

# Correlation of Thermodynamic Properties with Structure, Bonding & Physical Properties of Groups II-VI Compounds

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## ABSTRACT

Thermodynamic properties of groups II-VI compounds have been discussed in the light of their structure, bonding, ionicity, energy gap, bond length, molecular weight, etc. An attempt has also been made to correlate various thermodynamic and physical properties of the compounds. The interrelationship between thermodynamic and physical properties have been discussed, wherever possible, with realistic justification.

## 1. INTRODUCTION

Group II B elements (zinc, cadmium and mercury) combine with the elements (sulphur, selenium and tellurium) of group VI A to form nine compounds of equiatomic composition. These binaries belong to the family of semiconductors, and are generally designated as groups II-VI compounds. These compounds are important semiconductor materials due to their applications in various electronic, optoelectronic and photoelectric devices. Some compounds of this family are potential candidates for infrared detectors used in military applications. Research on these compounds is mainly concerned with their physical and electronic properties; their thermodynamic properties have not been systematically investigated. The available thermodynamic data shows wide disagreement, inconsistencies and error limits. Because the knowledge of accurate and reliable thermodynamic data is of considerable importance for the growth of semiconducting crystals and for understanding of their stability

against changing environment, the thermodynamic properties of groups II-VI compounds have recently been precisely measured employing two independent techniques, namely, electrochemical and calorimetry<sup>1-8</sup>. Since the thermodynamic properties of semiconducting compounds play an important role in device development and fabrication, it is worthwhile to discuss the thermodynamic properties in terms of structure, stability, bonding and other physical parameters. In the present study, an attempt has been made to correlate, wherever possible, various

## 2. STRUCTURE & BONDING

Groups II-VI compounds crystallise either in zinc blende (*ZnS*, *ZnSe*, *ZnTe*, *CdTe*, *HgS*, *HgSe* and *HgTe*) or wurtzite (*ZnS*, *CdS* and *CdSe*) structure. In either case of the structural arrangements of the compound (say AB), each A (or B) atom is tetrahedrally surrounded by four B (or A) atoms. In

the zinc blende structure, each A (or B) atom has four nearest neighbours of B (or A) atoms at the equal distance of  $\frac{\sqrt{3}}{4}a$  at the corners of a regular tetrahedron, where  $a$  is the cubic lattice parameter. In the wurtzite arrangement, each A atom is bonded to four B atoms, approximately at the corners of tetrahedron<sup>9</sup>, one at the distance  $uc$  and three at  $\sqrt{\frac{1}{3}a^2 + c^2(\frac{1}{2}-u^2)}$ , where  $c$  and  $a$  are the hexagonal lattice parameters. In the ideal wurtzite structure (i.e.  $u = 0.375$  and  $c/a = 1.633$ ), all the bond lengths are equal. For a given coordination number, the bond length or interatomic distance ( $l_{AB}$ ) between nearest neighbours can be taken as sum of the component radii<sup>10</sup>,  $r_A$  and  $r_B$ . Thus, lattice parameters of a tetrahedral compound can be calculated from the component radii. The lattice parameters and bond length of groups II-VI compounds as estimated from tetrahedral covalent<sup>11</sup> and ionic<sup>12</sup> radii of the component elements have been listed in Table 1. For comparison, experimental values of lattice constants have also been incorporated in the table and it clearly indicates that experimental values of lattice constants are in excellent agreement with those calculated from the covalent component radii of the compounds. The wide disagreement of estimated lattice constants based on the ionic radii with the

experimental values reflects the poor ionic nature of groups II-VI compounds.

Table 1. Lattice constants

Compound	Experimental		Calculated			
	Lattice parameter (Å)	Bond length <sup>†</sup> (Å)	Covalent radii		Ionic radii	
					Lattice parameter (Å)	Bond length (Å)
ZnS (ZB)	$a = 5.426$	2.35			$a = 5.672$	2.42
ZnSe (ZB)	$a = 5.667$	2.45			$a = 5.958$	2.58
ZnTe (ZB)	$a = 6.069$	2.63			$a = 6.489$	2.81
CdS (W)	$a = 4.134$ $c = 6.711$	2.52			$a = 4.327$ $c = 7.067$	2.65
CdSe (W)	$a = 4.290$ $c = 6.994$	2.62	(Å)	(Å)	$a = 4.589$	2.81
	$a = 6.438$		$a = 5.427$	2.35	$c = 7.493$	
	$a = 5.851$		$a = 5.658$	2.45	$a_1 = 7.021$	3.04
	$a = 6.084$		$a = 6.074$	2.63	$a = 6.466$	2.78
	$a = 6.386$		$a = 4.115$	2.52	$a = 6.813$	2.94
		$c = 6.720$		$a = 7.344$	3.17	
		$a = 4.278$	2.62			

**Table 2. Standard enthalpy of formation of groups II-VI compounds at 298 K**

Compound	$\Delta H^\circ$ (kJ/mol)		
	Experimental	Pauling (ionic)	Phillips (spectroscopic)
ZnS	204.6	156.3	176.1
ZnSe	177.6	123.5	166.5
ZnTe	119.0	48.3	108.4
CdS	153.3	123.5	149.8
CdSe	144.3	94.6	129.3
CdTe	103.6	30.9	105.0
HgS	53.3	69.5	68.6
HgSe	43.5	48.3	29.3
HgTe	36.5	7.7	42.7

experimental values<sup>1-8,14</sup> are also included in Table 2. There is wide disagreement between the experimental values of enthalpies of formation and those estimated from Pauling's equation for ionic compounds. This suggests that bonding in groups II-VI compounds is not substantially ionic. This discrepancy may be due to the presence of four resonating bonds in these compounds possessing tetrahedral structure because better agreement has been observed for compounds having single or double resonating bonds.

Phillips<sup>10</sup> improved the empirical formula for the calculation of enthalpy of formation by considering both ionicity and metallisation terms and presented the following expression based on spectroscopic data:

$$\Delta h_{AB}^\circ = \Delta h^K f_i \left( \frac{d_{Ge}}{d_{AB}} \right)^3 \left( 1 - b \left[ \frac{E_g}{\bar{E}} \right]_{AB}^2 \right) \quad (2)$$

where  $f_i$  is Phillips' ionicity of the bond A-B,  $d$  the bond length of the compound AB relative to  $Ge$ , the parameters,  $b = 0.05$  and  $\Delta h^K = -287$  kJ/mol;  $E_g$  represents the energy gap between bonding and anti-bonding states and  $\bar{E}$  is given by

$$\bar{E} = \frac{1}{2}(E_0 + E_1) \quad (3)$$

**Table 3. Standard entropy of groups II-VI compounds at 298 K**

Compound	$-\Delta S^\circ$ (J/K/mol)	
	Experimental	Theoretical (ionic)
ZnS	58.2	66.5
ZnSe	70.5	93.3
ZnTe	78.4	96.2
CdS	72.0	74.9
CdTe	84.7	101.7
CdSe	97.3	104.6
HgS	82.4	85.4
HgSe	100.8	112.1
HgTe	104.9	115.1

where  $E_0$  and  $E_1$  are the orbital energies, averaged over spin-orbit split multiples. The enthalpy of formation of these compounds as obtained by Eqn (2) has also been presented in Table 2. It is observed that for these compounds, the values predicted by Phillips spectroscopic formulation are in better agreement (compared to Pauling's formulation; Table 2) with those measured experimentally.

Latimer<sup>15</sup> proposed a method for calculation of the standard entropy of ionic compounds by adding the entropies of cationic and anionic constituent elements. The value of standard entropy of groups II-VI compounds, estimated by assuming the presence of electropositive elements (zinc, cadmium and mercury) as bivalent cations and electronegative elements (sulphur, selenium and tellurium) as bivalent anions, have been listed in Table 3 together with the experimental values. This table clearly indicates that the values of standard entropy due to ionic model are considerably higher than those based on the experimental data except in *CdS* and *HgS*. Thus, analysis of standard entropy further reflects the poor ionic character of the bond in groups II-VI compounds except for *CdS* and *HgS*.

#### 4. IONICITY, ENTHALPY OF FORMATION & ENERGY GAP

The ionic character of bond is also related with the electronic properties of semiconducting compounds. The more ionic crystals show larger

energy gap between the valence and the conduction bands. That is why more ionic crystals are less polarisable and associated with smaller dielectric constants. This is further associated with larger exothermic enthalpy of formation of compounds. Thus, it is quite relevant to search for quantitative value of ionicity in a given compound. Phillips<sup>10</sup> defined the ionicity as the fraction  $f_i$  of ionic character in the bond compared to fraction  $f_c$  of covalent character such as

$$f_i + f_c \quad (4)$$

Clearly in the elemental crystals like silicon and germanium,  $f_i = 0$  and  $f_c = 1$ . On the other hand, one needs the values for other semiconducting crystals. Two different theories are available for the quantitative calculation of ionicity in compounds. One theory is of Pauling<sup>11</sup> based on electronegativity of component elements and the other is of Phillips<sup>10</sup> based on band model. The values of ionicity for different compounds based on these theories are incorporated in Table 4 together with enthalpy of formation<sup>1-8,14</sup> and energy gap<sup>16</sup> of compounds. From the table it is clear that the values of ionicity obtained by two independent approaches differ widely. Pauling's values are much lower than the Phillips values. It has been observed from the table that Pauling's ionicity values show a systematic trend and are consistent with enthalpy of formation and energy gap. For the same homologous series of compounds the numerical values of ionicity, enthalpy of formation and energy gap increase with decrease of anion size [Table 4(a)] as well as cation size [Table 4(b)]. The increase of ionicity with decrease of cation size is inconsistent with the existing hypothesis of increase of cation formation tendency with increasing atomic number of element in a given group of the Periodic table. This discrepancy is presumably due to complicated role of successive ionisation energies in partially ionic compounds. On the other hand, Phillips' ionicity values show a very random trend. On the Phillips' scale, semi-metals (*HgSe* and *HgTe*) are more ionic than the *Zn-VI* compounds. Obviously, neither the

Table 4. Ionicity, enthalpy of formation and energy gap of groups II-VI compounds

Compound	Ionicity		$\Delta H^\circ$ (kJ/mol)	$E_g$ (eV)
	Pauling	Phillips		
	(a)			
<i>ZnS</i>	0.18	0.62	204.6	3.84
<i>ZnSe</i>	0.15	0.63	177.6	2.82
<i>ZnTe</i>	0.06	0.61	119.0	2.39
<i>CdS</i>	0.15	0.69	153.3	2.58
<i>CdSe</i>	0.12	0.70	144.3	1.84
<i>CdTe</i>	0.04	0.72	103.6	1.61
<i>HgS</i>	0.09	0.79	53.3	2.09
<i>HgSe</i>	0.06	0.68	43.5	sm
<i>HgTe</i>	0.01	0.65	36.5	sm
	(b)			
<i>ZnS</i>	0.18	0.62	204.6	3.84
<i>CdS</i>	0.15	0.69	153.3	2.58
<i>HgS</i>	0.09	0.79	53.3	2.09
<i>ZnSe</i>	0.15	0.63	177.6	2.82
<i>CdSe</i>	0.12	0.70	144.3	1.84
<i>HgSe</i>	0.06	0.68	43.5	sm
<i>ZnTe</i>	0.06	0.61	119.0	2.39
<i>CdTe</i>	0.04	0.72	103.6	1.61
<i>HgTe</i>	0.01	0.65	36.5	sm

sm - Semi-metal

Pauling's formulation nor the Phillips' formulation represents the true quantitative values of ionicity though Pauling's values are more justified. However, on the basis of analyses of structural, thermodynamic and energy gap data, the following balance opinion may be drawn: (i) bonding in groups II-VI compounds is neither substantially ionic nor covalent, and (ii) in a given homologous series of groups II-VI compounds, the ionicity increases with the decrease of atomic size of either of the component elements. This is further associated with increase of exothermic enthalpy of formation and energy gap of the compounds.

## 5. CORRELATION OF THERMODYNAMIC & PHYSICAL PROPERTIES

Table 5 lists the thermodynamic properties (at room temperature) of groups II-VI compounds along with their melting point, bond length, energy

gap, ionicity (based on Pauling's equation) and molecular weight. From the table it is clear that as the bond length increases within the same homologous series, the thermodynamic stability

and ionicity of the compound decreases. This is further associated with the decrease in negative value of the enthalpy of formation, melting point and energy gap of the compounds. Table 5(a) also

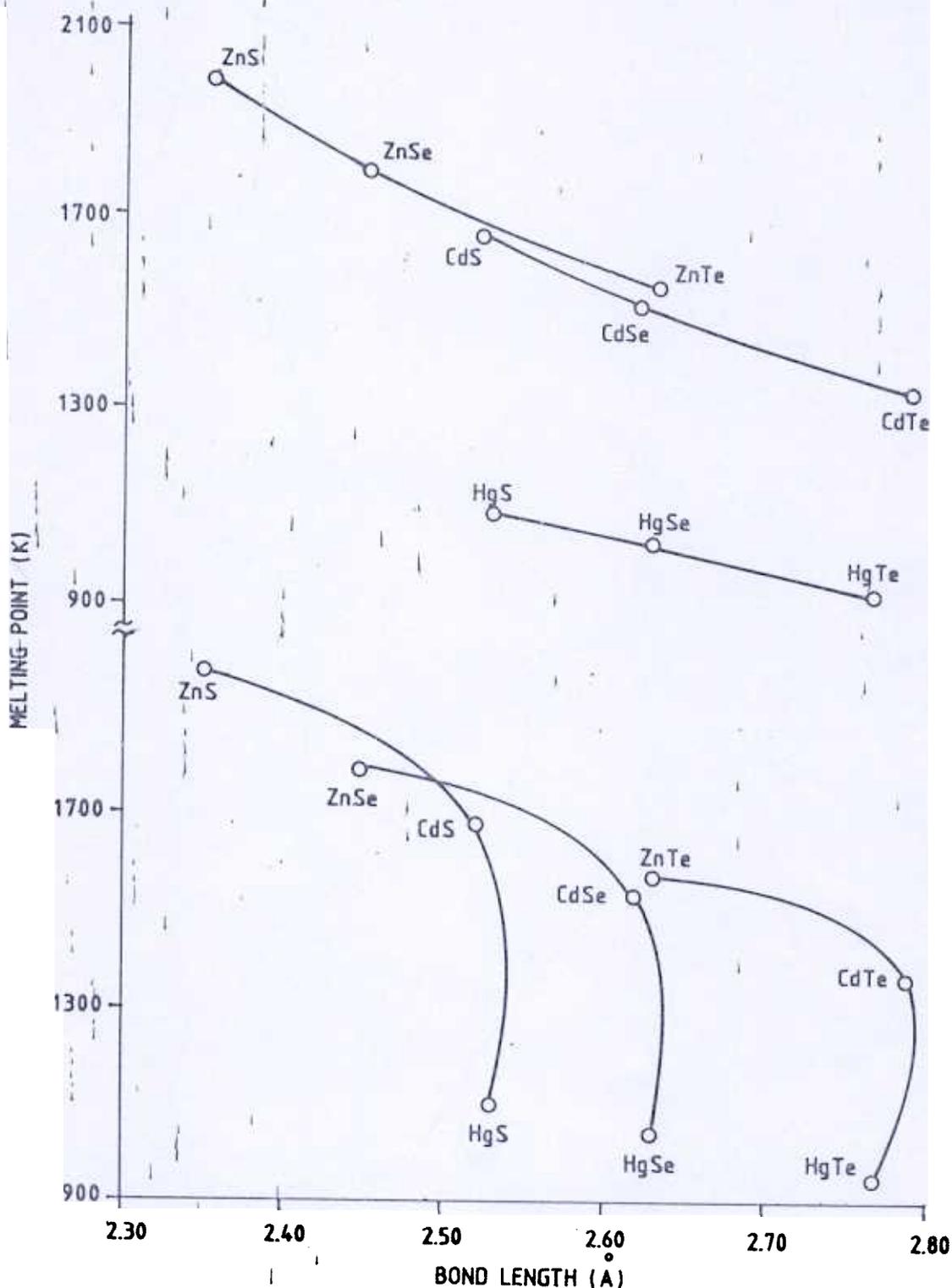


Figure 1. Plot of melting point with bond length

Table 5. Thermodynamic and physical properties of groups II-VI compounds

Compound	$-\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$S^\circ$ (J/K/mol)	Melting point (K)	Bond length (Å)	$E_g$ (eV)	Ionicity (Pauling's)	Molecular weight
(a)								
<i>ZnS</i>	200.0	204.6	58.2	1991	2.35	3.84	0.18	97.43
<i>ZnSe</i>	173.6	177.6	70.5	1799	2.45	2.82	0.15	144.33
<i>ZnTe</i>	115.2	119.0	78.4	1571	2.63	2.39	0.06	192.97
<i>CdS</i>	149.8	153.3	72.0	1678	2.52	2.58	0.15	144.46
<i>CdSe</i>	141.5	144.3	84.7	1537	2.62	1.84	0.12	191.36
<i>CdTe</i>	102.4	103.6	97.3	1365	2.79	1.61	0.04	240.00
<i>HgS</i>	45.8*	53.3	82.4	1098	2.53	2.09	0.09	232.65
<i>HgSe</i>	38.1*	43.5	100.8	1043	2.63	sm	0.06	279.55
<i>HgTe</i>	30.4	36.5	104.9	943	2.77	sm	0.01	328.19
(b)								
<i>ZnS</i>	200.0	204.6	58.2	1991	2.35	3.84	0.18	97.43
<i>CdS</i>	149.8	153.3	72.0	1678	2.52	2.58	0.15	144.46
<i>HgS</i>	45.8*	53.3	82.4	1098	2.53	2.09	0.09	232.65
<i>ZnSe</i>	173.6	177.6	70.5	1799	2.45	2.82	0.15	144.33
<i>CdSe</i>	141.5	144.3	84.7	1537	2.62	1.84	0.12	191.36
<i>HgSe</i>	38.1*	43.5	100.8	1043	2.63	sm	0.06	279.55
<i>ZnTe</i>	115.2	119.0	78.4	1571	2.63	2.39	0.06	192.97
<i>CdTe</i>	102.4	103.6	97.3	1365	2.79	1.61	0.04	240.00
<i>HgTe</i>	30.4	36.5	104.9	943	2.77	sm	0.01	328.19

sm – Semi-metal, \* – Estimated values

reveals that the value of exothermic enthalpy of formation increases, within the homologous series, with the increase of energy gap and melting point and with the decrease of standard entropy and molecular weight. On the other hand, standard entropy generally increases with the increase of molecular weight (i.e. atomic size of either of the component elements) and bond length (i.e. molecular size) and with decrease of thermodynamic stability, exothermic enthalpy of formation, melting point, ionicity and energy gap. The only exception is *HgTe* which does not follow the above trend of bond length when *Te* is kept constant in a homologous series [Table 5(b)]. Variation of melting point with bond length presented in Fig. 1 shows that when electro-positive element is kept constant in a homologous series, melting point decreases almost linearly with the bond length. However, linear variation is not observed when electronegative element

(i.e. group VI A) is kept constant though trend of variation remains the same except for *HgTe*.

A very interesting interrelationship between melting point and molecular weight has been observed in Fig. 2. This figure clearly shows that the melting point of compounds, within the homologous series when either of the component element is kept constant, decreases linearly with the molecular weight.

## 6. CONCLUSIONS

The thermodynamic properties of groups II-VI compounds have been analysed in terms of structure, bonding and other physical properties. It has been observed that bonding in groups II-VI compounds is neither substantially ionic nor covalent. In a homologous series of compounds, ionicity increases with decrease of atomic size of

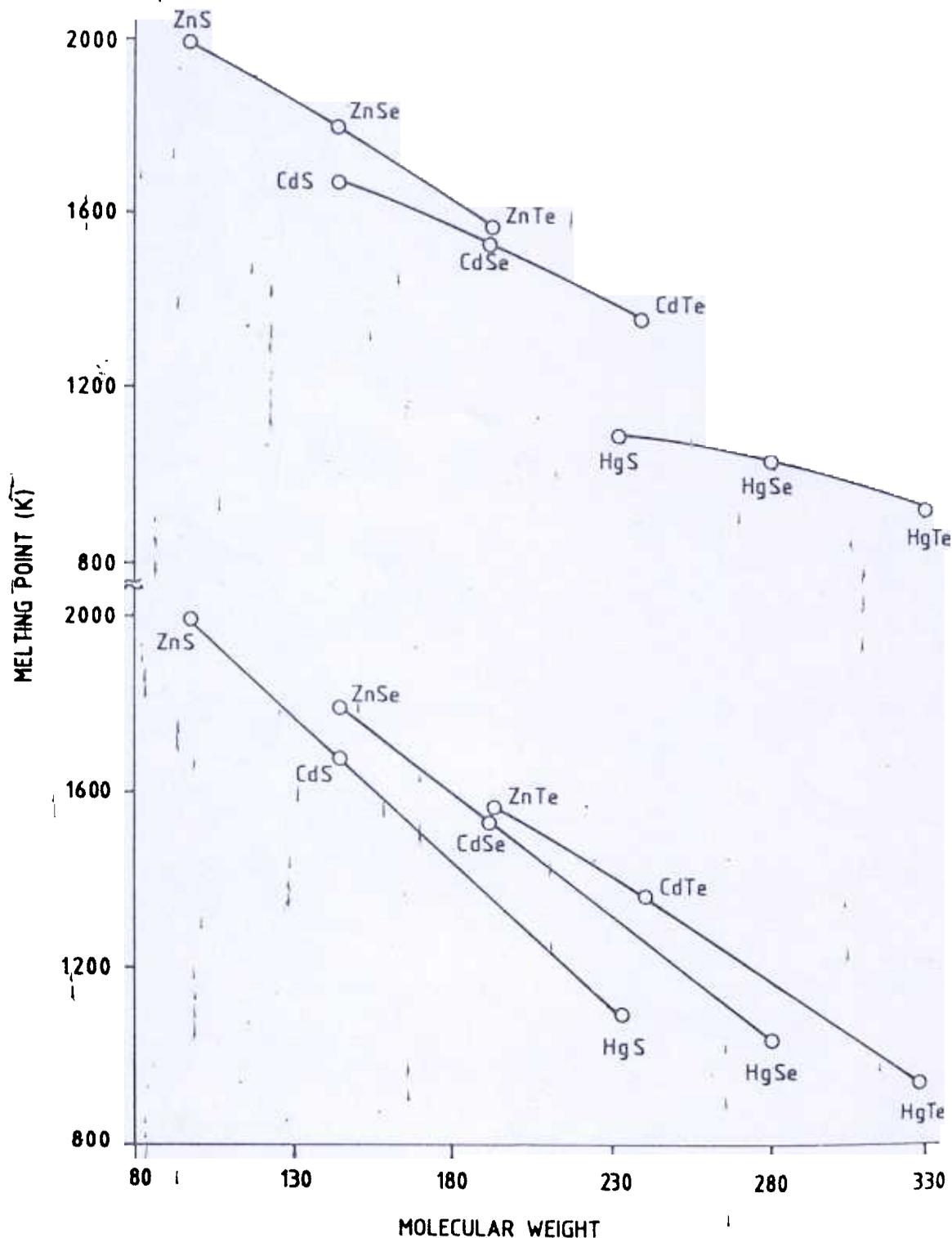


Figure 2. Plot of melting point with molecular weight

cationic as well as anionic component elements. There is good correlation between melting point and bond length. A better correlation exists between melting point and molecular weight.

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## Contributors

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