

Electronegativity, Work Function, and Heat of Adsorption of Hydrogen on Metals

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A new list of work functions for polycrystalline metal surfaces is proposed and correlated with Pauling's electronegativity. Simple linear relationships exist between the above two quantities, which divide metals into four groups, roughly: *sp*, transition, alkali and alkali earth metals. The difference between the electronegativity for atoms in molecules and that for solid metal surfaces is discussed. The use of these work functions in the Eley-Stevenson method for calculating the adsorption heat of hydrogen on metals shows that the ionic contribution to the bond energy is essentially correct, and better agreement with experimental data than in previous calculations is generally obtained if metal-metal bond energies are derived from surface tension measurements rather than from atomization heats.

Pauling¹ defined electronegativity as "the power of an atom in a molecule to attract electrons to itself". This quantity is not capable of direct measurement, so that the best way to test electronegativity values is to correlate them with other properties capable of precise and direct experimental measurement. The electronegativity of an atom in a molecule will in general be different from that of an isolated atom or that of the surface of the corresponding solid, nevertheless correlations among these quantities may be expected because all of them are governed by the electronic configuration of the element. Gordy and Thomas² proposed a linear relationship, for all metals, between electronegativity ($x_{M,e}$, where *e* stands for "element") and work function Φ , viz.,

$$x_{M,e} = 0.44\Phi - 0.15. \quad (1)$$

Conway and Bockris³ reported a similar relationship for 19 elements:

$$x_{M,e} = 0.40\Phi - 0.3. \quad (2)$$

One purpose of this paper is to show that the above correlations are unsatisfactory and, as such, cannot be given a definite physical meaning. The reason is first a lack of accuracy in the values for the work function used by the above authors, and secondly an underestimation of the importance of deviations in the derived plots. In this paper, more reliable correlations between $x_{M,e}$ and Φ are presented, and their significance is analyzed and a formulation for calculating the adsorption heat of hydrogen on metals is given. Though different methods have been proposed for evaluating electronegativity, the values generally accepted are those derived by Pauling¹ from bond energies, and in the following, unless stated, reference will be always made to these values.

WORK FUNCTIONS

Work function measurements are greatly affected by the surface state of solids and therefore they are easily changed by the presence of traces of impurities.⁴ Work functions for 32 metals have been selected in a previous paper⁵ and correlated with the electrochemical behaviour.^{6, 7} Values of Φ for 20 more metals have been added

TABLE 1.—WORK FUNCTIONS AND ELECTRONEGATIVITIES OF METALS

(a) This work, from work functions, eqn (3)-(6); (b) Pauling's values ¹; (c) Gordy and Thomas' values ²; (d) Pritchard and Skinner's values ²⁶; (e) electronegativities of metal surfaces, eqn (8).

metal	Φ /eV	electronegativity in Pauling's scale				
		(a)	(b)	(c)	(d)	(e)
Ag	4.30	1.86	1.9	1.8	1.7	1.37
Al	4.19	1.55	1.5	1.5	1.5	1.33
Au	5.32 ⁴	2.37	2.4	2.3	2.1(I)	1.69
	4.78*	2.10*				1.52*
Ba	2.35 ⁴	0.90	0.9	0.9	0.9	0.75
Be	5.08 ¹⁴	1.52	1.5	1.5	1.4 to 1.5	1.62
Bi	4.36	1.90	1.9	1.8	1.8	1.39
Ca	2.71 ¹¹	0.98	1.0	1.0	1.0	0.86
Cd	4.12	1.77	1.7	1.5	1.4	1.31
Ce	2.80 ^{8, 10}	1.11	1.1	1.1	—	0.89
Co	4.70	1.80	1.8	1.7	—	1.49
Cr	4.40	1.65	1.6	1.6(III)	—	1.40
Cs	1.90 ¹¹⁻¹³	0.72	0.7	0.75	0.7	0.60
Cu	4.70	1.80	1.9	1.8(I)	1.7(I)	1.49
Fe	4.65	1.77	1.8	1.8(III)	—	1.48
Ga	4.25	1.58	1.6	1.5	1.6	1.35
Hf	3.65 ⁴	1.28	1.3	1.4	—	1.16
Hg	4.50	1.96	1.9	1.8(II)	1.9(II)	1.43
K	2.30 ^{4, 12}	0.81	0.8	0.8	0.8	0.73
In	4.08	1.76	1.7	1.5	1.5	1.30
La	3.40 ^{8, 10}	1.15	1.1	1.1	—	1.08
Li	3.10 ¹⁵	0.99	1.0	0.95	1.0	0.99
Mg	3.66 ¹²	1.20	1.2	1.2	1.2 to 1.3	1.16
Mn	3.90	1.40	1.5	1.5(III)	—	1.24
Mo	4.30	1.86	1.8	1.6(IV)	—	1.37
Na	2.70 ^{12, 17}	0.90	0.9	0.9	0.9	0.86
Nb	4.20	1.55	1.6	1.7	—	1.34
Nd	3.1 ^{8, 10}	1.26	1.1	1.2	—	0.99
Ni	4.73	1.82	1.8	1.8	—	1.50
Os	4.83	2.13	2.2	2.0	—	1.54
Pb	4.18	1.80	1.8	1.8(IV)	1.8(IV)	1.33
Pd	5.00	2.21	2.2	2.0	—	1.59
Po	4.6 ⁸	2.01	2.0	2.0	—	1.46
Pr	2.7 ⁸	1.06	1.1	1.0	—	0.86
Pt	5.40	2.14	2.2	2.1	—	1.72
	5.03*	2.23*				1.60*
Rb	2.20 ¹¹⁻¹³	0.79	0.8	0.8	0.8	0.70
Re	4.95	1.92	1.9	1.8	—	1.58
Ru	4.80	2.11	2.2	2.0	—	1.53
Sb	4.56	1.99	1.9	1.8	1.9	1.45
Sc	3.5 ¹⁰	1.20	1.3	1.3	1.3	1.11
Sm	2.95 ^{8, 10}	1.19	1.2	1.2	—	0.94
Sn	4.35	1.89	1.8	1.8(IV)	1.8 to 1.9(IV)	1.38
Sr	2.76 ¹¹	0.98	1.0	1.0	1.0	0.88
Ta	4.22	1.56	1.5	1.3 to 1.7	—	1.34
Te	4.70 ⁸	2.06	2.1	2.1	2.1 to 2.2	1.49
Th	3.71 ⁴	1.31	1.3	1.0 to 1.4	—	1.18
Ti	4.10	1.50	1.5	1.6	1.6	1.30
Tl	4.02	1.73	1.8	1.9 (III)	1.4 (I)	1.28
U	3.50 ⁴	1.46	1.7	1.4(IV)	—	1.11
V	4.44	1.67	1.6	1.7(IV)	—	1.41
W	4.55	1.72	1.7	1.6(IV)	—	1.45
Zn	4.30	1.60	1.6	1.5	1.5	1.37
Zr	4.00 ⁴	1.45	1.4	1.5	1.5	1.27

* "Operative" work function (see text). Numbers in brackets indicate valence states. Work functions with no reference have been selected in previous papers.^{5, 7}

in this work. The criteria of selection have been the same as previously.⁵ The values of work function are reported in the first column of table 1.

The Φ value for gold selected in the previous paper⁵ was 4.78 eV in the place of about 5.3 eV as suggested by a number of authors.⁴ Only the first value, which would correspond to an untreated surface, seems to include gold in electrochemical correlations,^{6, 7} i.e., the first value represents an “operative” work function corresponding to the state of the metal as used in electrochemistry or catalysis. Something similar seems also to be the case with platinum which lies near gold in the periodic table.

Objections may be raised to the selection of a single value of work function for each metal. The work function depends on the surface structure, varying from one plane to another.⁴ One polycrystalline sample may not possess the same work function as another and much of the variation between reported values for any given metal may well be due to variation in the proportions of different facets. For films the work function increases with sintering temperature⁹ because the crystallinity of the sample increases with the degree of order.⁴ However, some justification may be given for selecting a single value of the work function. First, work functions are here not considered by themselves but in relation to quantities in electrochemistry^{6, 7} or catalysis, where metals are usually employed in the polycrystalline state. In this case, the selection of a single value of Φ has the same significance as the choice of a single value for the potential of zero charge,⁷ or the exchange current for hydrogen discharge. Statistically, the surface of a polycrystalline sample may be considered as reproducible, otherwise no meaning could be attached to any measurement in catalysis and electrochemistry. The problem of the selection of work functions is to accept only values which best approximate to the state of a metal as commonly used in practice. Indeed recent calculations¹² show that the experimental work functions for polycrystalline sample approximate well to the mean value for the three main faces.

Accordingly the “operative” work function of films should be that *measured* at room temperature. However, Shurmann and Wedler¹⁸ used films directly *deposited* at different temperatures. In this case, the best temperature for comparison with actual polycrystalline samples may be below the room temperature. In other words, sintering may be less effective than the direct deposition of the film at the selected temperature.¹⁹ Results would suggest that this may be so for nickel²⁰, and results for lead and Bi seem to support the above view.⁴

The results of electrochemical correlations^{6, 7} seem to corroborate this type of analysis. Values of work function chosen as above⁵ from the data of Shurmann and Wedler¹⁸ are in satisfactory agreement with data for polycrystalline samples.^{4, 5} As a further example, Φ values for polycrystalline samples of Ru^{4, 21} are in agreement with each other and also that for Ru films deposited at 78 K and sintered at about 300 K.¹⁹

CORRELATION BETWEEN $x_{M,e}$ AND Φ

The Φ values are plotted in fig. 1 against Pauling's¹ electronegativity values. The previous correlation of Gordy and Thomas² ignores the detailed structure of the plot. The equations for the four straight lines a-d are:

$$x_{M,e} = 0.50 \Phi - 0.55, \quad (3)$$

$$x_{M,e} = 0.50 \Phi - 0.29, \quad (4)$$

$$x_{M,e} = 0.23 \Phi + 0.28, \quad (5)$$

$$x_{M,e} = 0.23 \Phi + 0.36, \quad (6)$$

respectively. A plot similar to fig. 1 has already been reported⁷ but eqn (5) and (6) could not be confirmed for lack of data.

The potential of zero charge²² and the exchange current for hydrogen evolution²³ increase as gold is anodically activated, as though the work function is increased by this activation. The value of 5.40 eV for Φ places platinum in an anomalous position with respect to the other metals of its group.⁷ The experimental behaviour of Pt is better described by a value of 5.03 eV.

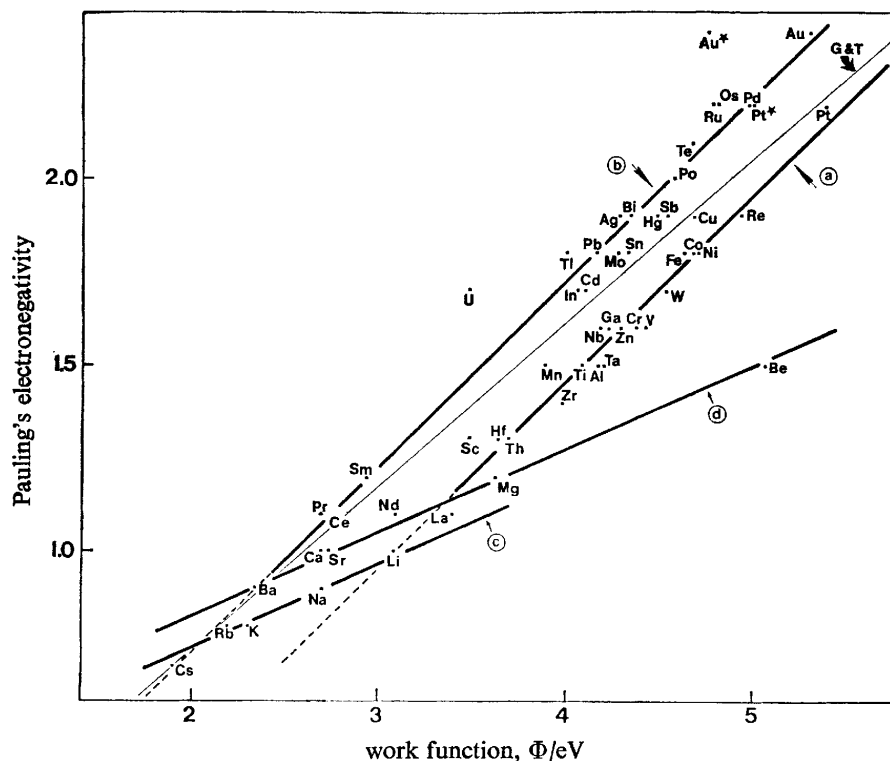


FIG. 1.—Pauling's electronegativity as a function of work function of polycrystalline metal surfaces. Starred points refer to "operative" work functions. G & T indicates the correlation proposed by Gordy and Thomas.²

Fig. 1 suggests that the essential factor governing the separation into the two main groups is the nature of the d electrons. It seems that the properties of the elements in the atomic rather than in the solid state are responsible for this separation, i.e., the variation of the work function with the position in the periodic table is more regular than that of $x_{M,e}$. Therefore, $x_{M,e}$ in group b is higher than expected from periodicity. Since $x_{M,e}$ is a measure of the power of an atom in a molecule to attract electrons to itself, then elements in group b may present a nuclear charge less screened and therefore more attractive. In other words, $3d$ electrons screen the nuclear charge better (or at least differently) than f or other d electrons do. The alkali metals and alkali earths seem to constitute separate classes, probably because the d electrons are well below the valence shell.

The alignment of the points in the four groups in fig. 1 may be considered as a check of the reliability of both quantities involved in the plot. For all metals, the value of $x_{M,e}$ from eqn (3)-(6) is generally within ± 0.05 unit of the electronegativity value of Pauling,¹ i.e., the accuracy claimed by Pauling.

Mo falls unexpectedly in group b. If $x_{M,e} = 1.8$ for this metal, then Φ should be about 4.7 eV; Eastman¹⁰ reports a photoelectric value of 4.6 eV, but this differs from other data which place the work function at 4.3 eV.⁶ If $\Phi = 4.3$ eV then $x_{M,e}$ should be about 1.6 which coincides with the value given by Gordy and Thomas² for Mo^{IV}. The values of electronegativity given by the above authors seem more appropriate also for U and Nd.

ELECTRONEGATIVITY OF SOLID METALS

The plot of $x_{M,e}$ against Φ is a simple correlation between two quantities pertaining to a system in two completely different, though in some respect interrelated, states. Eqn (3)-(6) cannot be used to derive the electronegativity of a metal and then in turn, for instance, to calculate adsorption heats, as in fact has been done.³ $x_{M,e}$ is the electronegativity of an atom in a molecule, and therefore bound to atoms of different nature, whereas the appropriate absolute electronegativity of bulk metals is in principle the work function. If adsorption bond energies are calculated from Pauling's formula,¹ the work function must be expressed in the same scale as that of $x_{M,e}$, the electronegativity of the adsorbed atom.

Stevenson,²⁴ following Mulliken's suggestion,²⁵ proposed to calculate the electronegativity of "solid" metals from the equation:

$$x_{M,s} = 0.355 \Phi. \quad (7)$$

More recent considerations by Pritchard and Skinner²⁶ of the scaling factor from Pauling's to absolute electronegativity, give

$$x_{M,s} = 0.318 \Phi. \quad (8)$$

Eqn (8) is implied in the scheme of Steiner and Gyftopoulos²⁷ to calculate the work function of metals from their electronic configuration. However, they express $x_{M,s}$ in terms of Gordy's formula² in which the electronegativity of atoms is related to the electrostatic potential of the core acting on a valence electron. This formula cannot be applied simply to all metals.

Results are reported in the last column of table 1. The electronegativity of a solid metal surface is always lower than that of the corresponding isolated atom. This is apparent also from Steiner and Gyftopoulos' equation.²⁷ This implies a greater screening of the nuclear charge in the solid than in the isolated atom. However, as expressed by eqn (8), the electronegativity of a solid is a collective, anisotropic property, as evidenced by results obtained by Hopkins *et al.*^{28, 29}

Since a list of work functions is proposed in this work, and this quantity is involved in the Eley-Stevenson^{24, 30} method for the calculation of the adsorption heat of hydrogen on metals, we now test the validity and limitation of the method by using these more accurate values.

HEAT OF ADSORPTION OF HYDROGEN

For hydrogen adsorption, which best lends itself to this type of calculation, the adsorption heat is expressed by Eley³⁰ as

$$q = E(M-M) + 46.12 \times 4.184 (x_{M,s} - x_H)^2 \text{ kJ mol}^{-1}, \quad (9)$$

where $E(M-M)$ is the metal atom-metal atom bond energy taken as 1/6 of the atomization heat. Stevenson²⁴ used eqn (7) to calculate $x_{M,s}$, and the fact that his calculated values give satisfactory agreement with experimental data must be considered as fortuitous, in that the inaccuracy in calculating $x_{M,s}$ was counter-balanced by the use of Michaelson's values⁸ for the work function, which are in general lower

than the actual values.⁵ The same criticism may be applied to calculations made by Conway and Bockris.³ These authors used eqn (2) to derive $x_{M,s}$, i.e., they derived $x_{M,e}$, the electronegativity of the atom in a molecule. However, results obtained by Stevenson²⁴ with the aid of eqn (7) have never been re-assessed by using eqn (8).

Experimental and calculated adsorption heats are compared in table 2. Experimental heats are usually values extrapolated to zero coverage,^{32, 34} thereby eliminating the effect of lateral interaction between adsorbed particles, which is not accounted for in eqn (9). However, for some metals, extrapolation may give a value of the heat which refers to sites of especially strong adsorption (low atom density planes) so that it may be higher than that calculated from eqn (9) by using the work function for polycrystalline surface and the atomization heat which is an isotropic quantity. Inspection of the data for various metals suggests that this effect is present in the results of Eley and Norton,³⁵ whereas for most of the metals the heat at zero coverage may be considered to be relative to the polycrystalline surface as a whole.

TABLE 2.—EXPERIMENTAL AND CALCULATED HEAT OF ADSORPTION OF HYDROGEN ON METALS

metal	expt.	heat of adsorption, $q/kJ\ mol^{-1}$			
		(a)	(b)	(c)	(d)
Cr	189	161	124	100.5	—
Fe	117-151	144	109	132.3	129
Mo	168	213	172	179.9	175
Ni	109-134	141	105	121.0	119
Pd	117	114	83.5	94.3	—
Pt	109	{122 142*	{101 114*	94.6	108*
Ta	189	238	200	208.0	191
Ti	163	202	157	—	—
W	189	223	185	191.0	171
Cu	117	126	92.5	98.1	118

* “Operative” work function; experimental heats of adsorption from Cerny and Ponec³¹ and Bond³²; atomization heats from Nyholm’s paper.³³

(a) This work, eqn (8) and (9); (b) this work, eqn (7) and (9); (c) Stevenson’s values²⁴; (d) this work, from surface energies.^{40, 41}

Table 2 shows that use of eqn (8) generally leads to more understandable values than eqn (7) does. For transition metals below group 8, the calculated values of q are always higher than the experimental data. Cr seems to be an exception, which suggests that the experimental value may be higher than the true adsorption heat (cp ref. (36)). Eqn (9) appears on the whole unsatisfactory, because it does not take into account the surface electronic configuration. According to the model of Dowden³⁷ for metals on the basis of Goodenough’s considerations,^{38, 39} formation of surface M—H bonds between a hydrogen atom and an e_g emerging orbital requires some energy to promote an electron from the Fermi level to the orbital in question. This energy should be greater the lower the Fermi level, i.e., other things being equal, the lower the electron concentration. Thus, erratic predictions by eqn (9) are expected, inasmuch as the promotion energy is not accounted for in the above equation. In fact, table 2 shows that the disagreement between experimental and calculated values increases as the number of d electrons decreases.

From the foregoing, it follows that the error in eqn (9) is to be sought essentially in the first term. This is implicit in Ehrlich’s reasoning.⁴⁰ The results in table 2 suggest that the atomization heat is also a measure of the surface capability of metals

to form chemisorption bonds only when the energy of the Fermi level overlaps that of the localized orbital emerging from the surface. In this respect, surface energies should better approximate the actual value of $E(\text{M}-\text{M})$ in the surface. If such values, taken from Ehrlich's papers,^{40, 41} are used in eqn (9), the agreement between experimental and calculated values of heats of adsorption is good for all metals. The value for W is lower than the experimental heat, but this is not surprising since this value appears to be invariably high in correlations.³⁶ This may be also due to the fact that the heat of adsorption at zero coverage is not always the more appropriate value for comparison with calculated values.³⁵ The value calculated for W in this work is, in fact, in good agreement with that of 163 kJ mol⁻¹ obtained by Eley and Norton³⁵ by extrapolating to zero coverage the middle portion of their (q, θ) curve.

The results shown in column c and d of table 2 suggest that the calculations made by Stevenson²⁴ must in part be fortuitous. Column d shows that the second term in eqn (9) is substantially correct and that the adsorption heat depends on the collective properties of solids inasmuch as the work function is a collective property. Eqn (9) also predicts a dependence of the adsorption heat on the orientation of the surface. The surface potential in the chemisorption of various simple species certainly does so.^{28, 29} Clearly, a correct calculation should start from data relative to well-defined crystal planes, but there are fewer data so that a similar treatment cannot be applied. The approximations introduced by using data for polycrystalline samples are thought not to be so great as to affect the analysis made and the results obtained in this work.

CONCLUSIONS

Use of reliable values for the work function of polycrystalline metals give close correlations of Φ with a number of physico-chemical properties. The correlation between electronegativity (reactivity of isolated atom) and work function (reactivity of solid phase) is less qualitative than thought previously. This shows that the periodic behaviour of elements is closely retained in the solid state. These correlations suggest that in theories of catalysis one may resort to collective properties strictly related to properties of isolated atoms. In fact, even though localized d orbitals may be present in the surface of metals,^{38, 39} possible promotion of electrons to or from the Fermi level³⁷ makes the free energy of electrons always an important factor in the chemisorption process. Thus, the energy of the electrons rather than their detailed configuration should be simply related to the behaviour of solid metals. In this respect, the density of energy states may be another relevant factor. The variation in this factor from metals of groups 8 to 2B can account for the strongly decreasing catalytic reactivity of these metals.

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