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A new compilation, based on a literature search for the period 1969–1976, is made of experimental data on the work function. For these 44 elements, preferred values are selected on the basis of valid experimental conditions. Older values, which are widely accepted, are given for 19 other elements on which there is no recent literature, and are so identified. In the data for the 63 elements, trends that occur simultaneously in both the columns and the rows of the periodic table are shown to be useful in predicting correct values and also for identifying questionable data. Several illustrative examples are given, including verifications of predictions published in 1950.

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INTRODUCTION

New evaluations of the work functions of the elements are of continuing interest because the data are pertinent to the theory of metals and to the understanding of the properties of metals and semiconductors. In practice, work functions are used in calculating corrosion rates, and properties of materials for electron-emitting and photosensitive devices.

Several extensive compilations of work-function data have appeared in the literature.[1–5] Of special interest in recent years are the critical reviews published by Rivière[3] in 1969 and Trasatti[5] in 1971, both of whom discussed the rationale for selecting preferred values for 41 elements. Fomenko[4] includes not only experimental data but also theoretical estimates for unmeasured elements and provides a preferred list that comprises almost every known element.

Since those evaluations were made, much new information has become available and refinements in technique have continued. Since 1970, in particular, vacuum equipment has become widely available for providing improved background pressures down to 10^{-10} Torr or lower, and identification of surface structure by Auger electron spectroscopy has become an important and definitive analytic tool for the experimentalist. In addition, there have been new studies of the work function in single crystallographic directions, research on specific effects of annealing polycrystalline specimens, and new findings on trace contamination of surfaces.

The present selection of published values is the result of a study of recent data as compared with older preferred values and an assessment of the experimental conditions. The new listing greatly extends the usefulness of a previous observation[2] that work functions obey a periodic law. The present paper indicates how this behavior not only permits successful prediction of the work function of unmeasured elements but also defines certain trends of data. As is the case for many physical properties, these trends and sequences in the periodic table are most useful for comparing and evaluating data and for planning research.

THE PREFERRED VALUES

The choice of preferred values for polycrystalline specimens is always complicated by the well-known variations among work functions published for each element. The variables include the purity of the specimen, the measurement method, and, in particular, the surface distribution of crystal facets. In general, the many years of research and of improvement in technique have now narrowed the variously reported measurements on a given element (with specified surface conditions) to within one-tenth or two-tenths of an electron volt. This margin of experimental error would seem to apply to the data in the Appendix. The rationale for assuming that a single value exists for each element requires that the polycrystalline specimen being measured have the same surface condition as that of materials commonly used in practice. In addition to polycrystalline data, the Appendix includes measurements on various crystal planes for 21 of the elements.

The compilation is the result of a search of *Physics Abstracts* and *Science Abstracts*, 1969 to 1976, and a subsequent comparative study of the original sources. The selection of values for each of element is based on

(1) the validity of experimental technique (e.g., use of background pressures of 10^{-9} Torr or lower, lack of surface contamination, and identification of crystal-face distribution and other surface conditions), and

(2) for those data published before 1969, the best general agreement with preferred values and theoretical values of the true work function (given variously by Fomenko,[4] Rivière,[3] and Trasatti[5]).

Certain limitations of the data must be recognized. Measurements made on the 19 elements before 1969 do seem acceptable and valid but some were not carried out in ultrahigh vacua and might have been affected by trace impurities. These data, therefore, are of unknown reliability and are underscored for the most part. Exceptions are W and Ta, which have been studied so thoroughly that hardly any question remains about their validity. In addition, the 1967 measurements on U were made under rigorous experimental conditions. The method of measurement deserves attention for any given element, as pointed out in detail by Rivière.[3] The thermionic method, for example, does not give the absolute value for polycrystalline or other patchy surfaces, and the photoelectric method does not yield the true work function for semiconductors because the emission contains contributions of both volume and surface origin. Consequently some of the values listed must be accepted simply as being the best available and

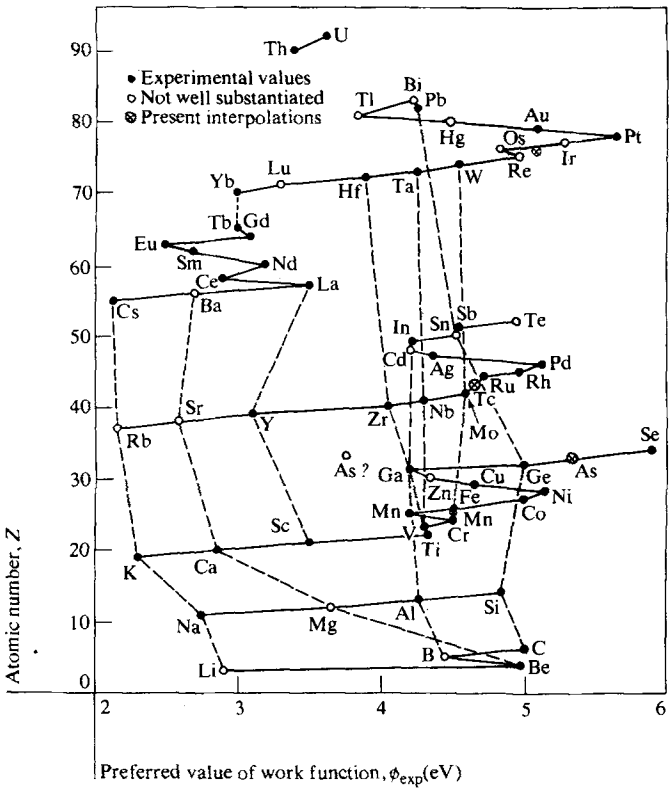

FIG. 1. Relation of experimental values of the work function to the periodic system of the elements. Solids lines correspond to rows in the table of the elements and dashed lines to columns.

not necessarily as absolute physical quantities. In particular, the recent data on As, Te, and Se are underscored because the photoelectric method was used.

There are several notable features of the Appendix. The value for Be, for example, is now known to be about 5 eV, as determined first by Dixon and Lott[6] and confirmed subsequently by Gustafsson *et al.*[7] Previously accepted values centered around 3.9 eV, the low values being due to mercury vapor contamination. Other measurements made on vapor-deposited pure elemental films under rigorous conditions[8] give values higher than formerly accepted, by several tenths of an electron volt, for Co, Hf, Mn, Ni, Pt, and Ti. Included in that work[8] were also the first reported measurements on Sc, Y, and Eu. In addition, many new single-crystal data are cited from 17 sources since 1969.

TABLE I. Experimental confirmation of work-function data predicted by interpolation between neighboring elements in the periodic table.

Element	Predicted value (eV) (Ref. 2)	Measured value (eV)
Y	3.3	3.1 (Ref. 8)
Sc	3.3	3.5 (Ref. 8)
In	4.0	4.08 (Ref. 9) 4.12 (Ref. 10).

DATA TRENDS IN THE PERIODIC TABLE

The periodicity in the work functions of elementary solids is somewhat similar to the periodicity of the electronic structure of atoms. As might be expected, in each period of the table of the elements, work-function values ϕ tend to rise with increasing atomic number Z, as electron shells and subshells gradually become filled in successive atoms. The relation between ϕ and Z becomes complex in the intervals occupied by the transition metals, as indicated in Fig. 1. Regardless of the complexity of the curve the same data, when arranged in a periodic chart (Table II), show some fairly regular features. The quantities in each row and column are sequences that permit interpolation, in both hori-

TABLE II. Periodic system of the elements, with work function ϕ_{exp} in electron volts. Data are for polycrystalline specimens.

IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA
3	4											5	6			
Li	Be											B	C			
2.9	4.98											4.45	5.0			
11	12											13	14	15	16	
Na	Mg											Al	Si	P	S	
2.75	3.66											4.28	4.85	. . .	. . .	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
2.30	2.87	3.5	4.33	4.3	4.5	4.1	4.5	5.0	5.15	4.65	4.33	4.2	5.0	3.75	5.9	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
2.16	2.59	3.1	4.05	4.3	4.6	. . .	4.71	4.98	5.12	4.26	4.22	4.12	4.42	4.55	4.95	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
2.14	2.7	3.5	3.9	4.25	4.55	4.96	4.83	5.27	5.65	5.1	4.49	3.84	4.25	4.22	. . .	
87	88	89	90	91	92											
Fr	Ra	Ac	Th	Pa	U											
. . .	. . .	. . .	3.4	. . .	3.63											
			58	59	60	61	62	63	64	65	66	67	68	69	70	71
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			2.9	. . .	3.2	. . .	2.7	2.5	3.1	3.0	. . .	. . .	. . .	. . .	. . .	3.3
			90	91	92	93										
			Th	Pa	U	Np	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
			3.4		3.63											

TABLE III. Preferred values of the electron work function. (See explanation in the Appendix.)

Element	ϕ (eV)	Expt. method	Ref.
Ag	4.26	P	14
	4.64 (100)	P	14
	4.52 (110)	P	14
	4.74 (111)	P	15
Al	4.28	P	16
	4.41 (100)	P	17
	4.06 (110)	P	16
	4.24 (111)	P	17
As	3.75 (111)	P	11
Au	5.1	P	8
	5.47 (100)	P	18
	5.37 (110)		18
	5.31 (111)		18
B	4.45	T	19
Ba	2.7	T	20
Be	4.98	P	7
Bi	4.22	P	21
C	5.0	CPD	22
Ca	2.87	P	23
Cd	4.22	CPD	24
Ce	2.9	P	8
Co	5.0	P	8
Cr	4.5	P	8
Cs	2.14	P	25
Cu	4.65	P	9
	4.59 (100)	P	26
	4.48 (110)	P	26
	4.98 (111)	P	26
	4.53 (112)	P	26
Eu	2.5	P	8
Fe	4.5	P	8
	4.67 (100)	P	27
	4.81α (111)	P	28
	4.70α	P	29
	4.62β	P	29
	4.68γ	P	29
Ga	4.2	CPD	30
Ge	5.0	CPD	31
	4.80 (111)	P	32
Gd	3.1	P	8
Hf	3.9	P	8
Hg	4.49	P	33
In	4.12	P	10
Ir	5.27	T	34
	5.42 (110)	FERP	35
	5.76 (111)	FERP	35
	5.67 (100)	F	36
	5.00 (210)	F	36
K	2.30	P	37
La	3.5	P	8
Li	2.9	F	38
Lu	3.3	CPD	39
Mg	3.66	P	40
Mn	4.1	P	8
Mo	4.6	P	8
	4.53 (100)	P	41
	4.95 (110)	P	41
	4.55 (111)	P	41
	4.36 (112)	P	41
	4.50 (114)	P	41
	4.55 (332)	P	41
Na	2.75	P	42
Nb	4.3	P	8
	4.02 (001)	T	43
	4.87 (110)	T	43
	4.36 (111)	T	43
	4.63 (112)	T	43
	4.29 (113)	T	43
	3.95 (116)	T	43
	4.18 (310)	T	43
Nd	3.2	P	8
Ni	5.15	P	8
	5.22 (100)	P	44
	5.04 (110)	P	44
	5.35 (111)	P	44
Os	4.83	T	34
Pb	4.25	P	49
Pd	5.12	P	36
	5.6 (111)	P	45
Pt	5.65	P	8
	5.7 (111)	P	45
Rb	2.16	P	33
Re	4.96	T	34
	5.75 (1011)	F	38
Rh	4.98	P	36
Ru	4.71	P	36
Sb	4.55 (amorph.)	. . .	46
	4.7 (100)	. . .	47
Sc	3.5	P	8
Se	5.9	P	48
Si	4.85n	CPD	49
	4.91p (100)	CPD	50
	4.60p (111)	P	51
Sm	2.7	P	8
Sn	4.42	CPD	52
Sr	2.59	T	53
Ta	4.25	T	34
	4.15 (100)	T	54
	4.80 (110)	T	54
	4.00 (111)	T	54
Tb	3.0	P	55
Te	4.95	P	48
Th	3.4	T	56
Ti	4.33	P	8
Tl	3.84	CPD	57
U	3.63	P, CPD	58
	3.73 (100)	P, CPD	59
	3.90 (110)	P, CPD	59
	3.67 (113)	P, CPD	59
V	4.3	P	8
W	4.55	CPD	60
	4.63 (100)	FERP	35
	5.25 (110)	FERP	35
	4.47 (111)	FERP	35
	4.18 (113)	CPD	61
	4.30 (116)	T	62
Y	3.1	P	8
Zn	4.33	P	21
	4.9 (0001)	CPD	63
Zr	4.05	P	8

zontal and vertical directions, of missing data. The sequences are also the basis for empirical relations.

These trends were observed in 1950,[2] at a time when published data were less reliable than now because of surface contamination of the specimens. Nevertheless, even at that time obvious trends in the existing data justified predictions for three elements that were later confirmed by measurements within 0.2 eV, as shown in Table I. Because the Appendix is a considerable refinement over the 1950 data, it should offer a firmer basis for extrapolations for other elements.

The method is used here to examine data for three metals on which very few measurements have ever been published, and thus have little confirmation by other workers. These elements are Os, As, and Mn.

First we consider As. Like most elements, As is situated in a fairly regular sequence of incremental change across its row and also down its column, as can be seen in Table II. The only modern measurement for As, in 1975,[11] is for the (111) plane. Disregarding this value for the moment, we make one estimate (5.4 eV) by interpolation in the row and another (4.9 eV) by extrapolation in the column. An older measurement of 5.11 eV, published by Schulze,[12] falls within this range of 4.9 to 5.4 eV and may fortuitously be correct, even though Schulze did not use a ultrahigh vacuum technique.

Cross interpolation for Os yields 5.0 or 5.1 eV instead of the 4.83 value listed in the Appendix. Interpolation for Mn gives 4.5 eV instead of the measured 4.1 eV. From these estimates it would seem that further experimental studies of As, Os, and Mn would be worthwhile.

One of the unmeasured elements, technetium (No. 43), can be estimated at 4.7 eV by inspection in Fig. 1 or by cross interpolation in Table II. This estimate seems quite reasonable from another point of view. From theoretical calculations based on bond energies, Trasatti[13] determined the work determined the work function of Tc to be 4.88 eV, which differs from the current estimate by only 3.8%.

CONCLUDING REMARKS

The compilation of newly published values of the work function is the result of a search of the recent literature and critical examination of the data. A number of older values are included because they are generally accepted by workers in the field. Those elements that were not studied with a modern ultrahigh vacuum technique nor with precise determination of surface structure are identified as data "of unknown reliability". Most seem valid, however, and are included to provide a comprehensive view of work-function data.

The compilation was used in a new study of the work function in terms of a periodic law. Our predictions for Sc, Y, and In, made in 1950, were later confirmed to within 0.2 eV by published experimental data. Present estimates are As = 5.2 eV; Os = 5.1 eV; Mn = 4.5 eV; and Tc (as yet unmeasured) = 4.7 eV.

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APPENDIX

Preferred values of the electron work function are given in Table III. (Numbers which are underscored may be valid but are of unknown reliability because they are not confirmed by any measurements made in recent years with ultrahigh vacuum technique.)

Crystallographic directions for single-crystal data are indicated in parentheses.

Abbreviations apply to the experimental method: T, thermionic; P, photoelectric; CPD, contact potential difference; F, field emission; FERP, field emission-retarding potential. Important distinctions among such measurements are discussed in the Rivière paper (Ref. 3, pp. 180–198).

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