

Solubility of hydrogen in metals

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Abstract - Products of interactions of transition metals with hydrogen exhibit retentions of essential metallic properties accompanied by decreases of density. With reference to temperature and to hydrogen gas-pressures, p , in equilibrium, different metals exhibit very different levels of hydrogen content, c . For elements in subgroups III, IV and V and palladium in group VIII, initial regions of solid solubilities can be succeeded at quite low pressures by transformations to crystallographically distinct hydride phases. Proportionalities between hydrogen solubility and square roots of hydrogen pressure have suggested stepwise solubility processes of surface molecular dissociation followed by occupation of interstitial sites by the dissociated hydrogen entities: opinion is divided concerning alternative protonic or anionic character of the interstitial hydrogen. The general high mobility of hydrogen between interstices assists internal equilibration. Higher temperatures increase mobilities and also favour developments of rapid surface equilibration processes additionally important for accurate determinations of relationships between pressure, p , and content, c . Hydrogen solubilities have been equated with changes of physical parameters including electrical resistivity. Measurements of electrical resistivities in equilibria with gaseous hydrogen extend up to very high pressures. There is interest in the magnitudes of hydrogen contents introduced into metals by electrolysis. Resistivity measurements with variously surface-activated palladium cathodes indicate attainments of hydrogen contents below contents introduced by equilibration with gaseous hydrogen pressures of the order of 10,000 atmospheres. Generation of hydrogen gas pressures of such an order of magnitude within voids in some metals either acting as cathodes or during processes of corrosion would seem responsible for surface blistering phenomena. Related experimental possibilities are those of developments of pressures in voids of gaseous molecule products of interactions of migrating interstitial hydrogen with inclusions of elements such as carbon, nitrogen and sulphur; and of helium resulting from decomposition of tritium in metal tritides.

ABSORPTION OF HYDROGEN BY METALS AND FORMATION OF METALLIC HYDRIDES

The first clear appreciations of the absorption and embrittling effects of hydrogen in iron and steels seem to have developed in the latter part of the 19th century (refs. 1-3) contemporaneously with the findings of substantially larger absorption (occlusion) of hydrogen in palladium as compared to iron and platinum (ref. 4). Subsequently it has been established (refs. 1,2,5-8) that the very high apparent solubilities of hydrogen in palladium had been a consequence of a combination of an initial range of hydrogen content where the hydrogen could be simply regarded as a solid solution in the metal lattice - succeeded at higher hydrogen contents by the formation of a crystallographically distinct formal hydride phase. Also it has now been appreciated that the formation of structurally distinct metallic hydride phases at low hydrogen chemical potentials was a characteristic pattern of behaviour shown by the more electropositive metals of transition element subgroups III, IV and V. Extensive data are now available concerning the (p - c - T) phase relationships of these and some other metal/hydrogen systems (refs. 5-10).

PRESSURE-COMPOSITION RELATIONSHIPS OVER REGIONS OF SOLID SOLUTION AND ADJACENT REGIONS

While changes of concentration c corresponding to phase transitions are distinguished by a constancy of equilibrium pressure, p - there are continuous increases of equilibrium pressure over regions of increasing concentrations of solid solubility. Primarily from

experimental findings by Sieverts and his collaborators (refs. 1,2,5-7) of dependences of c on the square root of pressure, it has been widely inferred that in these regions the hydrogen exists in the metal as individually dissolved atoms located in interstitial lattice positions. In the case of the palladium hydrogen system these positions have been identified as octahedral interstitial positions of the face centred cubic lattice from neutron scattering (ref. 11) and channelling (ref. 12) experimental measurements.

HYDROGEN ADSORPTION AT EXTERNAL AND INTERNAL SURFACES: SUB-SURFACE ABSORPTION

In practice it is found that the regions where solid solution criteria of a square root ($p^{1/2}$) dependence of pressure on hydrogen content (c) are often limited. In terms of overall hydrogen uptake, such regions have been preceded by ones corresponding to surface adsorption which are relatively more extended in cases of specimens in particulated form (ref. 13). Furthermore relatively recently (refs. 14-16) there seems increasingly clear evidence of intermediate sub-surface states which still require further additional clarifying study. A further issue in this area of consideration is that of increased hydrogen uptake into finely divided cold-worked specimens which reflects its introduction into voids and dislocations (refs. 8,17). Further attention to this factor will be drawn below with reference to corrosive and deliberate electrolytic sources of hydrogen incorporation.

VERY HIGH PRESSURE HYDRIDE PHASE TRANSITIONS

Transition Metals from Subgroups VI and VII, members of Subgroup VIII with the exception of palladium, and copper, silver and gold in Subgroup I exhibit only very low solubilities of hydrogen at pressures up to one atmosphere over a wide range of temperatures (refs. 1,2,6,8,18-20). Further studies up to 30-60 k.bar have provided evidence for the formation by nickel at pressures of ~ 6000 bar of an analogous phase to the β -phase hydride of palladium and also for formations of hydride phases at still higher pressures by rhodium, manganese, chromium and iron. No evidence for hydride formation was found in the cases of the six platinum metals other than palladium (refs. 20,21). As further discussed below in the case, at least, of the platinum/hydrogen system, p - c relationships would have a supercritical form with respect to a hydride phase transition analogous to that of the $\alpha \rightleftharpoons \beta$ transition of palladium (refs. 21,22).

REGIONS ADJACENT TO PHASE TRANSITIONS AND OF CRITICALITY AND SUPERCRITICALITY WITH RESPECT TO REGIONS OF PHASE TRANSITION: CATASTROPHE MODELS

Deviations from dependences of hydrogen content changes on the square root of equilibrium hydrogen pressure, associated with surface and immediate subsurface sorption, have already been mentioned above. Importantly, from a bulk lattice structural standpoint, however, in regions of latent phase transition, significant deviations from a square root of pressure dependence on hydrogen content also begin increasingly to appear, in the sense of findings of substantially larger increases of hydrogen content per incremental increases of pressure (refs. 1,2,5-9,22). X-ray crystallographic and electrical resistance measurements have been invoked (refs. 8,23,24) to suggest that this reflects the gradual development of domains of the nucleating new phase within a matrix of virtually saturated solid solution - and has encouraged a proposition that the overall process of the phase transition could be described in terms of a catastrophe model (refs. 8,24,25).

Any theoretical model has to take account of decreases with temperature of the pressure-invariant regions of hydrogen content, up to a critical temperature where a clear pressure-invariant region is no longer evident and there is a virtual absence of hysteretic differences between p - c relationships derived over alternative courses of increases or decreases of hydrogen content. The possible catastrophe model has attempted to take this into account together with likelihoods of some continued presence of residual regions of solid solution structure even at the conclusion of pressure invariant regions and also of existences of quasi two phase regions at hydrogen contents corresponding to inflected regions of critical and even supercritical p - c isotherms. Support for these possibilities appears to gain some encouragement from recent analyses (ref. 26) of relationships between hydrogen content and electrical resistivity over a range of temperatures for the Pd/H system (refs. 23,27) and of inter-relationships between electrical resistance, hydrogen content and equilibrium hydrogen pressure for an extensive series of palladium/platinum alloys (ref. 22).

PROTONIC OR ANIONIC NATURE OF THE HYDROGEN

One criterion of retention of general metallic properties is that of the relatively small orders of magnitude of changes of electrical resistivity produced by the hydrogen in

metallic hydrides. This could be regarded as consistent with a quite widely held view (refs. 7,9) of a protonic or essentially electron donating and pseudo alloying behaviour of the hydrogen either in metallic hydride phases or in the initial hydriding stage of solid solution formation. On the other hand consideration has to be given to the electropositivity with respect to hydrogen of most transition elements and of those of Subgroups III, IV and V in particular (refs. 8,24,26). An alternative model has been advanced (refs. 8,24,28) proposing that partial electron transfer from the metal atoms to the hydrogen interstitials takes place but to an extent insufficient for conversion of the metal atoms to positive ions with the concurrent collapse of effective radius and increase of density produced in the cases of alkali and alkaline earth hydrides (refs. 8,9,24). Thus the continued metallic character could be associated with a retention of original metallic character modified by a lattice expansion in a somewhat analogous way to the thermal expansion produced by increasing temperature and in the case of palladium might be alternatively responsible for the observed decrease of paramagnetism on hydrogen absorption (refs. 8,29).

DIFFUSION RATES

Potential combinations of high concentrations of interstitial hydrogen and vacant interstitial sites in a maintained elastic medium has provided attractive possibilities for utilising metallic-hydride-forming transition elements and their alloys as hydrogen permeation membranes for hydrogen purification and related purposes. Aside from technical problems of membrane geometry and constructional junction strains in relation to lattice volume expansions and contractions - generally desirable permeation rate criteria are those of high concentration gradients, dictated by forms of pressure-composition relationships, together with high values of hydrogen diffusion coefficients. Various techniques have been utilised to derive data for the substantial compilations of diffusion coefficient and activation energy parameters which are available (refs. 30,31).

GORSKY AND DIFFUSION-ELASTIC EFFECTS RELATED TO STRAIN GRADIENTS IN HYDROGEN PERMEATION MEMBRANES

During hydrogen permeation in the steady state, the concentration gradients existing across the thickness of the membrane are complementary with a gradient of lattice expansion. Latterly it has been appreciated that such Diffusion Elastic Effect initiated strain gradients can produce Gorsky Effect induced permeation rate components in the opposite direction to that of concentration gradient-imposed flux (refs. 32,33).

Related effects have been demonstrated by experiments with certain compositions of palladium/platinum and palladium/silver alloys with p-c relationships at temperatures near to 25°C which are supercritical with respect to regions of phase transition analogous to those of the palladium/hydrogen system. In these experiments (refs. 34-38) the reimpositions of strain gradients at one surface of membranes, initially containing homogeneously distributed hydrogen contents, also have been found to produce temporary reductions in surface hydrogen chemical potentials at the opposite surface.

ELECTROLYTIC INTRODUCTION OF HYDROGEN

Utilisation of this convenient means of introducing hydrogen into metals was reported as part of Graham's initial studies of the absorption of hydrogen by palladium (refs. 1,4,6). Electrolytic techniques have since been frequently employed and quite recently there has been much interest in the specific case of introduction of deuterium into palladium with regard to anticipation of concurrent nuclear fusion processes. An initiative for investigation of this possibility had been estimations that very high concentrations of deuterium (refs. 39,40) could be introduced at high current densities corresponding in turn to very high pressures. Latterly, however, practical limitations to such equivalent high pressure development have been more appreciated. Thus for instance at cathodes with surfaces of sufficiently high catalytic activities for open circuit electrode potentials to be reliably equatable with pressure through Nernstian relationships - hydrogen isotope concentrations within cathodes were limited to those in equilibrium with hydrogen gas pressures of the order of 100 atmospheres concurrently with the general onset of gas bubble evolution (refs. 6,8,22,41-44).

These conclusions were drawn from results of measurements with palladium cathodes of open circuit electrode potential and component-separated hydrogen overpotential originally developed by Knorr and co-workers (ref. 44). They have also been importantly substantiated by measurements of the electrical resistivity of cathodes of both palladium and of certain palladium alloys for which resistivity and hydrogen content changes have high sensitivities as functions of hydrogen pressure over ranges of pressure spanning

values near to 100 atmospheres (refs. 8,22,42,43). At cathode surfaces of lower catalytic activity for equilibration processes involving surface hydrogen species, larger effective concentrations of hydrogen ad-atoms can develop during electrolysis (refs. 8,13,24) and correspondingly higher hydrogen contents can be introduced into cathode substrates. Again in the case of palladium and palladium alloy cathodes, these higher contents have been estimated by measurements of electrical resistivity (refs. 8,45,46) which could be equated with effective hydrogen pressures through relationships derived in studies of equilibration with high gaseous pressures of hydrogen (refs. 19,22,47). Some guidance to structural and hydrogen content changes has also been obtained recently from X-ray studies (refs. 48,49) which also have been of importance in indicating (ref. 49) a decreased expansive effect of deuterium as compared to protium interstitials at 77K (ref. 49) in some contrast to earlier indications (ref. 6).

EMBRITTEMENT AND MACROSCOPIC DAMAGE: BLISTERING

Even while retaining a similar appearance and other general metallic characteristics, many metals exhibit increased tendencies for brittle fracture under stress on absorption of hydrogen. In cases of some elements such as titanium, vanadium and their group congeners (ref. 9) brittle behaviour can be a clear consequence of formation of distinct hydride phases and may be effectively reversed by 'regeneration' of the hydrogen-free metal on hydrogen desorption. Such cycles of formation and decomposition of specific hydride phases generally result in substantial macroscopic dimensional alterations (refs. 1-9). However, in the case of palladium, large numbers of hydrogen absorption/desorption cycles can be effected with little macroscopic alterations provided the limits of absorption are restricted to ranges of hydrogen content corresponding to solid solution compositions (ref. 8).

In cases of other technologically important elements and alloys such as nickel, iron and steels, embrittlement may be a consequence of relatively small concentration absorptions of hydrogen into the bulk lattice and seems importantly associated with relatively high localised concentrations of hydrogen in lattice defects such as dislocations and voids. From a structural damage standpoint, it is significant that pressures of hydrogen gas contained in such voids can attain pressures of some thousands of atmospheres. This is complementary with the high surface hydrogen chemical potential which can develop on catalytically inactive surfaces during specific electrolytic cathodisation or during local cell corrosion processes. Developments of such high hydrogen pressures can lead to distensions of the voids as exemplified by the appearance of surface blisters (refs. 8,50). Further sources of such blisters are those originating from gaseous molecules produced as products of interaction of migrating hydrogen with inclusions of elements such as carbon and sulphur (ref. 8). Finally a special case of blistering is provided by the secondary formation of pockets of helium gas resulting from nuclear transformation of tritium contained in metal tritides (refs. 8,51,52).

REFERENCES

1. D.P. Smith, Hydrogen in Metals, Chicago University Press (1948).
2. M. Smiałowski, Hydrogen in Steel, Pergamon Press, Oxford (1962).
3. C.D. Beacham, Hydrogen Damage, American Society of Metals, Metals Park, Ohio (1977).
4. T. Graham, Phil. Trans. R. Soc. Lond., 156, 415-431 (1866).
5. Ted B. Flanagan, (ed), Engelhard Ind. Tech. Bull. (Thomas Graham Commemorative Issue), 7-62 (1966).
6. F.A. Lewis, The Palladium/Hydrogen System, Academic Press, London (1967).
7. E. Wicke, H. Brodowsky and H. Züchner, Topics in Applied Physics, (ed. G. Alefeld and J. Völkl) Springer: Berlin, 29, 73-155 (1978).
8. F.A. Lewis, Platinum Metals Rev., 26, 20-27, 70-78, 121-128 (1982), Z. Phys. Chem. Neue Folge, 146, 171-185 (1985); Int. J. Hydrogen Energy, 12, 643-655 (1987).
9. W.M. Mueller, J.P. Blackledge and G.G. Libowitz (eds.), Metal Hydrides, Academic Press, New York (1968).
10. E. Fromm, R. Kircheim and E. Wicke (eds.), Proc. Conf. on Hydrogen in Metals Fundamentals and Applications, (2 vols.) Stuttgart 1988, Oldenbourg Press Munich (1989).

11. K. Sköld and G. Nelin, J. Phys. Chem. Solids, **28**, 2369-2380 (1967).
12. H.D. Carstanjen, Z. Phys. Chem. Neue Folge, **165**, 141-163 (1989).
13. F.A. Lewis and J.J. Rooney, Proc. 4th Int. Conf. Hydrogen and Materials (eds. P. Azou and N.P. Chen) I.S.M.C.M, St. Ouen, **1**, 29-39 (1989).
14. E. Wicke, Z. Phys. Chem. Neue Folge, **143**, 1-21 (1985).
15. F.A. Lewis and S.G. McKee, Surf. Technol., **24**, 355-363 (1985).
16. K. Kandasamy, F.A. Lewis and S.G. McKee, Surf. Technol., **35**, 93-99 (1988).
17. Ted B. Flanagan and J.F. Lynch, J. Less-Common Met., **49**, 25-35 (1976).
18. B. Baranowski, Topics in Applied Physics (ed. G. Alefeld and J. Völkl), Springer, Berlin, **29**, 157-200 (1978).
19. B. Baranowski, Z. Phys. Chem. Neue Folge, **114**, 59-81 (1979).
20. V.E. Antonov, I.T. Belash, V. Yu. Malyshev and E.G. Ponyatovsky, Platinum Metals Rev., **28**, 158-163 (1984).
21. E.G. Ponyatovsky, V.E. Antonov and I.T. Belash, Problems in Solid-State Physics, eds. A.M. Prokhorov and A.S. Prokhorov, Mir Publishers, Moscow, 109-172 (1984).
22. B. Baranowski, F.A. Lewis, W.D. McFall, S. Filipek and T.C. Witherspoon, Proc. R. Soc. Lond., **386A**, 309-332 (1983).
23. F.A. Lewis, W.D. McFall and T.C. Witherspoon, Z. Phys. Chem. Neue Folge, **114**, 239-249 (1979).
24. F.A. Lewis, I. Lewis and S.G. McKee, J. Less-Common Met., **101**, 503-521 (1984).
25. K. Kandasamy, F.A. Lewis, W.D. McFall and R-A. McNicholl, Z. Phys. Chem. Neue Folge, **163**, 41-46 (1989).
26. F.A. Lewis, S.G. McKee and R-A. McNicholl, Abstracts of 32nd IUPAC Congress, Stockholm, 2-7 August 1989, Abstract 429, p. 90 (1989).
27. H. Brüning and A. Sieverts, Z. Phys. Chem. Lpz., **163**, 409-441 (1938).
28. F.A. Lewis, Nature Phys. Sci., **242**, 45-46 (1973).
29. T.R.P. Gibb, Engelhard Ind. Tech. Bull., **7**, 28-35 (1966).
30. G. Alefeld and J. Völkl, Topics in Applied Physics, (ed. G. Alefeld and J. Völkl) Springer: Berlin, **29**, 321-348 (1978).
31. A. Kufudakis, J. Čermák and F.A. Lewis, Z. Phys. Chem. Neue Folge, **64**, 1013-1018 (1989).
32. J. Čermák, G. Gardavská, A. Kufudakis and P. Lejček, Z. Phys. Chem. Neue Folge, **145**, 239-250 (1985).
33. K. Kandasamy, Scripta Metall., **22**, 479-481 (1988).
34. F.A. Lewis, J.P. Magennis, S.G. McKee and P.J.M. Ssebuwufu, Nature Lond., **306**, 673-675 (1983).
35. B. Baranowski, J. Less-Common Met., **154**, 329-353 (1989).
36. B. Baranowski and F.A. Lewis, Ber. Bunsenges. Phys. Chem., **93**, 1225-1227 (1989).
37. F.A. Lewis, K. Kandasamy and S.G. McKee, Z. Phys. Chem. Neue Folge, **164**, 1019-1024 (1989).
38. F.A. Lewis and X.Q. Tong, Abstracts of 32nd IUPAC Congress, Stockholm, 2-7 August, 1989, Abstract 4501, p. 109 (1989).
39. M. Fleischmann, S. Pons and M. Hawkins, J. Electroanal. Chem., **261**, 301-308 (1989); **263**, 187 (1989).
40. S.E. Jones, E.P. Palmer, J.B. Czirr, D.L. Decker, G.L. Jensen, J.M. Thorne, S.F. Taylor and J. Rafelski, Nature Lond., **338**, 737-741 (1989).
41. F.A. Lewis, R.C. Johnston, M.C. Witherspoon and A. Obermann, Surf. Technol., **18**, 147-166 (1983).

42. F.A. Lewis, M.N. Hull, R.C. Johnston and M.C. Witherspoon, Surf. Technol., 18, 167-184 (1983).
43. F.A. Lewis, R.C. Johnston, S.G. McKee, A. Obermann and M.C. Witherspoon, Int. J. Hydrogen Energy, 9, 303-307 (1984).
44. L. Kandler, C.A. Knorr and C. Schwitzer, Z. Phys. Chem. Lpz., 180A, 281-304 (1937); C.A. Knorr, Z. Elektrochem, 57, 599-604 (1953); 59, 647--659 (1955); R. Clamroth and C.A. Knorr, Z. Elektrochem., 57, 399-405 (1953).
45. G. Bambakidis, R.J. Smith and D.A. Otterson, Phys. Rev., 177, 1044-1048 (1969).
46. R.J. Smith and D.A. Otterson, J. Phys. Chem. Solids, 31, 187-189 (1970).
47. R. Wiśniewski, Rev. Sci. Inst., 40, 464-465, (1970).
48. E. Batalla, E.G. Zwartz and B.A. Judd, Solid State Commun., 71, 805-807 (1989).
49. J.E. Schirber and B. Morosin, Phys. Rev., 12B, 117-118 (1975).
50. A. Kufudakis and G. Gardavskā, J. Less-Common Met., 63, 65-74 (1979).
51. T. Schober, J. Golczewski, R. Lässer, C. Dieker and H. Trinkaus, Z. Physik. Chem. Neue Folge, 147, 161-169 (1986).
52. R. Lässer, K. Bickmann and H. Trinkaus, Phys. Rev., 40B, 3306-3310 (1989).