ESTIMATION OF ABSOLUTE COHESION ENERGIES OF Zn AND Cd IN MATERIALS

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Abstract

The basic property of Zn and Cd metals is to estimate absolute cohesion energies in materials, to measure the intermolecular energies of Zn and Cd metals and to study the majority of their physical properties. In the present study the absolute values of cohesive energy of Zn and Cd metals in liquid and solid has been reported. The melting point of metals was used as another correlation parameter with the reference value. As a simplified result it has been found that the cohesion energy of solid metals at 0 K can be calculated by dividing the melting point of the metal. In this paper accurate data is taken from the literature to study the structural differences between solid and liquid metals. The concept of absolute cohesion energies is suggested to explain the perfection of pure metals and the metallic atoms of different elements in a gas or liquid.

Key words: Cohesion Energy of metals, Binding Energy, Absolute Scale, Correlation and Melting Point.

INTRODUCTION

Cohesive energy is one of the most important physical quantities that quantify the thermal stability of the materials such as melting temperature, boiling temperature, solubility etc. It has been well established both experimentally and theoretically that the cohesive energy and the melting temperature of nanoparticles with relatively free surface decreases with decreasing particle size. The major reason for that is there are no straight forward experimental or theoretical methods to obtain the absolute value of the cohesion energy. Cohesion energy is basic energetic property of metals, influencing the majority of their other physical properties. The cohesion energy of solid and liquid metals is energy connecting atoms in the solid and/or liquid state. Although any change in the state of the matter is perfectly described by the Gibbs energy change accompanying this process, the cohesion energy in Zn and Cd metals would require an absolute scale. The binding or cohesive energy ε_c of a substance is the energy required to break all the bonds associated with one of its constituent molecules. It is, therefore a measure of the inter-molecular energy for a substance. We know that intra-molecular bonds that hold atoms together in a molecule (e.g. the O-H

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bond in water) are generally much stronger than inter-molecular bonds. This means that the thermal energy of H_2O even at high temperature is not enough to break the intra-molecular bonds, thus implying that these intra-molecular bonds are stronger than those holding the substance together.

According to chemical thermodynamics, the heat of formation of pure elements in their most stable state is taken equal zero. Thus, the heat of formation of all solid metals is zero at 298.15 K and 1 bar. Consequently, the ideal gas of all metals at 298.15 K and 1 bar is characterized by some positive values of the heat of formation. Therefore, using formal logic, the heat of sublimation of metals should be characteristic to the energy of broken bonds in the solid or liquid phase, as in ideal gas such bonds do not exist. Therefore, the classical equation to calculate the cohesion energy in Zn and Cd metals at 0 K can be written as:

$$U^c_{coh(s.ok)} = \Delta_f H^o_{s(ok)} = \Delta_f H^o_{g(ok)} \qquad (1)$$

Where $-\Delta_f H^o_{g(ok)}$ - the enthalpy of formation of gaseous metals at 0 K (kJ/mol),

$\Delta_f H^o_{s(ok)}$ - the enthalpy of formation of solid metals at 0 K (kJ/mol).

It is often used as a correlation parameter for different physical properties in the scientific literature [1]. In the text books on material science cohesion energy or binding energy metals is usually considered only qualitatively, without the values of the binding energies [2-9]. However, the various properties of metals described mostly phenomenological way, without an attempt to make the bridge between them, using the concept of binding energies. In relation to ionic crystals, where the concept has been found more useful in explaining certain trends in properties of this class of materials. It is also important to remember, that for ionic crystals the definition of the cohesion energy is more sophisticated than that given by Eq.(1). Moreover, the values of cohesion energies calculated from thermodynamic Born-Haber cycle is in fairly good agreement with calculations based on the simplest energetic model of ionic crystals. One of the possible and elegant ways 'around the problem' is to scale the cohesion energy by some macroscopic properties of the material [10-11], such as melting point and molar volume at 0 K. Although the absolute values of the cohesion energies are lost in this way, the potential to apply the concept of cohesion

is saved, using a relative scale. However, the stability of gaseous atoms themselves of different elements is different, due to the different stability of their outer electron shells.

The literature values of cohesion energies of solid metals at 0 K and liquid metals at their melting point are collected and shown in table-1. It is suggested to use these tables to search for correlations between different properties of metals and cohesion energies. Empirical constants found in this way between different properties and the cohesion energy can be rationalized and compared with 'absolute' theories.

Table -1 Literature Values of Cohesion Energies of Solid Metals

Metal	(U coh. s.0K)	Tm. K	(U coh. l.0K. corr)	Tm. K	(U coh. s.0K. corr)	Tm. K
Zn	129.467	6927	171.46	6927	194.97	6927
Cd	111.000	594	147.03	594	167.07	594
Hg	62.418	234.29	57.99	234.29	65.70	234.29
Cu	336.236	1358	336.14	1358	383.66	1358
Ag	283.484	1234	305.45	1234	348.75	1234
Au	368.034	1338	331.19	1338	379.05	1338
Ni	427.828	1728	427.72	1728	497.76	1728
Pd	375.594	1825	451.73	1825	520.03	1825
Pt	563.428	2045	506.19	2045	584.70	2045

Let us present this controversies on the example of the dependence of the melting points of metals on cohesion energy by Eq.(1) (see Fig.1), especially that melting point was suggested and successfully applied by Beke et al. [10-11] in correlation of some properties of metals. The two metals have the same crystal structure (hcp for Zn and hcp for Cd). Therefore, the 'contradiction' is obviously explained by different electron structures of metals in the Zn and Cd metals. For 'normal' metals without extra stability of gaseous atoms the electron affinity has a negative value, while for metals with extra stable electron configuration in gaseous state the electron affinity is positive (Zn and Cd, i.e. the $3d^{10}4s^2$ and $4d^{10}5s^2$ metals). It's observed from Fig 1 the cohesive energy increases as a function of melting point of the Zn and Cd metals. The cohesive energy of the Zn metals was found to be 678.3178K and the cohesive energy of the Cd metals was found to be 608.888K.
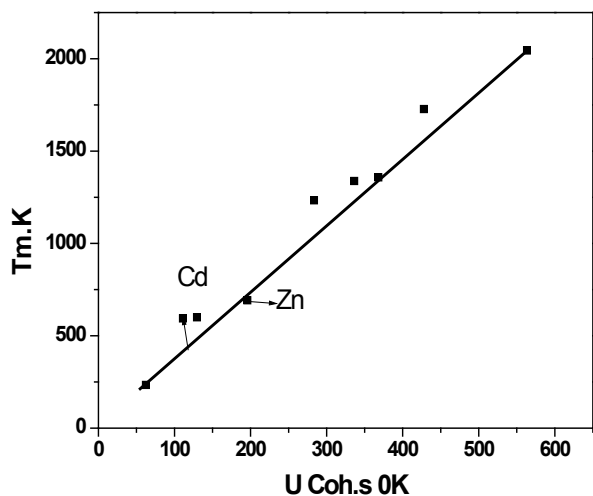
Fig.1 Melting Point of Metals as a Function of Their Cohesion Energy of Defined by Eq.1

Estimation of Cohesion Energy for Zn and Cd metals

In order to make the absolute scale for the cohesion energy of metals, one single liquid metal should be chosen with known well measured value of the surface tension and molar volume at the melting point, i.e. with well known value of parameter. Using the theoretical coefficient 0.172, the absolute value of the cohesion energy for this metal can be found. From this value, the proportionality constant between the cohesion energy of liquid metals and the melting point of metals can be found.

First, a liquid 'reference' metal should be chosen, having the following properties

i.   not corrosive,

ii. not sensitive to oxidation,

iii. normal metal', i.e. having an fcc structure in solid state, with no allotropes at 1 bar,

iv. having well established data for surface tension and molar volume in liquid state.

The theoretical proportionality constant between the melting point and the cohesion energy of the liquid at its melting point can be found from the value for Zn and Cd. In the first approximation, the same slope can be used to find absolute values of cohesion energies of other liquid metals at their melting points, as well:

$$U^{o}_{coh(1Tm)} \equiv \frac{Tm}{4.04} \quad (2)$$

with T_m in [K] and U_{coh} in [kJ/mol].

Once the cohesion energies for liquid metals are estimated by Eq.(1), the cohesion energies of solid metals can be re-calculated by Eq.(2). In this way, the cohesion energy of two solid metals with the same melting point, but different structures will be different, as the melting entropy is a structure sensitive property.

As an example, for Al one can find: $U^{o}_{coh(1,Tm)}$ = 933/-4.04 = -230.9 kJ/mol, $U^{o}_{coh(s,OK)}$ = -263.6kJ/mol. This value is more positive by 20%, compared to the classical value of -327 kJ/mol. For Mg: $U^{o}_{coh(1,Tm)}$ = 922/-4.04 = -228.2 kJ/mol. $U^{o}_{coh(s,OK)}$ = -259.6kJ/mol. This value is more negative by 78% compared to the classical value. Hence, the value for Zn with extra high stability of the gaseous atom was shifted to the negative direction much more, than the value of Al was shifted to the positive direction, with obviously somewhat higher than the average instability of gaseous atoms.

In Fig.2 the dependence of parameter on the corrected values of the cohesion energy is shown. One can see that for low-cohesion energy metals the data points are situated around the ideal line with a scatter normal to surface tension of metals. For high cohesion energy metals, however, the ideal line is significantly above the measured points. This might be the indication that the surface tension of high melting point metals is still known with not a sufficient accuracy, due to difficult measurements and to the role of adsorbed oxygen. It is observed from Fig 2 the cohesive energy of the Zn metal was found to be 1249.836 K and the cohesive energy of the Cd metals was found to be 618.0676K.
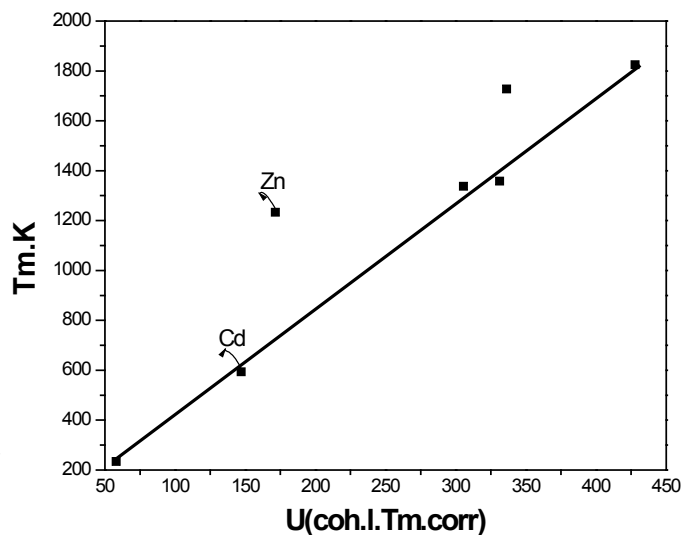

Fig.2 Dependence of Parameter on the Corrected Cohesion Energy of the Liquid Metals

In Fig.3 the correlation between the corrected cohesion energy at 0 K for solid metals and the melting point is shown. The correlation is 'too good', but this is due to Eq.(2). However, it can be seen that the scatter of maximum 5 kJ/mol is still present, due to the structural differences between different solid metals. From Fig.3 one can see that any correlation given in the literature between properties of metals and their melting point, can be converted into the more sensible correlation between those properties and the cohesion energy in metals. 'Theoretical' proportionality constant values have been established between the melting point and the cohesion energy of solid metals at 0 K (see Fig.3). It is observed from Fig.3 the cohesive energy of the Zn metal was found to be 1236.080 K and the cohesive energy of the Cd metals was found to be 590.5567K.
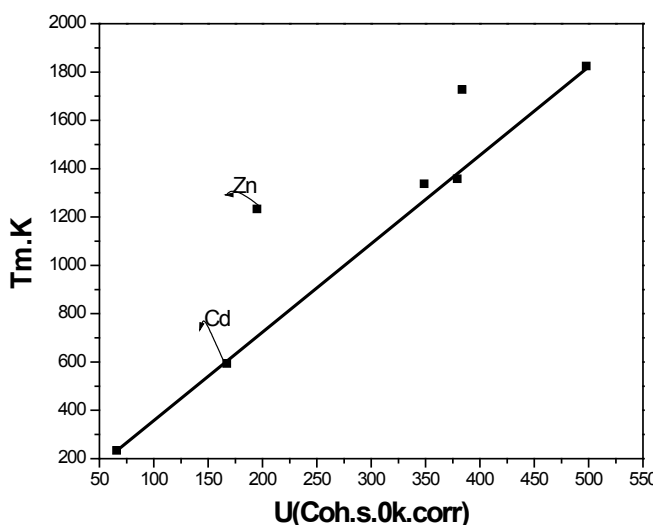

Fig.3 Correlation between the Corrected Cohesion Energy Values of Solid Metals at 0 K and Melting Point of Metals

CONCLUSION

The absolute cohesion energy of pure solid and liquid Zn and Cd metals has been constructed using the collection of their melting point and their values were found to be, for solid Zn= 678.3178K and for Cd=608.888 K, for liquid correlation Zn=1249.836K, Cd=618.0676K, for solid correlation Zn=1236.080K,Cd=590.5567 K. The table of absolute cohesion energies of pure solid and liquid metals are discussed, based on the surface tension of liquid noble metals, the melting point of metals was used as a correlation

parameter. Empirical constants found in this way between different properties and the cohesion energy can be rationalized and compared with absolute theories.

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