

SHORT COMMUNICATION

CHEMICAL CONSIDERATIONS ON PASSIVITY*

P. J. GELLINGS

Technische Hogeschool Twente, Enschede, Netherlands

Abstract—It can be shown that the value of the charge/radius ratio of metallic ions determines whether the metal on dissolution tends to become passive or not. Using this criterion it is possible to clarify the influence of pH and electrode potential on the occurrence and breakdown of passivity.

INTRODUCTION

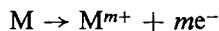
IN MANY cases a base metal is less reactive than would be expected from its standard electrode potential. This important phenomenon is called passivity and when a metal is passive it shows a much lower corrosive rate than otherwise.^{1,2} Well-known examples are aluminium, chromium and chromium alloys, titanium, etc. In aqueous solutions the explanation usually given for this phenomenon is that the surface of the metal is covered by a layer of oxide or adsorbed oxygen which isolates the metal from its environment.

From thermodynamic considerations it can be deduced under which circumstances passivity may be expected. The Pourbaix diagrams³ are extremely valuable in this respect.

On the other hand, however, thermodynamics is not able to furnish an explanation why passivity occurs. In the present paper the chemical background of passivity is considered on the basis of the chemical reactions and the properties of the metal ions involved in passivation. The discussion is limited to cases of "non-specific" passivity and cases such as Pb in H₂SO₄, which is protected by an insoluble film of PbSO₄, are not considered, and it is assumed that no complexing agents are present in the solution. Finally we shall limit ourselves to metals with inert-gas configurations and to the transition metals.

Basic reactions

The basic corrosion reaction is usually written as the anodic half-reaction of a galvanic couple.



For our considerations we must take into account that all ions in aqueous solution are hydrated, i.e. a number of water molecules are bound strongly to the metal ion:



*Manuscript received 15 March 1966.

It will be shown that the properties of these aquo-ions have a large influence on the corrosion-reaction.

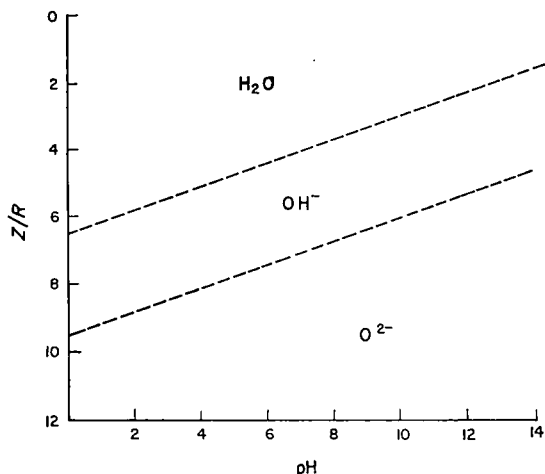
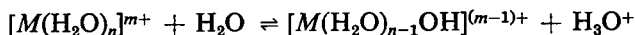


FIG. 1. Common ligands of metal ions as a function of the charge/radius ratio and pH in aqueous solution.

Those properties which are of main interest are conveniently summarized in Fig. 1 which is a modification of a similar diagram due to Jorgensen⁴ and which is based on the ideas of Cartledge.⁵ The ionic radii used in the calculations are those given by Pauling.⁶

For low values of z/r , the effective ionic potential, the predominant form of metal ions in solution is the ordinary aquo-cation over most of the pH range (e.g. Na^+ , Ca^{2+} , etc.). When z/r increases there is an increasing tendency for the following reaction to occur.



This equilibrium is shifted to the right at higher pH due to hydrolysis.

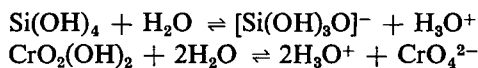


We see that this is explained by the higher field around the metal ion which causes a repulsion of the proton. At the same time the oxygen ion is attracted more strongly. This explains quite neatly the more amphoteric character of, for example, $\text{Be}(\text{OH})_2$ compared with $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ compared with $\text{Sc}(\text{OH})_3$ etc. In the same way this explains the larger tendency for hydrolysis of iron (III)-salts compared with those of iron (II).

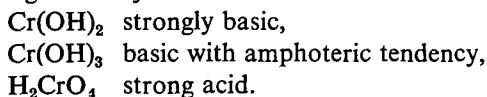
If z/r is increased further, particularly at high pH, more protons tend to be lost finally leading to ions such as $[\text{Al}(\text{OH})_6]^{3-}$. At still higher values of z/r and/or pH the hydroxyl-groups also start to lose protons:



For example

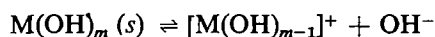


Thus O^{2-} becomes the predominant ligand. For metals with different valencies we see a strong tendency to increased acidic behaviour with increasing charge:

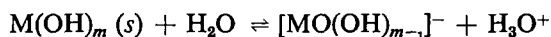


In cases such as this the decreasing radius with increasing charge of course causes an extra strong effect.

An important consequence which can be deduced is that in intermediate cases a low solubility of the hydroxide results owing to the high attraction between metal ion and oxygen and the reaction



occurs only to a slight extent. At the same time it is still a weak acid so that the equilibrium



also lies to the left. Taken together this means that the solubility product will be small for amphoteric hydroxides.

A second point of interest is that in many cases it is not the hydroxide which precipitates but the oxide or a hydrated oxide (such as e.g. $\text{FeO} \cdot \text{OH}$, $\text{AlO} \cdot \text{OH}$).⁷ The reason for this is that the lattice energy of a compound MX_n is less favourable than that of a compound MY_p with $p < n$ due to the decrease in the Madelung constant with increasing n ⁸ and the higher charge of Y. This is shown in Fig. 2 for a particular series of structures.

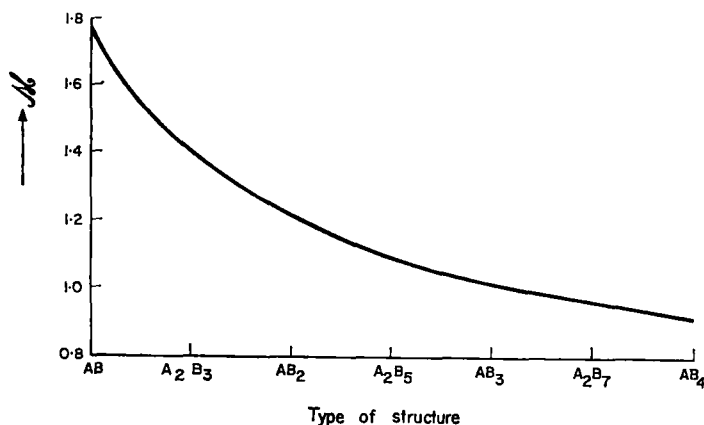


FIG. 2. Madelung constant for crystal structures with a hexacoordinated positive ion.⁸

DISCUSSION

Application to passivity

We can now apply this to passivity. In the first place we see that in order to obtain an insoluble hydroxide or oxide in the intermediate range of pH (i.e. pH 5–9) z/r must be between about 4–7. As is shown in Table 1 this is in good agreement with the facts when predominant valency under normal conditions is taken (Cr³⁺, Mo⁴⁺, Fe²⁺, etc.).

TABLE 1. CHARGE/RADIUS RATIO AND PASSIVE BEHAVIOUR OF METALS AS A FUNCTION OF POSITION IN THE PERIODIC TABLE

Li ⁺	Be ²⁺ <i>P</i>	B ³⁺							
1.67	6.4	15							
Na ⁺	Mg ²⁺ (<i>P</i>)	Al ³⁺ <i>P</i>	Si ⁴⁺	P ⁵⁺					
1.05	3.1	6.0	9.8	14.7					
K ⁺	Ca ²⁺	Sc ³⁺ ?	Ti <i>P</i>	V <i>P</i> ?	Cr <i>P</i>	Mn(<i>P</i>)	Fe(<i>P</i>)	Co	Ni
0.75	2.0	3.7	2 ⁺ 2.2	3 ⁺ 4.1	2 ⁺ 2.4	2 ⁺ 1.5	2 ⁺ 2.6	2 ⁺ 2.7	2 ⁺ 2.8
			3 ⁺ 4.0	4 ⁺ 6.7	3 ⁺ 4.3	4 ⁺ 7.4	3 ⁺ 4.7	3 ⁺ 4.8	3 ⁺ 4.8
			4 ⁺ 5.9	5 ⁺ 8.5	6 ⁺ 11.5	7 ⁺ 15.1	6 ⁺ (12)		
Rb ⁺	Sr ²⁺	Y ³⁺	Zr ⁴⁺ <i>P</i>	Nb ⁵⁺ <i>P</i>	Mo(<i>P</i>)	Re?	Ru <i>N</i>	Rh <i>N</i>	Pd <i>N</i>
0.67	1.77	3.2	5.0	7.1	4 ⁺ (6)	—			
					6 ⁺ 9.7				
Cs ⁺	Ba ²⁺	La ³⁺	Hf ⁴⁺	Ta ⁵⁺ <i>P</i>	W <i>P</i>	Tc?	Os <i>N</i>	Ir <i>N</i>	Pt <i>N</i>
0.59	1.48	2.6	(4)	(6)	6 ⁺ (8)	—			

P = Usually passive.

(*P*) = Passive under a limited set of conditions.

N = Noble.

Usual valence state under normal conditions are shown in bold type.

An important point is the effect of strongly oxidizing conditions, e.g. due to a high electrode potential caused by anodic polarization or by oxidizing media such as nitric acid. For those metals with a higher valency state this will lead to destruction or weakening of passivity due to formation of oxy-anions (Cr^{VI}, Mo^{VI}, Fe^{VI}) corresponding with transpassive behaviour.^{2,9} In the cases of chromium or chromium alloys this leads to dissolution as chromate ions. When no higher valency is available (Al, Ti, Zr) passivity will be destroyed even under highly oxidizing conditions.^{2,11}

Sometimes mildly oxidizing conditions are favourable for the onset of passivity, the most important case being iron. This also follows from the theory, and providing iron dissolves directly as Fe³⁺ ions the formation of a protective, insoluble film then becomes possible. On the other hand, if iron dissolves as Fe²⁺ ions which are subsequently oxidized in the solution, e.g. by dissolved O₂, at some distance from the metal, loose hydroxide is precipitated which does not lead to passivity.

It follows that reducing conditions will lead to a destruction of passivity where a lower valency is available (Cr, Fe) but will have a relatively small influence otherwise (e.g. Al).

The above is valid at intermediate values of the pH. When the pH is decreased there will be a larger tendency for the metal to go into solution in the form of aquocations. This will only lead to destruction or weakening of the passivity for low values z/r (Fe, Cr and to a lesser extent Al).^{2,10}

On the other hand, at a high pH there will also be a tendency toward diminished passivity due to dissolution in the form of oxy-anions, particularly for metals with a high value of z/r : Al, Ti, Nb.^{2,10}

It is seen that this theory explains several important facts about passivity. In the first place it shows that the metals which show passive behaviour will be found in a slightly downward sloping region in the middle of the periodic table. Those to the left and below have low values of z/r and dissolve preferably as aquo-cations, those metals to the right and above tend to dissolve as oxy-anions.

Reduction and low pH favour aquo-cations, whereas oxidation and high pH favour oxy-anions. Depending on the value of z/r and the availability of high or low valencies this may lead to destruction of passivity in one or both directions. When under oxidizing conditions a higher valence state with more favourable z/r is possible (Fe) this may lead to enhanced passivity.

Even when z/r and pH are favourable for passivity to occur another condition to be fulfilled is that the oxide lattice has to fit reasonably well on the metal lattice. However, for the very thin layers which are assumed to be responsible for passivity (50–200 Å) this condition is not very stringent because their plasticity is high enough to avoid cracking of the layer in cases where a perfect fit is not possible. It is clear from the above, however, that these topochemical considerations can never explain the occurrence of passivity as this is decided by the z/r -pH conditions. It may explain, however, the absence of passivity when the misfit is too large. There is no clear case known where this occurs, except perhaps vanadium and niobium.

CONCLUSION

From the discussion given above it follows that the simple model of ionic bonding of inorganic compounds is able to explain satisfactorily the occurrence of passivity of certain metals and the influence of the external conditions thereon.

Of course this only applies to the static aspects. The kinetics of passivation is influenced by several other variables also, e.g. availability of reactants, diffusion in the passive layer and the kinetics of the cathodic reaction which have not been considered. But, similar to the topochemical considerations above, the kinetics can only explain the absence of passivity as the occurrence of passivity is determined by the chemical variables z/r and pH.

REFERENCES

1. H. H. UHLIG, *Corrosion and Corrosion Control*. Wiley, New York (1963).
2. U. R. EVANS, *The Corrosion and Oxidation of Metals*, ch. 7. Arnold, London (1960).
3. M. POURBAIX, *Atlas d'Equilibres Electrochimiques*. Gauthier-Villars, Paris (1963).
4. C. K. JØRGENSEN, *Inorganic Complexes*. Academic Press, New York (1959).
5. G. H. CARTLEDGE, *J. Am. Chem. Soc.* **50**, 2855, 2863 (1928).
6. L. PAULING, *The Nature of the Chemical Bond*. Cornell University Press, Ithaca, New York (1940).
7. T. P. HOAR, The anodic behaviour of metals, in *Modern aspects of electrochemistry*. (Ed. J. O'M. BOCKRISS.) Vol. 2, p. 262. Butterworths, London (1959).
8. T. C. WADDINGTON, Lattice energies and their significance in inorganic chemistry, in *Advances in Inorganic Chemistry and Radiochemistry*. (Ed. H. J. EMELEUS and A. G. SHARPE.) Vol. 1, p. 158. Academic Press, New York (1959).
9. M. PRAŽÁK and V. ČIHÁL, *Z. Elektrochem.* **62**, 739 (1958).
10. J. DRALEY and W. RUTHER, *J. electrochem. Soc.* **104**, 329 (1957).
11. O. RÜDIGER and W. R. FISCHER, *Z. Elektrochem.* **62**, 803 (1958).