

## Non-periodic Trends in the Oxidative Dissolution of Transition Metals by Manganese(III) Acetate

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### Abstract

As part of a study designed to synthesize the proposed high temperature superconductor MoN, molybdenum powder was reacted with manganese(III) acetate and sodium azide in refluxing glacial acetic acid. No MoN was found. Instead, rapid and complete oxidative dissolution of the metal to soluble forms of Mo(VI) were observed. Removal of the azide or replacement of the azide by chloride had no qualitative effect. Other metals were studied and four groups may be discerned: (1) quantitative dissolution in cold, pure acetic acid – Mn, Fe, Co; (2) quantitative dissolution in refluxing Mn(III) solution – Cu, Mo, In, Sn; (3) partial dissolution in refluxing Mn(III) solution – Ni, V; (4) no reaction – Ti, Zr, Nb, Ta, Cr, W, Re, Rh, Ru, and Pt. Use of preformed metal nitrides, e.g. MoN<sub>0.6</sub>, and variation of the oxidant, e.g. replacing Mn(III) by Fe(III) or by Co(III), resulted in little qualitative change. Some unsuccessful attempts to explain this include literature periodic trends for transition metal chemistry and Pourbaix's electrochemical 'thermodynamic and practical nobility scales' for corrosion by aqueous media.

### Introduction and Periodic Trends

The redox chemistry of transition metals is a highly interesting, important and complicated problem with ramifications in synthetic and mechanistic inorganic and organic chemistry, as well as

analytical and biochemistry. Most of the interest and importance, as well as the complications, arise from the plethora of potentially available oxidation states. For example, molybdenum(VI) forms stable binary species with both oxygen and fluorine [1a], MoO<sub>3</sub> [1b] and MoF<sub>6</sub> [1c]. These two species are found in both the condensed and vapor phases and are highly bound relative to the elements in their standard state [2]. By contrast, the formally related nitride MoN<sub>2</sub> does not contain octahedrally coordinated hexavalent Mo (and tri-coordinated trivalent N) in the solid and a linear N≡Mo≡N structure in the vapor. Instead it consists of a weakly bonded complex of atomic metal and an essentially unmodified dinitrogen molecule, Mo·N<sub>2</sub>, and is seen only in a dinitrogen (N<sub>2</sub>) matrix [3]. As such, it is unbound relative to the elements in their standard state.

The lower valence states of the transition metals display the opposite tendency of being much less stable when bound to oxygen and fluorine than to nitrogen\*. For example, while MoO, a species for-

\*Most of the rules or regularities of chemical phenomena presented in this paper are either taken directly or are immediately derivable from the textbooks by F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980 or by J. E. Huheey, 'Inorganic Chemistry: Principles of structure and reactivity', 3rd edn., Harper and Row, New York, 1983. For example, this statement about the stability of transition metal nitrides, oxides and fluorides may be deduced from the stoichiometry of known compounds presented in these sources. The reader should realize that nitrides are far less 'popular' in the textbook literature than either oxides or fluorides. More explicit relationships are also given on the attainable valence states for the metals with oxygen, fluorine and the less electronegative, heavier halogens, from which one may extrapolate to the less electronegative nitrogen.

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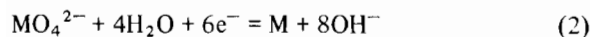
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mally containing Mo(II), is stable in the gas phase [2, 4], solid MoO is formed by a rather exotic disproportionation reaction: 'By reduction of oxygen-containing Mo compounds with potassium,  $K_{0.6}MoO_2$  and  $K_{1.5}MoO_3$  are obtained. When these react with alcohol or water, the products are  $K_2MoO_4$ , hydrogen and a black insoluble residue whose composition approaches MoO' [5]. In contrast, MoN and  $Mo_2N$  are thermodynamically [2, 6] and kinetically stable, indeed refractory, solids [7]. The above relative stability of higher and lower valence nitrides, oxides and fluorides is commonly seen and so provides a good governing principle for the classification and prediction of transition metal compounds.

Another general principle is that the lower oxidation states are generally observed for the 1st transition series, while higher oxidation states are generally observed for the 2nd and 3rd transition series [8]. For example, while Mo(VI) and W(VI) enjoy a rather rich oxide and oxyanion chemistry (e.g. all the iso- and hetero-polymolybdates and tungstates) [9], Cr(VI) oxygen chemistry is essentially limited [10] to  $CrO_3$  and the important, but rather more predictable and so boring, chemistry of chromate and dichromate ions,  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$ . By contrast, Cr(III), with a variety of oxygen ligands such as water, constitutes a staple of descriptive transition metal coordination chemistry [11, 12], while the corresponding mononuclear Mo(III) and W(III) compounds are much less characterized and seemingly less stable\*. Redox potentials can be used to quantitatively document these relative stabilities\*\*. In particular, consider the following half-reactions and associated standard emfs:



$$M = Cr, -0.744 \text{ V}; M = Mo, -0.20 \text{ V}$$



$$M = Cr, -0.74 \text{ V}^*; M = Mo, -1.05 \text{ V}; M = W, -1.05 \text{ V}$$

\*For example, in F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, only five lines (on p. 867) are devoted to aqueous mononuclear  $Mo^{3+}$ . They assert on p. 868 'no aqua ions of tungsten in any oxidation state have ever been reported.' In C. L. Rollinson, in J. C. Bailar, Jr., H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson (eds.), 'Comprehensive Inorganic Chemistry', Vol. 3, Pergamon, Oxford, 1973, the coordination chemistry of Mo(III) is summarized in all of two pages, pp. 719–720.

\*\*See J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper and Row, New York, 1983, pp. 579–589, for a thorough discussion of redox potentials and for the numbers we have used either directly or as input numbers for a half-reaction via the Nernst equation.

This illustrates the general rule that lower valence state species of the 1st transition series are generally more stable than their analogs containing 2nd or 3rd transition series elements, while higher valence state species are generally more stable with 2nd and 3rd transition series elements than they are when they contain the corresponding 1st transition series element. This stability analysis further exemplifies another even more powerful governing principle: the chemistry of corresponding elements in the heavier transition series are rather similar and generally quite different from that of their lighter congener in the 1st transition series [13].

We additionally note that, in general, as one proceeds from left to right in the periodic table, the higher oxidation states become more oxidizing and the lower oxidation states become less reducing. For example,  $FeO_4^{2-}$  oxidizes [14]  $Cr^{2+}$  to  $CrO_4^{2-}$ .  $FeO_4^{2-}$  may also be shown to be a stronger oxidizing agent than  $MnO_4^{2-}$  by noting that the reaction



is energetically favorable\*\*. ( $FeO_4^{2-}$  is also a stronger oxidizing agent than  $MnO_4^-$  [15].) Likewise one finds that  $Fe^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  are increasingly poor reducing agents. Most ferrous salts and many complexes of  $Fe^{2+}$ , such as the aquo-iron(II) complex  $Fe(H_2O)_6^{2+}$  are readily oxidized [16]. By contrast cobaltous salts and many complexes of  $Co^{2+}$  such as the aquo-cobalt(II) complex  $Co(H_2O)_6^{2+}$  are stable to air [17], and indeed,  $Co^{3+}$  readily oxidizes water to  $O_2$  [18]. It takes strong oxidizing agents such as the hydroxyl radical to affect oxidation of cationic complexes of Ni(II) to Ni(III) [19]. Both trends may be quantified by consideration of the emf of the appropriate half-reactions:  $MO_4^{2-} + 4H_2O + 3e^- = M(OH)_3 + 5OH^-$  for  $M = Cr, -0.13 \text{ V}$ ;  $M = Mn^{\dagger}, 0.32 \text{ V}$ ;  $M = Fe, 0.72 \text{ V}$ . A similar trend is noted for the half reaction emfs for  $M^{2+} + 2e^- = M$ , where M is a 1st transition series metal. Proceeding across the Periodic Table, one finds for  $M = Ti, V, Cr, Mn, Fe, Co, Ni$  and  $Cu$ , the values are:  $-1.628 \text{ V}$ ,

\*This value was derived by combining the two half-reactions:  $CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3$  at  $-0.13 \text{ V}$  and  $Cr(OH)_3 + 3e^- = Cr + 3OH^-$  at  $-1.34 \text{ V}$ .

\*\*This result was derived by combining the four half-reactions:  $FeO_4^{2-} + 3e^- + 4H_2O = Fe(OH)_3 + 5OH^-$  at  $+0.72 \text{ V}$ ,  $Fe(OH)_3 + e^- = Fe(OH)_2 + OH^-$  at  $-0.56 \text{ V}$ ,  $MnO_4^{2-} + 2e^- + 2H_2O = MnO_2 + 4OH^-$  at  $+0.60 \text{ V}$ , and  $MnO_2 + 2e^- + H_2O = Mn(OH)_2 + H_2O$  at  $-0.05 \text{ V}$ .

<sup>†</sup>This result for Mn was derived by combining the three half-reactions:  $MnO_4^{2-} + 2H_2O + 2e^- = MnO_2 + 4OH^-$  at  $+0.60 \text{ V}$ ,  $MnO_2 + 2H_2O + 2e^- = Mn(OH)_2 + 2OH^-$  at  $-0.05 \text{ V}$  and  $Mn(OH)_3 + e^- = Mn(OH)_2 + OH^-$  at  $0.15 \text{ V}$ .

-1.186 V, -0.912 V\*, -1.180 V, -0.440 V, -0.277 V, -0.250 V and +0.377 V.

The value noted above for Mn might seem out of line, but it is not. Another general principle regarding transition metal oxidation states asserts that there is often anomalous stability [20] in species with either a  $d^0$  or  $d^5$  electron configuration, since these correspond to either a 'closed' shell or 'half-filled' shell (*i.e.*, parallel spin subshell filled). That  $Mn^{2+}$  breaks the monotonic nature of the emf sequence reflects the extra stability of its  $d^5$  electronic configuration. Furthermore, this extra stability makes the half-filled  $d^5$   $Mn^{2+}$  ion less reducing than otherwise anticipated by simple interpolation between the values for Cr and Fe. This extra stability of  $Mn^{2+}$  also enhances the tendency of  $Mn^{3+}$  to gain additional electron and so we are not surprised that  $Mn^{3+}$  is relatively strongly oxidizing. Likewise, the reducing power of the  $d^4$   $Fe^{2+}$  ion is enhanced because of the extra stability of the  $d^5$  electronic configuration of its oxidized product,  $Fe^{3+}$ . Quantitatively, the half-filled  $d^5$   $Fe^{3+}$  ion is less oxidizing than either of its 'neighbors'  $Mn^{3+}$  or  $Co^{3+}$ : for  $M = Mn, Fe$  and  $Co$ , the half-reaction emf of  $M^{3+} + e^- = M^{2+}$  equals +1.51 V, +0.771 V, and +1.808 V. Furthermore, we are not surprised that the closed shell Mo(VI) oxides are more stable than either Mo(IV) or Mo(V). The relative instability of most 'simple' species incorporating Mo in its 4+ and 5+ oxidation states is also shared by those of Mo's congeners, Cr and W. That there are three 'famous' types of species containing the 5+ oxidation state for Cr [21], Mo [22] and W [22] -  $CrO_8^{3-}$ , the molybdenum blues and the less studied tungsten bronzes - does not modify our statement. Indeed, the last two also contain a preponderance of hexavalent metal.

The reader will also recall that a goodly number of redox reactions of transition metals involve oxyanions (e.g.  $MoO_4^{2-}$ ), or solid oxides (and their hydrates, the hydroxides, e.g.  $Cr(OH)_3$ ), or 'free' (*i.e.* water-complexed) cations, e.g.  $Mn^{3+}$ . This is not altogether surprising: most half-reactions refer to processes in aqueous media. In such media we do not expect halide complexes to be particularly stable because of loss of solvation of the halide ions, although certainly species such as  $Cr(H_2O)_4Cl_2^+$  have played important roles in our understanding of transition metal chemistry [23]. Very much the same can be said for nitride complexes [24], although in 'protonated form' in solution such as  $Co(NH_3)_6^{3+}$  and as solids such as TiN, NbN and

$Mo_2N$ , many enjoy high thermal stability\*. Indeed, most transition metals form binary nitrides that are hard, refractory solids [7]. In that many of these binary nitrides are also superconductors and are of great interest as wear coatings, there has been extensive effort to make them, particularly in thin film form. They also attract the attention of the theoretical solid state community because their d and f band character provides a good testing ground for band structure calculations.

### Experimental Motivation

The original goal of our investigation was to test a new synthetic pathway to such nitrides, especially MoN. For reasons we will now discuss, from the inception it was clear that low energy pathways were not going to be efficacious. Consider reaction (4)



It is exothermic for numerous transition metals\*\*, but the high nitrogen-nitrogen bond strength in  $N_2$  and high lattice energy of the solid metals generally conspire to preclude direct nitriding at room temperature. The energy of activation is simply too high. (The 'recipe' [25] for making NbN films in this manner is to heat metallic Nb to 1400 °C for 24 h in a full atmosphere or more of  $N_2$ .)

While in principle reaction (5)



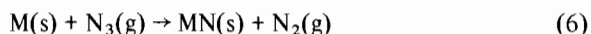
\*It is clear that  $Co(NH_3)_6^{3+}$  enjoys high stability: passing air through aqueous ammoniacal  $Co^{2+}$  solutions produces this ion, e.g., F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 773. To refer to complexes such as  $Co(NH_3)_6^{3+}$  as protonated nitrides might appear misleading or even wrong. However to see that it is not, consider the deprotonation of  $NH_3$ , considered first as a free molecule and then as a ligand, e.g., F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', Wiley, New York, 4th edn., 1980, pp. 123-127. Deprotonation of  $NH_3$  sequentially produces the free ions  $NH_2^-$ ,  $NH^{2-}$ , and  $N^{3-}$ , all of which have known ionic salts. Numerous complexes containing these ligands (or their organic derivatives) are known and generally go under the name of amido, nitrene and nitrido complexes. To the extent species such as  $OsO_3-N^-$  may be viewed as a nitrido complex of Os(VIII), one may also view CoN as a nitrido complex of Co(III), and so recognize it as a deprotonated and mostly deammoniated 'version' of  $Co(NH_3)_6^{3+}$ . Reversing this argument suggests calling  $Co(NH_3)_6^{3+}$  a protonated nitride.

\*\*For 'merely' a documentation of this fact, note that the heat of formation of these species is less than 0, see refs. 2 and 6.

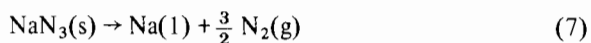
\*This value for Cr was derived by combining the two half-reactions:  $Cr^{3+} + e^- = Cr^{2+}$  at -0.408 V and  $Cr^{3+} + 3e^- = Cr$  at -0.744 V.

may be preferable, there are almost no chemical sources of atomic nitrogen. Excitation and dissociation of diatomic nitrogen in a microwave plasma is possible, but difficult in practice since the 'active nitrogen' formed typically abstracts oxygen from the quartz container walls and, since the binding energy of most metal oxides is substantially higher than the nitrides, substantial oxygen ends up being incorporated. (Indeed in SF<sub>6</sub> enhanced plasma nitriding of silicon, studies [26] with ultrapure N<sub>2</sub> and 10<sup>-5</sup> torr vacuum systems have often resulted in products with a nitrogen to oxygen ratio of 7:3.) Thus the material and especially the surface layer is rarely pure nitride. Moreover, the metal surface may act to facilitate atomic nitrogen recombination to form dinitrogen rather than be itself nitrated thereby requiring either very high power levels (to increase the degree of dissociation) or long reaction times. (For example, Oswald and Vepřek [27] report that it took over 400 h to nitride a 5 μm thick foil of Mo to the δ phase of MoN at 645 °C and 1 torr N<sub>2</sub> pressure.)

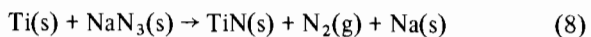
A third possible source of nitrogen is trinitrogen or azido radical, N<sub>3</sub>, cf. reaction (6)



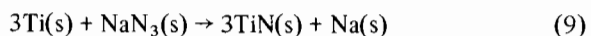
In this regard, [Co(NH<sub>3</sub>)<sub>6</sub>](N<sub>3</sub>)<sub>3</sub> has been reported to explode when dropped with the concomitant formation of CoN [28], yet when thermally decomposed no nitride was reported [29]. Azido radical has been seen in the gas phase but, the seemingly simple photochemical cleavage of the H–N bond in HN<sub>3</sub> [30, 31] or of any R–N bond in gaseous, covalent azides RN<sub>3</sub> [31] is at best a comparatively unclean reaction [30, 31]. It is not obvious how much trinitrogen (and/or atomic nitrogen) is initially formed in the thermal decomposition at 300 °C of alkali metal azides to form the pure metal and nitrogen [32], e.g.



However, in as much as reaction (7) is exothermic for all three species in their standard state, it is plausible that metal nitriding may occur with NaN<sub>3</sub>, e.g.



or even



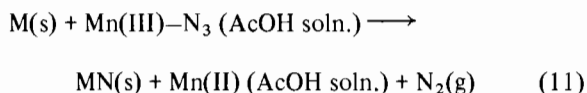
Indeed, this last reaction, (9), has been tried and, once initiated by passing an electric current through the sample, the reaction is exothermic enough to generate a 2500 °C flame and resultant clouds of sodium vapor [33]. While it is not obvious how general this reaction is, it is hardly a convenient

reaction in that the resulting material is essentially a sintered powder with trapped 'pockets' of impurities such as Na. Moreover, it is inobvious how to reduce the reaction temperature in order to allow formation of phases not stable at such high temperatures. (For example, when Mo is substituted for Ti, only metallic Mo, and no MoN<sub>x</sub>, is observed [34]. This is not surprising since when sputter depositing Mo in a full atmosphere of N<sub>2</sub>, no nitrogen is incorporated if the substrate temperature is over 900 °C [35].

Recently, an *in situ* formed manganese(III)–azide complex in glacial acetic acid has been studied by one of us [36] and found to be a clean reagent for the functionalization of organic compounds with –N<sub>3</sub> groups. For example, alkenes are readily converted into vicinal 1,2-diazides, reaction (10)



In that many azides readily lose dinitrogen [37], the following reaction appeared feasible:



In the experiments reported in this paper, the general procedure involved stirring weighed samples of bulk metal (generally powdered) into a refluxing glacial acetic acid solution of manganese (III) acetate\*, sometimes with sodium azide added. While a glove box was not used, efforts were made to maintain a nitrogen atmosphere over the surface of the liquid. The condition of reflux was chosen because it provides a well defined temperature, 116 °C, far enough above room temperature to substantially accelerate the reaction.

While reaction (11) uses a general metal, M, the first metal chosen was Mo for two disparate reasons:

(1) Band theory calculations of superconducting transition temperatures predict a record high value for MoN in the B1 crystal structure [38, 39]. (Much

\*This name suggests incorrectly the formula Mn(CH<sub>3</sub>-COO)<sub>3</sub>. In fact, the highly useful oxidant manganese(III) acetate is the pentahydrate of the oxo-centered triangular complex [Mn<sub>3</sub>O(OAc)<sub>6</sub>(OAc)HOAc]. Some key references to the structural and reaction chemistry of this species include: (a) O. T. Christensen, *Z. Anorg. Allg. Chem.*, 27, 321 (1901). (b) B. N. Figgis and G. Robertson, *Nature (London)*, 205, 694 (1965). (c) L. W. Hessel and C. Romers, *Recl. Trav. Chim. Pays-Bas*, 88, 545 (1969); (d) P. J. Andrusis, M. J. S. Dewar, R. Dietz and R. L. Hunt, *J. Am. Chem. Soc.*, 92, 5473 (1970); (e) D. Arndt, 'Manganese Compounds as Oxidizing Agents in Organic Chemistry' (Engl. transl.), Open Court Publishing, La Salle, 1981, Chap. 1.

effort using more conventional solid state fabrication methods such as reactive sputtering and ion implantation has been expended trying to make this material [35]. Only recently has there been any success [40, 41]).

(2) Molybdenum containing species are among the most important catalysts. We note, for example, that ref. 42 published over 30 years ago devotes almost 200 pages solely to the catalysis chemistry of molybdenum and molybdenum–nitrogen chemistry figures prominently. A more recent biochemical example is the dinitrogen fixing enzyme nitrogenase found in legumes which serves to reduce  $N_2$  at room temperature and atmospheric pressure [43] to  $NH_3$ . A more recent industrially important example of the use of Mo as a catalyst is the process ‘ammoxidation’ [44, 45] in which  $CH_2=CHCH_3$  from hydrocarbon feedstock is converted into the important monomer  $CH_2=CHCN$  by reaction with  $NH_3$  and  $O_2$ .

### Experimental Results and Definitive Conclusions

In the first run, 2.0 mmol of –325 mesh Mo powder was combined with 30 mmol of Mn(III) acetate and 90 mmol of  $NaN_3$  in 100 ml of glacial acetic acid. After 2.5 h the dark brown color of the initial Mn(III) mixture had been converted the colorlessness characteristic of the reduced Mn(II). When the hot reaction mixture was poured into 4 volumes of  $H_2O$  and filtered, no solids were recovered from the initially colorless aqueous solution. Upon standing in air, the filtrate changed to the distinctive molybdenum blue color. The inescapable conclusion is that instead of nitriding the Mo powder to form solid MoN or even the more common  $Mo_2N$ , the metal was dissolving upon oxidation. (Should molecular MoN or any other Mo(III) species be formed in solution, it is likely it would have been oxidized by the Mn(III) to higher valence (Mo(V) and/or Mo(VI)) molybdenum (*vide infra*). The same is presumably truer yet for the still lower valence form of molybdenum found in  $Mo_2N$ .)

Since the azide ion was not irreversibly nitriding the metal, we first sought to define the role that the azide was in fact playing. Replacing the azide ion by chloride sped up the dissolution rate but had no other qualitative effect. That the reaction with both azide and chloride proceeded is preceded by the reaction of alkenes with *in situ* formed manganese(III) chloride complexes to form vicinal 1,2-dichlorides [46]. Moreover, when plain manganese(III) acetate was refluxed with the solid molybdenum in acetic acid, the Mo still dissolved, although more slowly than with added azide or with added chloride.

We conclude that the azide ion is not playing the desired role of nitrogen donor, but is instead acting

to mediate an electron transfer oxidation reaction. Indeed there are numerous other reactions involving soluble oxidants and a common reductant wherein the electron transfer proceeds more slowly through acetate complexes than via the corresponding chloro or azido complexes [47–49]. All three of these reactions – manganese(III) acetate and metallic molybdenum mixed with added azide or chloride or with nothing added – may thus be pictured in a common, simplified sense: electron donation from the metal surface to the Mn(III) complex, with azide, chloride or acetate ligands providing both a spatial anchor for the manganese to the metal and an electrical conduit for the electrons. (See Fig. 1.)

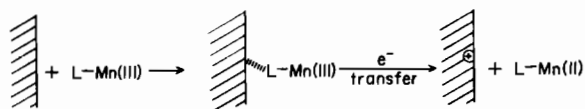


Fig. 1. A schematic drawing of the ligand-mediated electron transfer from the metal surface to the Mn(III) oxidant.

More precisely, an occupied, largely localized, orbital on the ligand bonds to the Mn(III) while another similarly binds the ligand to the surface. Electron density from an occupied surface orbital is then transferred to an unoccupied orbital of the Mn(III) by first forming an electronically delocalized complex, e.g., schematically  $Mo(\text{surface})-O-C(CH_3)-O-Mn$ , where the Mo is in its metallic or 0 oxidation state and Mn in its III oxidation state. It should be noted that the present electron transfer system is heterogeneous while the classic inner-sphere, with ligand bridging, and outer-sphere redox mechanisms were developed for homogeneous solutions. Thus the usual mechanistic probes were not applicable to this metal oxidation. In fact the uncharacterized and changing nature of the metal surfaces make precise representations of this electron transfer process impossible.

By using an amount of oxidant insufficient to oxidize all of the metal sample – the solution turns colorless while some solid metal remained – we determine the proper stoichiometry of the reaction to be 6 Mn to 1 Mo. The analysis corrects the exact experimental value of 4 to 1 (from entries 4–6, Table II) for some mechanical loss of metal in the workup (see entries 7 and 8, Table II), for the effective loss of metal due to prior oxidation of the surface, and for the possibility of reoxidation of Mn(II) to Mn(III) by  $O_2$  dissolved in the acetic acid. We presume the surface effect to be small. The reoxidation effect was explicitly investigated by testing whether Mo could be oxidized by only a catalytic amount of Mn(III) if  $O_2$  was purposely bubbled through the reaction vessel to reoxidize the Mn(II). The answer is yes, although the reaction is not very efficient – under the conditions employed after four days 80%

of the Mo was dissolved, whereas only 17% should have been dissolved if the Mn(III) added was used only once. This result is to be contrasted with the but several hours needed for a comparable completeness of the reaction given adequate initial Mn(III). Moreover, the formation of Mo(VI) is compatible with the visual observation that the reaction solution is colorless in the absence of excess Mn(III) which would itself impart a brown color. Both Mn(II) and molybdate (Mo(VI)) species are colorless, while whatever derivatives of lower valence states of Mo would be formed are expected to be highly colored\*. Since many soluble lower valence Mo complexes may be oxidized even by air (e.g.  $\text{Mo}_2(\text{OAc})_4$  [50] and  $\text{Mo}(\text{H}_2\text{O})_6^{3+}$  [51]), the isolation of these Mo species from an oxidizing mixture would be chemically unreasonable.

The dissolution of molybdenum suggests several other questions. Most importantly, what other metals react? To answer that question a set of reactions identical except for metal were performed wherein the metal was exposed to manganese(III) acetate in refluxing acetic acid. No chloride or azide were added as they did not qualitatively influence the Mo case. Table I reports our results.

Table I suggests that the earlier enunciated inter-row regularities are generally valid: the Group VB element V partially dissolves, while its congeners Nb and Ta are unreactive. In Group VIIIB, Fe and Co dissolve even in the absence of added Mn(III), while their heavier congeners Ru and Rh are untouched; Ni partially dissolves while its heaviest congener Pt is inert. Neither Group IVB element, Ti or Zr, is solubilized while the results for the remaining Group, VIIB, is somewhat ambiguous: Mn dissolves in the absence of added Mn(III), and Re, as found as a 3:1 W/Re alloy, was unaffected. (Their congener Tc was omitted from this study because of its intrinsic radioactivity.)

Moreover, a perusal of Table I shows that of the metals not solubilized by neat glacial acetic acid, Mo and Cu are the sole transition metals to be totally solubilized by added Mn(III). Our findings also invalidate another of our general rules. Proceeding across the rows in the Periodic Table, we can offer no explanation for the reactivity order indicated by Fig. 2

Mo is clearly an exception. The earlier enunciated rule of redox chemistry that 2nd and 3rd row transition metals behave similarly [13] suggests that since Mo dissolves, its heavier congener, W, should also. First row transition metals are generally more reactive

\*This is preceeded by the black color of  $\text{MoOCl}_3$  (Mo(V)), by the red color of  $\text{Mo}_2\text{O}_2^{4+}$  (Mo(IV)), the green of  $\text{Mo}(\text{H}_2\text{O})_3^{3+}$  (Mo(III)), and the yellow of Mo(II) as found in  $\text{Mo}_2(\text{OAc})_4$ , cf. F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 868-74.

TABLE I. Attempted Dissolution of Various Metals by Manganese(III) Acetate in Refluxing Acetic Acid<sup>a</sup>

Metal	Form	Reaction time (h)	Metal remaining (%)
Ti	powder	20	98
V	pieces	18	45
Cr	pieces	6	96
Mn <sup>b</sup>	pieces	—	0
Fe <sup>b</sup>	powder	—	0
Co <sup>b</sup>	powder	—	0
Ni <sup>c</sup>	shot	24	38
Cu <sup>c</sup>	20-30 mesh	15	0
Zr	foil	11	99
Nb	powder	5	100
Mo <sup>c</sup>	powder	5	0
Mo	foil	15	48
Ru	pieces	21	100
Rh	wire	11	100
In <sup>c</sup>	wire	21	0
Sn <sup>d</sup>	powder	18	0
Ta	foil	11	100
W	powder	24	95
W	rod	21	100
Pt	foil	11	99
W/Re(3:1)	wire	21	99

<sup>a</sup>The metal was heated to reflux in acetic acid with 15 equivalents of Mn(III) acetate (0.3 M) for the indicated time. The mixture was poured into ice-water, any excess Mn(III) reduced with sodium bisulfite, and the remaining metal filtered. The metal was successively washed with water and acetone, dried, and weighed. <sup>b</sup>Metal dissolved in glacial acetic acid at room temperature. <sup>c</sup>Metal was unaffected by refluxing acetic acid, >95% recovery. <sup>d</sup>Tin was recovered in 85% after refluxing in acetic acid for 15 h. Thus, it was partially dissolved by the hot acid alone.

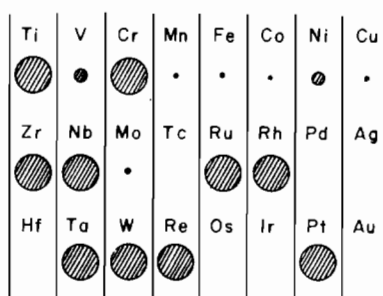


Fig. 2. A pictorial representation of the reactivity of the metals studied to manganese(III) acetate. (Radii are proportional to amount left.)

than those below [13]. For example, compare the rather reactive Cu with the noble Ag and Au. This suggests that since Mo dissolves, Cr should also. In fact, neither Cr nor W dissolve.

How are these facts to be understood? First we tried to delineate the circumstances necessary to get dissolution by varying the oxidation conditions and

TABLE II. Attempted Dissolution of Metals by Various Manganese(III) Oxidant Systems<sup>a</sup>

Entry	Metal	Equivalent Mn(III)/metal	Additive	Reaction time (h)	Metal remaining (%)
1	Mo	7.5	None	3	trace
2	Mo	7.5	NaN <sub>3</sub>	2	0
3	Mo	7.5	CaCl <sub>2</sub>	2	0
4	Mo	1.0	None	0.5	70 <sup>b</sup>
5	Mo	1.0	NaN <sub>3</sub>	0.25	79
6	Mo	1.0	CaCl <sub>2</sub>	0.18	76
7	Mo	0.0	None	6	92
8	Mo	0.0	NaN <sub>3</sub>	5	92
9	Nb	15	None	5	100
10	Nb	10	NaN <sub>3</sub>	4	91
11	Nb	0	NaN <sub>3</sub>	5	96
12	Ti	15	None	20	92
13	Ti	15	NaN <sub>3</sub>	4	95
14	Ti	0	NaN <sub>3</sub>	5	95

<sup>a</sup>Molybdenum and the additive (15 equivalents) were heated to reflux in acetic acid with the amount of manganese(III) acetate listed (0.3 M). The reaction time was the time required for complete reduction of Mn(III) → Mn(II) which was indicated by the color change of brown to colorless. The mixture was poured into water, filtered, dried and remaining metal weighed. <sup>b</sup>No difference was noted (recovery 74%, 30 min) when this reaction was conducted in the presence of 200 mol equivalent of NaOAc.

the oxidant. The first series of tests and their quantitative outcome are tabulated in Table II. Five types of conditions in otherwise identical refluxing acetic acid were tested: (1) Mn(III)/no additive, (2) Mn(III)/N<sub>3</sub><sup>-</sup>, (3) Mn(III)/Cl<sup>-</sup>, (4) no Mn(III) nor additive (*i.e.* neat acetic acid), and (5) N<sub>3</sub><sup>-</sup> in the absence of Mn(III). (Conditions 1–3 have been mentioned already in the mechanism discussion.) As Table II shows, molybdenum was unaffected by simply refluxing acetic acid (entry 7) or by sodium azide in refluxing acetic acid (entry 8). (A small loss of metal resulted from incomplete physical recovery of the powdered metal sample. To check this presumption of where some metal had gone, the reaction filtrate was treated with lead acetate. It produced no insoluble lead molybdate as would have been the case if any of the molybdenum metal had been dissolved and oxidized to the VI state [52]. Admittedly, we did not explicitly check for oxidation to any other state as we viewed it unlikely these would have formed a colorless solution.) Entries 1–3 indicate that complete dissolution of Mo is possible under the three conditions which include the Mn(III) oxidant, while entries 4–6 illustrate the decreasing reactivity of the three systems Mn(III) + Cl<sup>-</sup>, Mn(III) + N<sub>3</sub><sup>-</sup>, and Mn(III). The addition of extra acetate ion to the conditions of entry 4 resulted in no substantial change. Neither niobium nor titanium were dissolved to any appreciable extent under any of these conditions (entries 9–14). (Our choice of metals to study in this regard was governed by considerations of technological interest.)

We next recognized that manganese(III) acetate is not the only oxo-centered acetate oxidant, and so

tested the weaker oxidant containing iron(III) and the stronger oxidant containing cobalt(III)\*. While the emfs of bare cations in aqueous media do not necessarily relate to the oxidizing power of oxo-centered complexes in glacial acetic acid, they do in fact for the three metal(III) acetates: the emfs for the aqueous half reactions M<sup>3+</sup> + e<sup>-</sup> = M<sup>2+</sup> are Fe, 0.771 V; Mn, 1.51 V; and Co, +1.808 V. Table III shows that even with Fe, the weakest oxidant of the three, Mo is still solubilized, while even with the strongest, neither Nb nor W is.

Thus the oxidizing power of the oxidant does not appear to be the dominant factor in its ability to dissolve metals. A relative insensitivity to the ligands surrounding the oxidant has already been shown. Thus apparently only the nature of the solvent or some subtle combination of factors, remains to explain the selectivity which was observed. For example, solvents differ in their ability to donate H<sup>+</sup>. If such ions chemisorb to the metal surface, it is possible that the positive charge remains localized long enough to increase the probability of negatively charged reactive sites on the oxidizing agent (*e.g.* acetate, azide, chloride) attaching to the surface.

\*As with the manganese(III) compound, the description of these compounds as ferric and cobaltic acetate are simplistic. For Fe, the oxidant added to the glacial acetic acid is really [Fe<sub>3</sub>O(OAc)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>(HOAc)]NO<sub>3</sub> (B. N. Figgis and G. Robertson, *Nature (London)*, 205, 694 (1965)) and for Co, likewise [Co<sub>3</sub>O(OAc)<sub>6</sub>(HOAc)<sub>3</sub>] (J. J. Ziolkowski, F. Pruchniky and T. Szymanska-Buzar, *Inorg. Chim. Acta*, 57, 473 (1973).)

TABLE III. Effect of Other Oxo-Centered Acetate Oxidants on Metal Dissolution<sup>a</sup>

Entry	Metal	Oxidant <sup>b</sup>	Equivalent oxidant/metal	Reaction time (h)	Metal remaining (%)
1	Mo	Fe	30	7	0
2	Mo	Mn	15	5	0
3	Mo	Co	30	7	0
4	Nb	Fe	10	18	90
5	Nb	Mn	15	5	100
6	Nb	Co	25	6	94
7	In	Fe	10	24	0
8	In	Mn	15	21	0
9	W	Mn	15	24	95
10	W	Co	10	6	98

<sup>a</sup>Reactions were run as described in Table II. <sup>b</sup>Oxidants were Fe:  $[\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3(\text{HOAc})]\text{NO}_3$ , Mn:  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})(\text{H}_2\text{O})_5]$ , Co:  $[\text{Co}_3\text{O}(\text{OAc})_6(\text{HOAc})_3]$ .

The diligent reader may have noticed that the non-transition metal indium was included in both Tables I and III. It was included in the study in the hope of better understanding the role of gaseous acetic acid in greatly enhancing the perfection of the thermally produced oxide of indium [53]. Unfortunately very little is known about the gas phase chemistry of indium acetate. Thus we must resort to what we do know, namely what happens in the liquid phase in aqueous solution, and presume the presence of water has little effect. We note the stability constants,  $K$ , of 1:1, 1:2 and 1:3  $\text{In}^{3+}$  complexes with aqueous acetate ion are large [54, 55]. (By definition,  $K_{1:1} = [\text{InOAc}^{2+}]/[\text{In}^{3+}][\text{OAc}^-]$ , etc., and so a large stability constant indicates strong binding.) These high stabilities should encourage the loss of metal atoms from the surface since, once dissolved, the atom is unlikely to be redeposited on the surface. Unfortunately, comparably stable acetate complexes with  $\text{Cr}^{3+}$  are also known [54] and while In dissolves, Cr does not. Similarly, it is well established that Mo and Cu form quadruply bridged binuclear acetate complexes,  $\text{M}_2(\text{OAc})_4$ . Such complex forma-

tion would also encourage metal solubilization, and, in the Mo case, further oxidation. (See Fig. 3). However, Cr(II) [56a],  $\text{Ru}_{2.5}$  [56b] and Re(III) [56c] form analogous complexes but, unlike Mo and Cu, Cr, Ru and Re are not dissolved. The unexpected selec-

TABLE IV. Attempted Dissolution of Metal Nitrides by Manganese(III) acetate in Refluxing Acetic Acid<sup>a</sup>

Entry	Metal nitride	Equivalent Mn(III)/nitride	Metal nitride remaining (%)
1	$\text{MoN}_{0.6}$ <sup>b</sup>	0.66	83
2	$\text{MoN}_{0.6}$ <sup>c</sup>	0.66	85
3	$\text{MoN}_{0.6}$	1	71
4	$\text{MoN}_{0.6}$	1.3	70
5	$\text{MoN}_{0.6}$	2	60
6	$\text{MoN}_{0.6}$	3.3	34
7	$\text{MoN}_{0.6}$	4.6	12
8	$\text{MoN}_{0.6}$	8.7	0
9	$\text{MoN}_{0.6}$ <sup>d</sup>	2	60
10	$\text{MoN}_{0.6}$ <sup>e</sup>	0.2	91
11	$\text{MoN}_{0.6}$ <sup>e</sup>	0	97
12	$\text{Cr}_2\text{N}$	5	91
13	NbN	5	87

<sup>a</sup>The metal nitride and manganese(III) acetate (0.3 M) were heated to reflux in acetic acid. When the brown color of Mn(III) had disappeared, the mixture was cooled and poured onto water. Any remaining metal nitride was filtered, washed, dried, and weighed. <sup>b</sup>The molybdenum nitride used was a mixture of  $\text{MoN}$  and  $\text{Mo}_2\text{N}$  (1:2). <sup>c</sup>The molybdenum nitride used in this experiment was that which had been isolated after partial dissolution of entry 1. <sup>d</sup> $\text{Na}_2\text{MoO}_4$  (1 mol equivalent) was added to the reaction mixture before heating. <sup>e</sup> $\text{NaN}_3$  (10 mol equivalent) was added to the reaction mixture before heating.

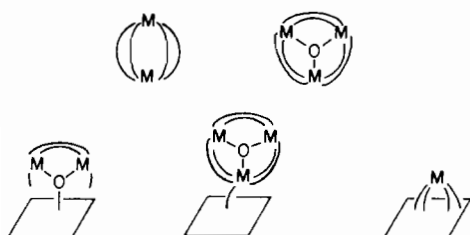


Fig. 3. Schematic drawings of acetate bridged complexes. (The top two represent known discrete species while the bottom three are conjectured species involving the metal surface.)



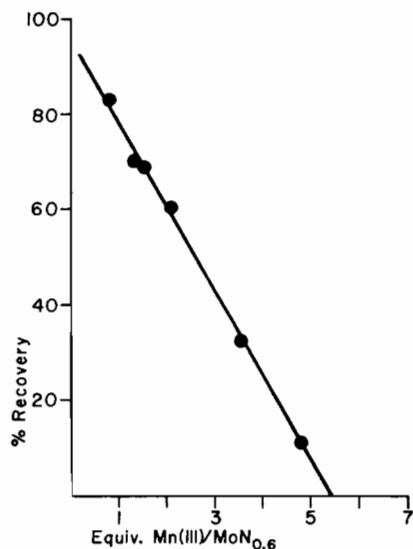


Fig. 4. A plot illustrating the % MoN<sub>0.6</sub> recovery vs. time of treatment with Mn(III) acetate.

tivity in metal dissolution observed is thus not simply related to the stability of the various metal acetate species which would be produced at least as an intermediate.

Having not succeeded in making bulk nitrides by any of our reactions, we then attempted to determine if part of the problem is that even premade nitrides dissolve in Mn(III). Entries 1–8 of Table IV are for molybdenum nitride (2:1 Mo<sub>2</sub>N:MoN = MoN<sub>0.6</sub>) and are additionally plotted in Fig. 4 wherein it is seen that MoN<sub>0.6</sub> is oxidized faster than pure Mo metal.

Comparison of entries 1 and 2 shows that the molybdenum nitride remaining after complete reduction of a substoichiometric amount of manganese(III) acetate can be resubmitted to identical conditions with the same result a second time. Moreover, that adding azide ion has no effect on the yield strongly suggests that neither nitride is being synthesized while the other is destroyed. Thus it appears unlikely that a particular form of nitride, e.g. MoN or Mo<sub>2</sub>N, is being selectively dissolved. This conclusion was further substantiated by comparing the X-ray diffraction patterns of the starting material and the recovered material – the patterns were essentially indistinguishable.

The stoichiometry of this dissolution process is approximately 5Mn(III)/MoN<sub>0.6</sub>. This corresponds to oxidation of the formal Mo(1.8) to Mo(VI) and either a partial oxidation of the nitrogen to some other form, or a larger than expected correction factor. The former interpretation is based on the assignment of 3– as the oxidation state of nitrogen in the nitride and so corresponds to that found in ammonia. That more than 6 – 1.8 = 4.2 equivalents of Mn(III) are needed per mol of MoN<sub>0.6</sub> is consis-

tent with the fact that Mn(III) was shown to slowly oxidize NH<sub>4</sub>OAc, although some ammonia can still be detected when the molybdenum nitride oxidative dissolutions were made basic. (This was shown in a control experiment wherein the other products were not identified.)

Two other nitrides, Cr<sub>2</sub>N and NbN, were briefly studied. It would appear that these, like MoN<sub>0.6</sub>, are somewhat more reactive than the parent metals. While this quantitatively minor change may seem perhaps qualitatively surprising, it is consistent with the hypothesis that the effect of the nitrogen bonding is to decrease the activation energy  $\Delta G^\ddagger$  for the formation of bonds to oxygen. A parallel argument has been advanced for the acceleration of the rate of oxide formation on silicon by traces of fluorine [57]. In that case, ½ at.% F is incorporated into the moving SiO<sub>2</sub>/Si interface. It is unfortunately not obvious how to quantify these arguments.

Another probe of the crucial features of the oxidizing agent was to study Mn(III) in a form without the central oxygen atom and the bridging acetates. While manganese(III) is destroyed readily in water under neutral or basic conditions, it is stable [58] at low pH. Table V compares several metals in

TABLE V. Attempted Dissolution of Metals by a Manganese(III) Acetate in Refluxing Acetic Acid<sup>a</sup>

Metal	Equivalent Mn(III)/metal	Form	Reaction time (h)	Metal remaining (%)
Mo <sup>b</sup>	1	powder	0.03	72
Nb <sup>b</sup>	1	powder	25	95
Ti <sup>c</sup>	1	powder	3.5	82
W <sup>b</sup>	1	powder	0.4	83

<sup>a</sup>The reactions were performed as described in Table I except the solvent was concentrated hydrochloric acid and the reaction temperature was 23 °C. <sup>b</sup>The metal is unaffected by hydrochloric acid at 23 °C. <sup>c</sup>Ti is partially dissolved (53% recovery) by hydrochloric acid within 3.5 h.

a different solvent system, concentrated aqueous hydrochloric acid. Mo is still dissolved as before, although at a much faster rate. In contrast to the acetic acid case, W is now dissolved to the extent expected assuming that the oxidation proceeds to W(VI). (Cr, the congener of Mo and W, was not studied because concentrated HCl alone will dissolve this metal.) Nb however still appears inert.

Ti was especially interesting in that more metal dissolved in neat HCl than in the Mn(III)/HCl solution. In the former case, the color of the Ti/HCl reaction solution was purple indicating the formation of a Ti(III) species [59] such as TiCl<sub>3</sub>. As the solution was exposed to air, it rapidly decolorized,

presumably through the conversion of trivalent  $\text{TiCl}_3$  to colorless derivatives of  $\text{Ti(IV)}$ . By contrast, when the reaction media contained  $\text{Mn(III)}$ , it never became purple prior to becoming colorless, indicating the reduction of  $\text{Mn(III)}$  to  $\text{Mn(II)}$  and corresponding oxidation of  $\text{Ti(0)}$  to  $\text{Ti(IV)}$  in the form of  $\text{TiCl}_4$  without stopping. Since less Ti was dissolved in the presence of  $\text{Mn(III)}$  than in its absence, the formation of a passivating surface layer which inhibits further oxidation of some oxidized Ti species as a result of the action of the  $\text{Mn(III)}$  is strongly suggested.

### The Surface Passivation Hypothesis

Indeed, the formation of such layers when metals are treated with an oxidizing acid, e.g. Cr/concentrated or dilute  $\text{HNO}_3$ , Mo/ $\text{HNO}_3$ , Fe/concentrated  $\text{HNO}_3$ , to provide corrosion resistance is well documented [60\*, 61]. To test the effect of such passivating layers on our reactions, we treated Mo foil with concentrated  $\text{HNO}_3$  for 15 h, washed and dried it, and then treated the foil exactly as described in Table I. This experiment returned 35% Mo, whereas without the attempted passivation 48% of the Mo would have been recovered under these conditions. It is obvious that the prepassivation did nothing to impede the  $\text{Mn(III)}$  dissolution process. Indeed one is encouraged to speculate that the layer the  $\text{HNO}_3$  produces on the metal's surface must be quite thick and, more importantly, consist of a compound which either is or is easily transformed into an intermediate quite late in the  $\text{Mn(III)}$  dissolution chain of reactions.

To further investigate the surface passivation hypothesis, dissolution of niobium in hydrofluoric acid was attempted. Niobium was slowly attacked by HF at room temperature, and gave 62% recovery after 5 h and 0% recovery after 15 h. When  $\text{Mn(III)}$  acetate was added to an identical mixture the manganese(III) was converted to its complex ion [62], the dark pink  $\text{MnF}_5^{2-}$  and only 41% of the Nb was recovered after 5 h. If one assumes that the effect of the  $\text{Mn(III)}$  species is to form a surface oxide on the metal, this rate enhancement is consistent with the observation that HF etches  $\text{NbO}_x$  more rapidly than it does  $\text{Nb}^{**}$  [63]. (The conventional Nb etches use a dilute HF/ $\text{HNO}_3$  mixture, the rationale being that the  $\text{HNO}_3$ , like many other acids, adds oxygen to the surface and the HF 'eats' the oxide. HF is the only known agent to dissolve  $\text{NbO}_x$  and works better in dilute than concentrated form [64]. It is interesting to note that depending on the concentra-

tion of  $\text{F}^-$  and HF, varying amounts of  $\text{NbOF}_5^{2-}$ ,  $\text{NbF}_6^-$  and  $\text{NbF}_7^{2-}$  are formed [65].

An obvious question in all of this is what role surface passivation is playing. Not only are passivating layers possible as a result of reactions in the solution, but it is clear that our sample materials started out with a native oxide coating since they had all been exposed to air for substantial periods of time. Of the seventeen metals we tested, four general classes may be gleaned. The first class is composed of those metals that directly and facily dissolve in glacial acetic acid: Mn, Fe and Co. The second class is composed of those metals that quantitatively dissolve in the solution of  $\text{Mn(III)}$  in refluxing acetic acid. These are Cu, Mo, and the non-transition metals In and Sn. The third class is composed of those that partially dissolve: Ni and V. The final class is composed of those that are essentially unreactive. This class is by far the largest and consists of Ti, Nb, Ta, Cr, W, Re (as W alloy), Rh, Ru and Pt. What explains this division?

Electrochemists have provided guidance to people interested in corrosion by carefully exploring the systematics of a relatively small number of species and conditions. Thus there exists an extensive, organized review that compares the dissolution of metals in aqueous media as a function of pH and applied potential [66]. (Varying the pH changes the  $\text{H}^+$  and HX concentrations which in turn affects the oxidizing power of the solution through the Nernst equation and the solubilizing power of the solvent by shifting the metal ion, metal oxide/hydroxide equilibrium). Unfortunately we know of no similar study for our solvent system. Any comparison of water and acetic acid is expected to be complicated by different kinetic and thermodynamic factors such as the overvoltages, by differences in the stabilities of the final oxides, hydroxides and acetates for each metal, and by differences in the concentration dependent variations of the oxidizing and solubilizing strengths of  $\text{H}_3\text{O}^+$  and undissociated HOAc. Admitting these problems we nonetheless proceeded to look at how our results compare to those expected in aqueous media. Accepting Pourbaix's definition [67], 'a metal is thermodynamically noble or non-noble according as its immunity domain (i.e. its thermodynamic stability domain) shows or does not show a section [a region of overlap] with the thermodynamic stability domain of water... the nobility of a metal is greater, the larger the surface common both to its immunity domain and to the stability domain of the water'. Using a parallel definition employing both 'immunity and passivation domains', Pourbaix defined 'practical nobility'. For both nobility definitions, the higher the number, the less noble and more reactive. The dividing line between noble and non-noble was placed between 23 and 24. Table VI shows that neither the literature

\*Cr, p. 721; Mo, p. 846; Fe, pp. 751-2, respectively, in ref. 60.

\*\*p. 558 (Nb) and p. 592 (Nb oxides) in ref. 63.

TABLE VI. 'Thermodynamic' and 'Practical' Nobility of the Metals in the Current Study (as Defined by Pourbaix)

Metal	Thermodynamic nobility	Practical nobility
Mn	37	43
Fe	25	28
Co	22	30
Cu	13	16
Mo	27	38
In	30	20
Sn	26	15
Ni	21	29
V	36	40
Ti	41	7
Zr	38	13
Nb	33	2
Ta	34	3
Cr	35	21
W	28	27
Re	20	35
Rh	4	1
Ru	5	9
Pt	3	6

thermodynamic nor practical nobility parallels the observed reactivity of the various metals we have studied.

An obvious complication if the explanation lies in surface passivation is that even in the extensively studied and better understood case of metal passivation in aqueous acids, the effect is often dependent on the exact conditions [60, 61]. For example, recall that pretreating the Mo according to the conventional corrosion protection scheme with  $\text{HNO}_3$  accelerates rather than impedes its dissolution by Mn(III) acetate. This dependence can sometimes be utilized to technological advantage in that it can make selective metal dissolution possible and combinations of acids, e.g. aqua regia (3:1 HCl:  $\text{HNO}_3$ ) can dissolve materials which individually they cannot effect, e.g. Au. Since passivation involves the inability of the solvent to dissolve or otherwise remove a chemically altered, non-porous surface layer, the details of the solvent (e.g. its acidity, molecular size, degree of dissociation, dielectric constant, etc.) are expected to play a vital role in the dissolution process. In the current paper we have demonstrated variation in the metals dissolved by the addition of Mn(III) to concentrated HCl ( $\text{MnCl}_5^{2-}$  as oxidant), HF (i.e.  $\text{MnF}_5^{2-}$  as oxidant), and acetic acid (i.e.  $\text{Mn}_3\text{O}(\text{OAc})_6\text{OAc}$  as oxidant) systems [69]. Moreover, the rate, although not the effect, of the reaction has been shown to be dependent of whether Mn(III), Fe(III) or Co(III) are present as an oxidant.

## Theoretical Observations and Speculations

We admit we were unable to determine the nature of the rate determining step in the dissolution process. Indeed we have not established an unambiguous sequence of steps for the reaction. However, if we are allowed to speculate about the type of reaction steps that are involved a beginning can be made on the question of why Mo but no Cr and W dissolve. Because Mo changes from Mo(0) in the metal to Mo(VI) in the final state, some electron transfer reactions must be occurring. (See our earlier discussion.) Unfortunately, our image of how the electron transfer occurs does not help distinguish among these three congeners as the surface states have not yet been extensively studied. Their bulk band structures [68] are very similar with the d bands, through which the Fermi level passes, increasing in width in the order Cr, Mo, and W. In all cases these bands overlap with the s band at at least some points in the Brillouin zone. The gap between the s and d orbitals for isolated atoms shows no pattern. Defining this gap as the energy required to convert an atom with the  $nd^5(n+1)s^1$  ( $^7S$ ) electron configuration into one with the  $nd^4(n+1)s^2$  ( $^5D$ ) configuration, the numerical values are Cr,  $n=3$ ,  $E=7751\text{ cm}^{-1}=0.96\text{ eV}$ ; Mo,  $n=4$ ,  $E=10966\text{ cm}^{-1}=1.36\text{ eV}$ ; and W,  $n=5$ ,  $E=-2951\text{ cm}^{-1}=-0.37\text{ eV}$  [69]. While Mo is thus the extreme case in this regard, we can think of no reason why a larger gap should correlate with larger reactivity. A more relevant quantity is the ionization potential, the cost of successively removing electrons. These numbers are shown for Cr, Mo, and Nb in Table VII

TABLE VII. Successive Ionization Potentials (eV) of Cr, Mo and Nb

	0 → +1	+1 → +2	+2 → +3	+3 → +4	+4 → +5	+5 → +6
Cr	6.8	16.5	31.0	49.1	69.3	90.6
Mo	7.1	16.2	27.2	46.4	61.2	68
Nb	6.9	14.2	25.0	38.3	50.6	

[70]. (No such comparable data is available for W.) A comparison of Mo and Cr might initially suggest that the greater ease of reaching the 6+ state for Mo may provide an explanation of why Mo dissolves but Cr does not. However, the ionization potentials of Nb are uniformly lower than the corresponding ones for Mo and yet Nb does not react with manganese(III) acetate. It appears that there is no correlation between atomic or crystal electronic structure and the tendency to dissolve in manganese(III) acetate.

However, in addition to electron transfer reactions, it is quite possible that oxygen is binding to the metal prior to its dissolution. Since Cr is most

stable in its 3+ oxidation state, perhaps the bonds of the surface atoms to the bulk are still strong when it reaches this state by bonding to one oxygen and one acetate group, and the surface is passivated. In contrast the Mo is most stable in its 6+ oxidation state and so the reactions of a surface atom are unlikely to stop at the relatively unstable 3+ state. By the time the oxidation state reaches 6+, the surface atom is no longer contributing any electrons to metal-metal bonding and so is presumably quite free to move away from the bulk surface, i.e. to dissolve. W is even less reactive than Mo and presumably the bond to the Mn(III) acetate is never strong enough to allow the necessary electron and atom transfer reactions to occur.

### A Practical Application

We close this article with a brief discussion of the oxidation of 316 stainless steel, an important ferrous alloy rich in Mo, Ni and Cr. (More explicitly, it is a solid solution of 2% Mo, 18% Cr and 10% Ni in austenite Fe.) While Mo and Ni both dissolve in Mn(III)-acetate, and Fe in neat, glacial acetic acid, 316 stainless steel is, by contrast, unreactive in both environments. Thus the alloy is more resistant to the acetic acid/oxidant solution than its constituents, and the Mn(III) oxidant had no effect in this environment. On the other hand, when 316 stainless steel was treated with concentrated HCl/Mn(III) for 0.75 h, 44% was recovered, while a control experiment without oxidant in concentrated HCl returned 71% of the metal.

### Summary and Conclusions

Thus we have found two cases wherein the addition of Mn(III) accelerated the rate of dissolution of a metal or metal alloy (Nb in HF and 316 stainless steel in hydrochloric acid), one case where it slowed it down (Ti in HCl), and one case where it turned on the dissolution (Mo in acetic acid). While there is some consolation in the fact that it is often the case that the properties of alloys do not follow simply from those of the component metals, we are nonetheless frustrated that the systematics of what will and will not dissolve in a given media are not more apparent.

Indeed the conclusion of this article is that reactive dissolution is far from a well understood process. Moreover, whereas the general rules of redox chemistry are followed by most transition metals in our manganese(III) acetate environment, they are not for molybdenum. None of our studies have shown precisely why, although many possibilities were investigated. That the dissolution occurs after

substantial oxidation of the surface atoms is suggested by the reaction rate data. A final oxidation state of 6+ for molybdenum, presumably in the form of tightly bound, covalent molybdenyl ('MoO<sup>4+</sup>' and/or 'MoO<sub>2</sub><sup>2+</sup>')-acetate complexes (cf. the related fluorides, chlorides, and chelates [71]) or molybdate MoO<sub>4</sub><sup>2-</sup> is well established. (An attempt to confirm the Mo(VI) species by IR absorption spectroscopy was frustrated by the superimposed strong acetate peaks.) Despite the near total lack of correlations to the data on dissolution in aqueous media, the most likely explanation remains some form of surface passivation. It is clear that many interesting, if complex, problems remain.

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### References

- (a) C. L. Rollinson, in J. C. Bailar, Jr., H. J. Emeleus, R. Nyholm and A. F. Trotman-Dickenson (eds.), 'Comprehensive Inorganic Chemistry', Vol. 3, Pergamon, Oxford, 1973, pp. 731-736; (b) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 847; (c) pp. 861-862.
- D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data*, 11, Suppl. 2 (1982).
- T. Foosnaes, M. J. Pellin and D. M. Gruen, *J. Chem. Phys.*, 78, 2889 (1983).
- K. P. Huber and G. Herzberg, 'Molecular Spectra and Molecular Structure Constants for Diatomic Molecules', Van Nostrand Reinhold, New York, 1979.
- C. L. Rollinson, in J. C. Bailar, Jr., H. J. Emeleus, R. Nyholm and A. F. Trotman-Dickenson (eds.), 'Comprehensive Inorganic Chemistry', Vol. 3, Pergamon, Oxford, 1973, p. 717.
- P. C. P. Bouten and A. R. Miedema, *J. Less Common Met.*, 65, 217 (1979).
- P. Ettmayer and A. Vendl, in R. K. Viswanadham, D. J. Rowcliffe and J. Gurland (eds.), 'The Science of Hard Materials', Plenum, New York, 1981.
- (a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 822-823; (b) J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper and Row, New York, 1983, p. 572.

- 9 (a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 847–861; (b) J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper and Row, New York, 1983, pp. 695–701.
- 10 (a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 733; (b) J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper and Row, New York, 1983, p. 695.
- 11 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 727–731.
- 12 C. K. Jørgensen, 'Inorganic Complexes', Academic Press, New York, 1963.
- 13 (a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 822–823; (b) J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper and Row, New York, 1983, p. 567.
- 14 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 765–766.
- 15 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 766.
- 16 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 754–755.
- 17 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 772.
- 18 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 768.
- 19 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 796–797.
- 20 (a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 625, 681; (b) J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper and Row, New York, 1983, pp. 30–32.
- 21 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 745–746.
- 22 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 848–50.
- 23 C. K. Jørgensen, 'Inorganic Complexes', Academic Press, New York, 1963, Chap. 3.
- 24 (a) C. K. Jørgensen, 'Inorganic Complexes', Academic Press, New York, 1963, chap. 4; (b) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 123–127.
- 25 J. P. Remeika, M. Gurvitch and W. P. Lowe, *Bull. Am. Phys. Soc.*, **29**, 483 (1984).
- 26 R. V. Giridhar and K. Rose, *Appl. Phys. Lett.*, **45**, 578 (1984).
- 27 H. R. Oswald and S. Vepřek, 'Thermogravimetric Studies in Nonisothermal Low Pressure Plasmas', in *Proc. 5th Int. Conf. Thermal Analysis*, Kyoto, Japan, 1977.
- 28 T. B. Joyner, West. States Sect., *Combust. Inst.* (1967); *Chem. Abstr.*, **72**, 113383g (1970).
- 29 T. B. Joyner and F. H. Verhoek, *J. Am. Chem. Soc.*, **83**, 1069 (1961).
- 30 A. Treinin, in S. Patai (ed.), 'The Chemistry of the Azide Group', Interscience, New York, 1971.
- 31 R. S. Berry, in W. Lwowski (ed.), 'Nitrenes', Interscience, New York, 1970.
- 32 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 421.
- 33 J. B. Holt, *Ind. Res. Dev.*, 88–91, (April 1983).
- 34 L. Francavilla, February, 1984, personal communication.
- 35 W. W. Fuller, S. A. Wolf, D. U. Gubser, E. F. Skelton and T. L. Francavilla, *J. Vac. Sci. Technol.*, **A1**, 517 (1983).
- 36 W. E. Fristad, T. A. Brandvold, J. R. Peterson and S. R. Thompson, *J. Org. Chem.*, **50**, 3647 (1985).
- 37 (a) S. Patai (ed.), 'The Chemistry of the Azide Group', Interscience, New York, 1971; (b) W. Lwowski (ed.), 'Nitrenes', Interscience, New York, 1970.
- 38 W. E. Pickett, B. M. Klein and D. A. Papaconstantopoulos, *Physica B*, **107**, 667 (1981).
- 39 D. A. Papaconstantopoulos, W. E. Pickett, B. M. Klein and L. L. Boyer, *Nature (London)*, **308**, 494 (1984).
- 40 E. J. Saur, H. D. Schlechinger and L. Rinderer, *IEEE Trans., Magn. Mag-17*, 1029 (1984).
- 41 G. Linker, R. Smithey and O. Meyer, *J. Phys. F.*, **14**, L115 (1984).
- 42 D. H. Killeffer and A. Linz, 'Molybdenum Compounds: Their Chemistry and Technology', Interscience, New York, 1952.
- 43 (a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 1341–1343; (b) J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper and Row, New York, 1983, pp. 892–895.
- 44 G. Somorjai 'Chemistry in Two Dimensions: Surfaces', Cornell University Press, Ithaca, 1981, p. 403.
- 45 D. M.-T. Chan, W. C. Fultz, W. A. Nugent, D. C. Roe and T. H. Tulip, *J. Am. Chem. Soc.*, **107**, 251 (1985).
- 46 K. D. Donnelly, W. E. Fristad, B. J. Gellerman, J. R. Peterson and B. J. Selle, *Tetrahedron Lett.*, **25**, 607 (1984).
- 47 H. Taube, 'Electron Transfer Reactions of Complexed Ions in Solution', Academic Press, New York, 1970, p. 51.
- 48 J. H. Espenson and H. B. Gjerde, *Inorg. Chem.*, **19**, 3549 (1980).
- 49 S. W. Barr, K. L. Guyer, T. T.-T. Li, H. Y. Liu and M. J. Weaver, *J. Electrochem. Soc.*, **131**, 1626 (1984).
- 50 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 874.
- 51 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 867.
- 52 T. M. Chatard, *Am. J. Sci.*, **1**, 416 (1871).
- 53 A. F. Hebard, J. P. Arthur and D. L. Allara, *J. Appl. Phys.*, **49**, 6039 (1978).
- 54 R. M. Smith and A. E. Martell (eds.), 'Critical Stability Constants', Vol. 1, Plenum, New York, 1974.
- 55 J. Catterick and P. Thornton, *Adv. Inorg. Radiochem.*, **20**, 291 (1977).
- 56 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York 1980, (a) pp. 725–727; (b) p. 931; (c) p. 893.
- 57 R. P. H. Chang, C. C. Chang and S. Darack, *Appl. Phys. Lett.*, **36**, 999 (1980).
- 58 D. Arndt, 'Manganese Compounds as Oxidizing Agents in Organic Chemistry' (Engl. transl.), Open Court Publishing, La Salle, 1981.

- 59 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 701–702.
- 60 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980.
- 61 A. Schwabe, *Angew. Chem., Int. Ed. Engl.*, 5, 185 (1966).
- 62 (a) D. Arndt, 'Manganese Compounds as Oxidizing Agents in Organic Chemistry', (Engl. transl.), Open Court Publishing, La Salle, 1981, pp. 1–25; (b) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 741–743.
- 63 D. Brown, in J. C. Bailar, Jr., H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson (eds.), 'Comprehensive Inorganic Chemistry', Vol. 3, Pergamon, Oxford, 1973.
- 64 R. Laibowitz, November, 1984, personal communication.
- 65 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, p. 834.
- 66 M. Pourbaix (ed.), 'Atlas of Electrochemical Equilibria in Aqueous Solutions', Pergamon, Oxford, 1965, Chap 2.
- 67 M. Pourbaix (ed.), 'Atlas of Electrochemical Equilibria in Aqueous Solutions', Pergamon, Oxford, 1965, p. 81.
- 68 A. Papaconstantopoulos, January, 1985, personal communication.
- 69 C. E. Moore, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, 35 (1971).
- 70 C. E. Moore, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, 34 (1970).
- 71 (a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text', 4th edn., Wiley, New York, 1980, pp. 866–867; (b) C. L. Rollinson, in J. C. Bailar, Jr., H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson (eds.), 'Comprehensive Inorganic Chemistry', Vol. 3, Pergamon, Oxford, 1973, pp. 733–735.