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Estimation of Physical Properties of Transition Metals Based on a Configuration Model of Solids **

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A new empirical formula for estimation of the entropy S°_{298} of transition metals is suggested. On the basis of this formula some equations that enable calculation of other physical properties, for example density and molar heat capacity, have been derived.

(Keywords: Configuration model of solids; Physical properties; Transition metals)

Die Abschätzung physikalischer Eigenschaften von Übergangsmetallen auf der Grundlage eines Konfigurationsmodells von Festkörpern

Es wird eine neue empirische Formel zur Abschätzung der Entropie S°_{298} von Übergangsmetallen vorgeschlagen. Auf der Basis dieses Ansatzes wurden weitere Gleichungen abgeleitet, die die Berechnung weiterer physikalischer Eigenschaften — etwa Dichte und molare Wärmekapazität — ermöglichen.

Introduction

A method of empirical determination of physical properties of materials is often used in physical chemistry [1, 2]. Thus, for example,

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Karapetyants [3] offers a formula for estimation of entropy. *Filippin* [4] developed a new method for an approximate estimation of entropy of compounds belonging to the same type. Having used a configuration model of solids [5, 6], we proposed an empirical equation for estimation of physical properties characterizing some transition metals. The application of our equation for estimation of some properties of these transition metals is discussed in this paper.

Results and Discussion

New Empirical Formula for Estimation of Entropy

The systematic analysis of the basic parameters of a configurational model of matter [5, 6] showed that the entropy of the elements depends on the statistical weight of atomic stable d^5-configuration (SWASC d^5) of the d-transition metals (W) and the quantity of localized electrons (I). On the basis of that fact we propose the following empirical equation:

$$S^\circ_{298} = A \cdot \ln (I \cdot W \cdot M) + B \tag{1}$$

where M is the molecular mass, A and B are constants (J/mol K).

Table 1 presents the values of constants A and B of some transition elements. The values for I and W we used from [5, 6] (Table 2) and the values for S°_{298} and M from the [8–10].

It is interesting to note that the values characterizing constants A and B for the same group of elements of the periodic system, as presented in Table 1, are the same.

Table 1. *The values of constants A and B of some transition elements (J/mol K)*

Constant	V; Nb; Ta	Fe; Ru; Os	Ni; Pd; Pt
A	6.685	3.780	5.254
B	− 32.592	− 11.015	− 15.499

Estimation of Density and Molar Heat Capacity

Using the dependence (1), the physical properties of some transition metals such as density and molar heat capacity can be determined.

I. *Density.* It is well known [4] that the dependence of entropy on molecular mass (M) and material density (d) can be expressed as follows:

$$S^{\circ}_{298} = k \cdot \ln \frac{M^2}{d} + n \tag{2}$$

where k and n are constants.

Having equalized the equation (1) and (2) an expression characterizing the dependence of density on SWASC and quantity of localized electrons was obtained:

$$d = N \cdot M^2/(I \cdot W \cdot M)^{A/k} \tag{3}$$

where $$N = \exp\left[(n - B)/k\right]$$

On the other hand, the density can be determined as follows:

$$d = 1.66 \frac{M \cdot Z}{V} \tag{4}$$

where d is the X-ray density, Z is the quantity of atoms in an elementary cell and V is the unit cell volume.

Table 2. *Statistical weight of atomic stable configuration of some transition metals* [5, 6]

Element	Configuration of valence electrons	Total localized part of electrone (I)	SWASC (W) (%)		
			d^0	d^5	d^{10}
V	$3d^3 4s^2$	3.2	37	63	0
Nb	$4d^4 5s^1$	3.8	24	76	0
Ta	$5d^3 6s^2$	4.1	19	81	0
Fe	$3d^6 4s^2$	7.3	0	54	46
Ru	$4d^7 5s^1$	6.0	0	80	20
Os	$5d^6 6s^2$	5.8	0	84	16
Ni	$3d^8 4s^2$	9.4	0	12	88
Pd	$4d^{10} 5s^0$	9.1	0	18	82
Pt	$5d^9 6s^1$	8.0	0	40	60

Using equations (3) and (4) and knowing the constants A and B, the constants k and n can be determined. The same is possible as constants A and B have equal values for a certain subgroup of transition elements of the periodical system of Elements. On this basis three equations can be derived allowing to determine values for k and n.

II. *Molar heat capacity.* The empirical formula for estimation of entropy, in case when a molar heat capacity (C_p) is known, will have the following form [3, 7]:

$$S^{\circ}_{298} = L \cdot C_p \cdot \ln M + f \tag{5}$$

where L and f are constants.

When equalizing equations (1) and (5) the following dependence is obtained:

$$C_p = \frac{1}{\ln M} a \cdot \ln (I \cdot W \cdot M \cdot) + b \tag{6}$$

where $a = A/L$ and $b = (B - f)/L$.

In case when the constants a and b (Table 3) are known, and using the equation (6), the molar heat capacity of transition elements can be calculated.

Table 3. *The values of the constants a and b of some transitions elements (J/mol K)*

Constant	V; Nb; Ta	Fe; Ru; Os	Ni; Pd; Pt
a	19.661	20.520	13.472
b	− 85.506	− 106.638	− 13.110

Comparison of Experimental and Calculated Values of Density, Entropy and Molar Heat Capacity

Using the equations (1), (3), and (6) the values characterizing entropy, density and molar heat capacity are calculated and given in Table 4. The experimental values for the same elements [8–10] are simultaneously given with the above mentioned ones.

The results obtained show that utilization of the empirical formula (1) for estimation of entropy gives results that are in good agreement with experimental data.

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Table 4. *Experimental (exp) and calculated (calc) values of entropy, density and molar heat capacity of some transition elements*

Element	S°_{298} (J/mol K)			d(g/cm^3)			C_p (J/mol K)		
	exp	calc	relative error (%)	exp	calc	relative error (%)	exp	calc	relative error (%)
V	29.52	29.16	1.21	6.091	6.062	0.47	24.70	24.45	1.02
Nb	34.80	55.58	2.25	8.630	8.752	1.41	24.89	25.37	1.94
Ta	41.40	40.97	1.03	16.623	16.471	0.91	25.40	25.17	0.91
Fe	21.18	26.79	1.45	7.872	7.921	0.62	25.02	24.50	2.08
Ru	28.90	29.77	3.02	12.437	12.118	2.56	23.85	24.86	4.25
Os	32.70	32.22	1.46	22.581	23.034	2.01	24.89	24.40	1.97
Ni	29.88	30.73	2.83	8.897	8.113	8.81	25.77	25.88	0.45
Pd	37.30	35.81	3.99	12.038	14.025	16.50	25.52	25.38	0.55
Pt	41.87	42.51	1.53	21.470	20.208	5.88	25.69	25.72	0.13

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