ = 0.46 Pd/C, 0.5 mg Pd	
Cation	Solvent	$C_{i½}$	Solvent	$C_{i½}$
Zn^{2+}	75% MeOH	$>1.5 \times 10^{-2}$	75% MeOH	$>4 \times 10^{-2}$
	89% HAc	9×10^{-3}	90% MeOH	$>4 \times 10^{-3}$
Mn^{2+}	89% HAc	8×10^{-3}	75% MeOH	$>1.6 \times 10^{-2}$
			90% MeOH	$>4 \times 10^{-3}$
Cd^{2+}	75% MeOH	6×10^{-6}[a]	75% MeOH	$>10^{-3}$[b]
	89% HAc	8×10^{-6}	90% MeOH	4×10^{-4}

[a] From crossover experiment. The apparent value is the same. Two runs with 0.05% Pt/graphite gave ca. 3×10^{-6} as apparent $C_{i½}$. [b] Rate nearly constant 1.6×10^{-4}–10^{-3}.

Table II shows results against nitrobenzene for Pt/C and Pd/C. [The Rh-catalyzed reductions of nitrobenzene are rather erratic (cf. part I), and no toxicities were run therewith in this series.] The toxic activity of cadmium on Pt is reasonably in line here, but it proved impossible to get half-poisoning concentrations of zinc and manganese in 75% methanol. Satisfactory data could be obtained in 89% acetic acid where these two ions had about equal low toxicities, $C_{i1/2}$ being almost 1000 times that with cadmium. The results with Pd/C and Zn^{2+} and Mn^{2+} are what might be expected from the above, but cadmium also was markedly less active. Its $C_{i1/2}$ had to be obtained in 90% methanol. The resultant value for α_i/α_s is 10^3 while that for reduction of cyclohexene by the same catalyst and in the same solvent is 2×10^5. The α_s figures cannot differ to that extent so this result is clearly anomalous.

The acetophenone data shown in Table III are fairly well in line: cadmium ion continues to be a strong poison; zinc and manganese are relatively weak except with platinum. It is to be noted, however, that even with platinum, manganese poisoning did not follow the theoretical curves, and with palladized charcoal, zinc and manganese inhibition was largely independent of concentration as though compensating forces were at work. At first sight, one might be surprised that $C_{i1/2}$ for Cd^{2+} vs. acetophenone with Pt/C is higher than the figure for nitrobenzene (1.5×10^{-5} and 6×10^{-6}). If, however, the substrate concentrations are considered, the relationship is revised: α_i/α_s for nitrobenzene is 6.6×10^4 and for acetophenone, 1.1×10^5.

When we examine the palladized-charcoal reductions of benzaldehyde, benzyl alcohol, and benzyl methyl ether, presented in Table IV, we again encounter standard behavior from cadmium. Zinc and manganese have little effect on the reduction of benzaldehyde but clearly promote the reduction of benzyl alcohol and benzyl methyl ether. Ferrous

Table III. Inhibition of Acetophenone Reductions by Cations

Catalyst	Solvent and acidity	Inhibitor	$C_{i1/2}$	Remarks
Pt/C (3%) C_s in = 1.7 10 mg Pt	75% MeOH Res	Zn^{2+}	2×10^{-5}	
Pt/C (3%) C_s in = 1.7 10 mg Pt	99% MeOH Res	Mn^{2+}	4×10^{-5}	Does not follow poisoning curve
Pt/C (3%) C_s in = 1.7 10 mg Pt	75% MeOH 0.023 M $HClO_4$	Cd^{2+}	1.5×10^{-5}	From crossover[a]
Pd/C (3%) C_s in = 1.33 5 mg Pd	90% MeOH 0.23 M $HClO_4$	Zn^{2+}	$>10^{-3}$	Fairly constant 2×10^{-5}–10^{-3}
Pd/C (3%) C_s in = 1.33 5 mg Pd	0.23 M $HClO_4$	Mn^{2+}	$>10^{-3}$	Fairly constant 2×10^{-4}–10^{-3}
Pd/C (3%) C_s in = 1.33 5 mg Pd	0.23 M $HClO_4$	Cd^{2+}	2×10^{-5}	
Rh/C (5%, cat. E) C_s in = 1.7 5 mg Rh	75% MeOH Neutral	Zn^{2+}	3×10^{-4}	
Rh/C (5%, cat. E) C_s in = 1.7 5 mg Rh	Neutral	Mn^{2+}	$>10^{-2}$	Rate $^2/_3$ of standard at 10^{-2}
Rh/C (5%, cat. E) C_s in = 1.7 5 mg Rh	Neutral	Cd^{2+}	6×10^{-5}	

[a] Apparent $C_{i1/2} = 2 \times 10^{-5}$.

ion, which is adsorbed on palladium, had little effect on the reduction of benzyl alcohol and promoted the reduction of benzaldehyde only slightly. It is reasonable to view this finding as due to compensating poisoning and promotion.

On the Nature of Promotion. The work of Carothers and Adams can be discussed only in general terms since they employed platinum and particularly because this was in the form of Adams' catalyst. This catalyst is of the highest practical use, and its introduction was a landmark in organic chemistry, but it is unsuited to kinetic studies. Aside from the variability of batches, its state of subdivision is not constant. When first formed and engaged in a rapid reduction, it is highly colloidal and extremely active. When reduction stops or slows, it coagulates and does not thereafter recover *full* activity. Thus, inherently slow reductions are depressed out of reasonable comparison. Whether qualitative as well as quantitative changes in activity occur is uncertain. This point was considered by Adams, who thought that the activity of his promoters might be due in part to effect on the subdivision of the catalyst. This may have contributed, but it seems unlikely to be the major influence. Promotion was observed with *lower* concentrations of promoter than required for poisoning. We may assume that as *poisons* these ions were adsorbed on the catalyst. It is hard to see how they could prevent coagulation when less adsorbed or not adsorbed. Therefore, it is more likely that the promoters prevented coagulation merely by increasing the hydrogenation rate.

In the present studies, zinc and manganese are poorly adsorbed on palladium but function as promoters while iron, which is moderately well adsorbed, seems to have a dual role.

It is pertinent to ask a question that seems hitherto to have been avoided. Why should aldehydes, generally not noted for inactivity, be resistant to reduction in the first place? A possible answer is that in hydroxylic solvents they are present mainly or entirely as solvates. To the catalyst, a solvated aldehyde is simply a substituted alcohol, in the case of benzaldehyde a benzyl alcohol. Platinized charcoal, which does not reduce benzyl alcohol appreciably, also does not reduce benzaldehyde (and the usual promoters are here of no assistance). Adams' catalyst has some debenzylative abilities but is not superior in this respect. Palladized charcoal is superior for debenzylations and reduces benzyl alcohol rapidly, benzaldehyde even more rapidly.

If one imagines benzaldehyde hydrate or alcoholate adsorbed on a planar surface, the phenyl, α-carbon, and one C–O bond can lie on the surface. The other C–O bond cannot but will alter the electronic environment. Accordingly, the palladized charcoal reduction of benzaldehyde is less sensitive to acid than that of benzyl alcohol. One might also suppose that the coordinated metal could take the place of acid to which these debenzylations are so sensitive. That is not so, at least in any dramatic fashion. Runs in neutral solutions containing zinc chloride were only marginally faster than the neutral rate, both in the reduction of benzyl alcohol and that of benzyl methyl ether. In the latter case the difference may have been significant. This point might be settled by use of larger amounts of catalyst. Under the conditions of these reductions, formation of hemiacetal and hydrate would probably be instantaneous. Formation of full acetal would be much slower.

It is suggested that in the presence of polar substrates, zinc, manganese, and iron are extensively coordinated with substrate, while cadmium, as would be expected on general principles, is less so (or not at all). With nitrobenzene and platinized charcoal, the principal result is to diminish the availability of the inhibitor so that a larger amount is necessary to poison the catalyst. Coordination could also be expected with acetophenone. The data of Table III do not reveal any major influence of this sort, but this could be the result of compensating interactions. With the benzyl compounds, the metal coordinate constitutes a second and probably preferred substrate.[10] The effect is not dramatic in these palladium-catalyzed reductions since the unpromoted rate is very considerable. A quantitatively comparable promotion starting from a low or zero rate could easily account for the promotion with Adams' catalyst. Iron is not superior as a promoter in the present experiments because it is simultaneously an effective poison while zinc and man-

Table IV. Inhibition and Promotion in Palladium-Catalyzed Reductions

Cation	Solvent	$C_{i½}$	Remarks
A. Substrate Benzyl Alcohol: C_S in = 2.1, $HClO_4$ = 0.23 M 5 mg of Pd as 3% Pd/C			
Zn^{2+}	90% MeOH		10% promotion at 10^{-3}
	80% MeOH		10% promotion at 8×10^{-3}
	75% HAc		25% promotion at 10^{-2}
Mn^{2+}	90% MeOH		10% promotion at 4×10^{-3}
	80% MeOH		10% promotion at 8×10^{-3}
	75% HAc		20% promotion at 10^{-2}
Cd^{2+}	90% MeOH	2×10^{-5}	
	80% MeOH	2×10^{-5}	
	75% HAc	3×10^{-5}	
Fe^{2+}	90% MeOH	?	Rate fairly constant 5×10^{-5}–2×10^{-4} marginal inhibition at 10^{-3}
B. Substrate Benzyl Methyl Ether: C_S in = 1.4, $HClO_4$ = 0.23 M 5 mg of Pd as 3% Pd/C			
Zn^{2+}	75% HAc		30% promotion at 8×10^{-3}
Cd^{2+}	75% HAc	$\sim 5 \times 10^{-5}$	
C. Substrate Benzaldehyde: C_S in = 2.08, $HClO_4$ = 0.23 M 3 mg of Pd as 3% Pd/C			
Zn^{2+}	90% MeOH		Rate fairly constant 2×10^{-5}–8×10^{-3}
	80% MeOH		Rate fairly constant 4×10^{-3}–2×10^{-2}
Mn^{2+}	90% MeOH		No inhibition at 4×10^{-3}
	80% MeOH		No inhibition at 2×10^{-3}–10^{-2}
Cd^{2+}	90% MeOH	3.5×10^{-5}	
Fe^{2+}	90% MeOH		Fairly constant 0–2×10^{-4} Slight promotion at 10^{-4} With no added acid (res) 25% promotion at 2×10^{-5}

ganese are not. Assuming that the toxicities to Adams' catalyst are comparable to those with other platinum catalysts (Maxted's and platinized charcoal), these three metals were on a comparable basis as poisons, and the superiority of iron as a promoter was manifested. Maxted and Akhtar's observation with stannous ion also falls into line since this was a poison of lower potency.

The only useful data on rhodium in the present work are with benzene and acetophenone (and, with reservations, cyclohexene). The pattern is intermediate between those of platinum and palladium. Cadmium ion is a strong poison, zinc considerably weaker, and Mn^{2+} is barely toxic.

Maxted[11] proposed a rule as to the metal ions that are toxic to hydrogenation catalysts. This rule depends on electron disposition in the incompletely filled shell below the valence electrons. It appeared to be valid for the catalysts he examined. It clearly is not of general validity. In the present investigation cations Maxted considered nontoxic were not tested, but in view of the failure of this rule, a reexamination of other ions is distinctly indicated.

Acknowledgment. The author wishes to express his gratitude to Dr. George B. Brown and his department for their hospitality, which was indispensable for the accomplishment of this work.

Registry No.—Zn^{2+}, 23713-49-7; Mn^{2+}, 16397-91-4; Cd^{2+}, 22537-48-0; Fe^{2+}, 15438-31-0; platinum, 7440-06-4; palladium, 7440-05-3; rhodium, 7440-16-6; cyclohexene, 110-83-8; benzene, 71-43-2; nitrobenzene, 98-95-3; acetophenone, 98-86-2; benzyl alcohol, 100-51-6; benzyl methyl ether, 538-86-3; benzaldehyde, 100-52-7.

References and Notes

(1) Parts I and II: R. Baltzly, *J. Org. Chem.*, preceding papers in this issue.
(2) The author wishes to express his gratitude to the Wellcome Research Laboratories and to the Public Health Service Grant CA-08748 from the National Cancer Institute for partial financial support of this investigation.
(3) E. B. Maxted and A. Marsden, *J. Chem. Soc.*, 469 (1940).
(4) For a review of catalyst poisoning cf. R. Baltzly, *Ann. N.Y. Acad. Sci.*, **145**, 31–45 (1967).
(5) W. H. Carothers and R. Adams, *J. Am. Chem. Soc.*, **45**, 1071 (1923); **47**, 1047 (1925). Some further references, mainly of doubtful relevance, are cited in these papers. It is of interest to note that the second of these Adams papers contains what may well be the first observation of poisoning by iodide ion.
(6) Faillebin, *C. R. Acad. Sci.*, **175**, 1077, 1118 (1922).
(7) Actually, Carothers and Adams introduced chromium as CrO_4^{2-}, Maxted as Cr^{3+}. In both laboratories, it seems to have been tacitly assumed that the metal would end up in the same state. This would doubtless be the case if all the ions possibly involved should be adsorbed on the catalyst. It is, however, perfectly possible for any particle thermodynamically reducible to remain unaltered because not adsorbed. The equivalence of Fe^{2+} and Fe^{3+} was established.
(8) E. B. Maxted and S. Akhtar, *J. Chem. Soc.*, 3130 (1959). Relevant to footnote 7, stannous and stannic tin *were not equivalent.*
(9) This is also true of Maxted's experiments in which metals were introduced as chlorides and acetates.
(10) It was observable in the zinc and manganese runs of Table IV with benzyl alcohol that the linear portion of the reduction plot was appreciably prolonged (lower value for C'_s lim).
(11) E. B. Maxted, *J. Chem. Soc.*, 1987 (1949).