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The infrared spectra of the vapours over chromium, iron and nickel di-iodide have been studied by high-temperature infrared spectroscopy. The gaseous molecules CrI_2 , FeI_2 and NiI_2 were all identified and the interpretation of the spectra is in agreement with a linear structure. Additional strong absorption bands in the spectra of the vapour phase above liquid CrI_2 and FeI_2 were assigned to dimeric $(\text{MI}_2)_2$ molecules. Valence force constants and thermodynamic quantities have been calculated.

INTRODUCTION

High temperature corrosion of metals and metal surfaces by iodine plays an important role in nuclear industry [1,2] as well as in halogen lamp technology [3]. Our current interest in the transition metal iodides CrI_2 , FeI_2 and NiI_2 arises from the nuclear reactor safety studies since these compounds can be formed during the interaction of the fission product iodine with structural materials like stainless steel or Inconel. Modelling of the interaction processes requires knowledge of the stability of the iodides, in particular the vaporization thermodynamics as gas-phase transport is an important corrosion mechanism. In addition to vapour pressure studies by effusion or mass spectrometric techniques, infrared spectroscopic measurements can give useful information on vapour composition and molecular parameters, necessary for the calculation of thermodynamic quantities.

Presently, little is known about the molecular parameters of the first row transition metal iodides; only the ZnI_2 molecule has been studied in inert gas matrices [4,5] and in the gas-phase [6]. The corresponding dichlorides have been studied in more detail [7-14], but in spite of a large number of studies there is still disagreement about the molecular structure of some of the species. This complicates the use of predictive models, e.g. [15], to estimate the

molecular parameters of the transition metal iodides.

In order to obtain accurate data on the molecular geometry and vibrational frequencies of the gaseous iodides of chromium, iron and nickel, the vibrational spectra have been studied by high-temperature IR spectroscopy, as described in the present paper.

EXPERIMENTAL

The spectra were recorded with a BOMEM DA3.02 Fourier transform spectrometer connected to a self-built optical gas-cell, as described in detail previously [16]. Briefly, the main body of the cell consists of a silica tube (95 cm long and 6 cm in diameter) and is heated in a 62.5 cm long three-zone furnace. Temperature measurement and control is done by a chromel-alumel thermocouple in each separate zone. Optical windows are mounted in water-cooled flanges at both ends of the tube. The cell was loaded in an argon-filled glove box. The gas atmosphere in the cell was argon at a pressure of $1.5 \cdot 10^{-2}$ atm at room temperature. Wedge formed silicon windows were used. The spectrometer was operated with a mercury lamp as light source, a DTGS detector for the 700 to 350 cm^{-1} range, a bolometer operating at 4.2 K for the 375 to 100 cm^{-1} range and a bolometer operating at 1.6 K for the 100 to 25 cm^{-1} range. The spectra were recorded at 0.5 cm^{-1} resolution; 128 scans were coadded.

The FeI_2 and FeBr_2 samples were purchased from Cerac (99.5 %), and used without further purification. CrI_2 was prepared from CrI_3 (Cerac, 99.5 %) by heating at 773 K under vacuum. NiI_2 was prepared by dissolving Ni metal (Cerac, 99.9 %) in $\text{HI}(\text{aq})$. After heating to dryness, the precipitate was dissolved in ethanol and heated at 423 K. X-ray diffraction analysis showed the samples to be pure.

RESULTS AND DISCUSSION

Band assignment

The IR spectra of the vapours above CrI_2 , FeI_2 , and NiI_2 are shown in Figure 1. In the 375 to 100 cm^{-1} region the vapour above FeI_2 at 900 K and CrI_2 at 1110 K showed two distinct absorption bands, whereas the spectrum of NiI_2 at 900 K in the same wavenumber region consists of only one strong absorption band. In the 100 to 25 cm^{-1} region a distinct absorption band was observed for FeI_2 , whereas for NiI_2 one and for CrI_2 two weak absorption bands

($I/I_0 < 7\%$) were observed. The dependence of the absorption intensities on the temperature indicated that most of the bands were due to vapour species in the cell, except the absorptions at 214 cm^{-1} for CrI_2 and 152 cm^{-1} for NiI_2 which were concluded to be due to the condensed phases. The low-intensity bands at 205 cm^{-1} in the FeI_2 spectrum could not be attributed to vapour species with certainty. To eliminate the possibilities of interference of volatile reaction products of molecular iodine, formed by some dissociation of the samples, and the container or cell materials, various containers and protection tubes (molybdenum, AISI 316 stainless steel, nickel) were used, but in all cases the spectra were identical, indicating that all bands are part of the vapour phase of the iodides under investigation; their band positions are summarized in Table 1.

The participation of the 3d orbitals in the chemical bonding decreases from the left to the right in the Periodic Table, corresponding to a decrease of the covalent and an increase of the electrostatic bonding character. As a consequence the metal ligand bonding in the closed shell ZnI_2 (d^{10}) molecule is primarily electrostatic, whereas the open shell molecules NiI_2 (d^8), FeI_2 (d^6) and CrI_2 (d^4) show an increasing covalent bonding character. Electrostatically the most stable configuration for a $\text{X-M}^{2+}\text{-X}$ molecule is a linear structure ($D_{\infty h}$ symmetry). Raman spectroscopic [4-5] and electron diffraction measurements [17] have shown that ZnI_2 is indeed linear. Experimental evidence for the linearity of the molecules NiI_2 , FeI_2 and CrI_2 is not available, but the corresponding bromides and chlorides of nickel and iron are shown to be linear too [18]. For CrCl_2 contrasting data are available indicating either linear [7,12,19] or bent [20] structures.

The presence of only one absorption band in the stretching frequency range of the spectrum of NiI_2 is in agreement with a linear geometry. As a consequence, the assignment is straightforward: $\nu_3 = 343.0\text{ cm}^{-1}$ whereas the weak absorption band at about 52 cm^{-1} corresponds to the bending mode ν_2 . The assignment of the bands in the spectra of CrI_2 and FeI_2 is somewhat more complicated. By comparison with ZnI_2 and NiI_2 and the corresponding chlorides we assign the highest wavenumber absorption bands to the asymmetric M-I stretching frequency: $\nu_3 = 335.2\text{ cm}^{-1}$ for $\text{FeI}_2(\text{g})$ and $\nu_3 = 319.7\text{ cm}^{-1}$ for $\text{CrI}_2(\text{g})$. The presence of an additional absorption bands at 280 cm^{-1} suggest a bent geometry, but, especially in the case of CrI_2 the intensities do not support this, rather indicating that the bands arise from vapour species other than molecular MX_2 . This conclusion is further supported by a spectrum of the vapour above FeBr_2 which also shows two strong absorption bands in the stretching frequency region at 332.8 and 392.6 cm^{-1} (Figure 2). The FeBr_2 molecule is shown to be linear in the gas-phase by electron diffraction measurements by Hargittai et al. [18], who estimated its asymmetric stretching frequency at 380 cm^{-1} .

Mass spectrometric investigations of the composition of the vapour above the condensed phases of the compounds studied here, have only been reported for FeI_2 [21–24]. These studies established $\text{FeI}_2(\text{g})$ as the major binary molecular species in equilibrium with solid FeI_2 at 700 K, the contribution of its dimer $(\text{FeI}_2)_2$ being about five to ten times lower at 665 K. Mass spectrometric studies for NiCl_2 and CrCl_2 have shown that dimeric molecules are present in the CrCl_2 vapour but absent in NiCl_2 vapour [21]. Hilpert et al. [23] also detected FeI_3 as a parent ion in the vapour above $\text{FeI}_2(\text{s})$, its pressure being about two orders of magnitude lower than that of $\text{FeI}_2(\text{g})$ at 665 K.

Due to the absence of additional strong absorption bands in the spectra, an assignment of bands around 280 cm^{-1} to $(\text{MI}_2)_2$ or MI_3 species is difficult. More information is obtained from the spectrum of the vapour phase above FeBr_2 . Here a band at 235 cm^{-1} is present which is clearly part of the vapour phase. Assuming the molecular structure of the FeBr_3 molecule to be pyramidal, similar to FeCl_3 [25], assignment of the absorptions at 235 and 380 cm^{-1} to the two stretching frequencies (ν_1 and ν_3) of this molecule seems unlikely since it opposes the general trends that $\nu_3 > \nu_1$ and $I(\nu_1) \gg I(\nu_3)$ [26]. On the basis of these considerations we conclude that the bands near 280 cm^{-1} in the spectra of CrI_2 and FeI_2 are due to metal–iodine stretching frequency of the dimeric $(\text{MI}_2)_2$ species. This interpretation is in agreement with a linear structure for monomeric FeI_2 and CrI_2 .

The distinct absorption band in the 100 to 25 cm^{-1} region which is observed in the vapour phase over FeI_2 is assigned to the bending frequency of the gaseous diiodide, since this is the major vapour species at the conditions of the experiments. The weak absorption band in vapour over CrI_2 in this wavenumber region is tentatively assigned to the bending frequency of monomeric CrI_2 since it is close to the value of about 40 cm^{-1} obtained by a linear extrapolation of the bending force constants (see below) of the ZnI_2 , NiI_2 and FeI_2 molecules.

Force constants

Force constants of the CrI_2 , FeI_2 and NiI_2 molecules have been calculated assuming a valence force field [27], the results being listed in Table 2. This is a relatively simple two parameter model and can therefore be applied to the present results where only two of the three fundamentals have been observed. It describes the force field of the first row transition metal halides adequately, which is evident from the reasonable agreement between the values for k_1 , as listed in Table 2, obtained from the two stretching frequencies for some relevant first row MX_2 species for which experimental data for ν_1 as well as ν_3 are available

Figure 3 shows the variation of k_1 in the first row transition metal dichlorides and diiodides. The variation of the stretching force constant of the iodides is identical to the chlorides and provides further support to the present assignment of the vibrational frequencies.

Thermodynamic properties

The values for the standard entropy of gaseous CrI_2 , FeI_2 and NiI_2 have been calculated from the molecular parameters listed in Table 3, using a harmonic oscillator, rigid rotor approach. The ν_2 and the ν_3 frequencies are the experimental values from the present study. The data for the infrared inactive symmetric stretching frequencies are the calculated values from the valence force constants (Table 2). The internuclear distances have been estimated from experimental data for the corresponding fluorides, chlorides, and bromides [17–20].

Due to the open shell structures of the CrI_2 , FeI_2 and NiI_2 molecules the contribution of the degeneracy of the ground state as well of as low-lying electronic energy levels to the electronic partition function has to be taken into account. There are almost no experimental data for the $d^n \leftarrow d^n$ electronic transitions for these iodides. DeKock and Gruen [28–30] studied the electronic spectra of the 3d transition chlorides as well as NiI_2 and characterized the ground states and various electronic transitions in the 4000 to 50000 cm^{-1} range. We adopt the ground state assignment of NiI_2 by DeKock and Gruen and assume the electronic ground states of FeI_2 and CrI_2 to be identical to those given by these authors for the dichlorides: $^5\Sigma$ for CrI_2 , $^5\Delta$ for FeI_2 and $^3\Pi_g$ for NiI_2 . Values for the low-lying electronic states of the CrI_2 and the FeI_2 molecules are also estimated from the data of DeKock and Gruen. The values for NiI_2 , which has several d–d transition below 4000 cm^{-1} , are obtained by combination/comparison of the experimental results of DeKock and Gruen and the theoretical study of NiCl_2 by Lever and Hollebne [31]. Only excited levels below 10000 cm^{-1} have been considered.

The results of the statistical thermodynamic calculations are listed in Table 4. The present results differ significantly from the values given by Brewer et al. [32]. Their estimates for the vibrational frequencies of CrI_2 , FeI_2 and NiI_2 are in reasonable agreement with the experimental values but they assumed the electronic level distribution in the diiodides to be identical to the M^{2+} ions, resulting in a electronic entropy which is too high. The present values for $\text{FeI}_2(\text{g})$ are considerably lower than those obtained by the JANAF team [33] from estimated molecular parameters, the major difference occurring in the vibrational entropy which is about 8.3 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ higher. Second-law entropies for $\text{FeI}_2(\text{g})$ derived from experimental vapour pressure or dissociation pressure measurements [21–24, 34–37] are

summarized in Table 5. There is an appreciable scatter in the second-law values and the agreement with the calculated values is in general poor (Fig. 4): the results from the mass spectrometric measurements show no systematic differences; the results from indirect techniques are somewhat higher, probably due to inaccuracies in the monomer/dimer equilibrium data used for the correction of the data. The second-law entropy value for CrI_2 , obtained by the transpiration method [38,39] and of NiI_2 by the torsion effusion technique [40] deviate considerable from our calculated values. However, these indirect techniques are severely hindered by the lack of information on dissociation and dimerization reactions.

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Table 1. Observed infrared bands

value/cm ⁻¹			assignment	nature
CrI ₂	FeI ₂	NiI ₂		
319.7	335.2	343.0	ν_3	asymmetric M-I stretch of MI ₂ species
280.9	278.3			M-I stretch of (MI ₂) ₂ species
88				I-M-I bend of (MI ₂) ₂ species
36	53.0	52	ν_2	I-M-I bend of MI ₂ species

Table 2. Valence force constants and the calculated ν_1 stretching frequencies, where k_1 and k_1' are the stretching force constants calculated from ν_2 and ν_3 , respectively, k_b is the bending force constant, r is the M-X internuclear distance

compound	$k_1/\text{N}\cdot\text{m}^{-1}$	$(k_b/r^2)/\text{N}\cdot\text{m}^{-1}$	$k_1'/\text{N}\cdot\text{m}^{-1}$	ν_1/cm^{-1}
CrI_2	130.0	0.87	-	132
FeI_2	151.5	1.69	-	142
NiI_2	165.2	1.90	-	149
ZnI_2^a	183.4	3.14	198.7	
NiCl_2^b	250.9	3.42	270.7	

^a $\nu_1 = 163 \text{ cm}^{-1}$ [4], $\nu_2 = 64 \text{ cm}^{-1}$ [4,6], $\nu_3 = 346 \text{ cm}^{-1}$ [4]

^b $\nu_1 = 360 \text{ cm}^{-1}$ [11,12], $\nu_2 = 85 \text{ cm}^{-1}$ [7], $\nu_3 = 515 \text{ cm}^{-1}$ [7]

Table 3. Input parameters for the entropy calculation; σ is the symmetry number, r the internuclear distance, B the rotational constant, ν_i the vibrational wavenumber and ϵ_i the electronic energy level, degeneracies are given in brackets.

	σ	$r(\text{M-I})/\text{nm}$	B/cm^{-1}	ν_i/cm^{-1}	$\epsilon_i/\text{cm}^{-1}$
CrI_2	2	0.253	0.01038	132, 37(2), 319.7	0(5), 4200(10), 7000(10)
FeI_2	2	0.249	0.01071	142, 53(2), 335.2	0(10), 3600(10), 5600(5)
NiI_2	2	0.240	0.01153	149, 52(2), 343.0	0(6), 690(3), 1900(6), 4500(6), 8300(1), 9000(2)

Table 4. Statistical entropies of the MI_2 species, in $J \cdot mol^{-1} \cdot K^{-1}$, $p^\circ = 101.325 \text{ kPa}$

	T/K	S_{trs}	S_{el}	S_{rot}	S_{vib}	S_{tot}
CrI_2	298.15	180.122	13.382	62.993	84.883	341.4
	1000	205.277	13.666	102.388	94.945	416.3
FeI_2	298.15	180.278	19.145	57.097	84.617	341.1
	1000	205.433	19.445	96.391	94.678	415.0
NiI_2	298.15	180.392	15.541	55.910	84.006	335.8
	1000	205.547	19.233	94.068	94.068	414.0

Table 5. Comparison of statistical and second-law entropies for $\text{FeI}_2(\text{g})$, $p^\circ = 101.325 \text{ kPa}$

authors	reaction ^a	T_{mean}/K	$S^\circ(T)/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
			exp. ^b	calc.
Mucklejohn et al. [24]	B	1005.0	400.4	415.3
	A	823.5	405.6	402.7
Zaugg and Gregory [36]	C	944.8	405.0	411.3
Bartovska et al. [37]	C	915.0	391.8	409.4
Schäfer and Hönes [34] ^c	A	916.7	398.8	409.5
	B	820.1	372.7	402.5
Sime and Gregory [35] ^c	A	678.2	387.7	390.6
Hilpert et al. [23]	A	665.0	400.3	389.4
	C	665.0	416.7	389.4
	D	665.0	372.8	389.4
Grade and Rosinger [22]	A	664.0	360.3	389.3

^a A: $\text{FeI}_2(\text{s}) = \text{FeI}_2(\text{g})$, B: $\text{FeI}_2(\text{l}) = \text{FeI}_2(\text{g})$, C: $\text{Fe}(\text{s}) + 2\text{I}(\text{g}) = \text{FeI}_2(\text{g})$, D: $\text{Fe}(\text{c}) + \text{I}_2(\text{g}) = \text{FeI}_2(\text{g})$

^b calculated with $C_p(T)$ from [33] and $S^\circ(298.15 \text{ K}) = 154 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ from [41] for $\text{FeI}_2(\text{s})$

^c corrected for dimer contribution according to Zaugg and Gregory [36]

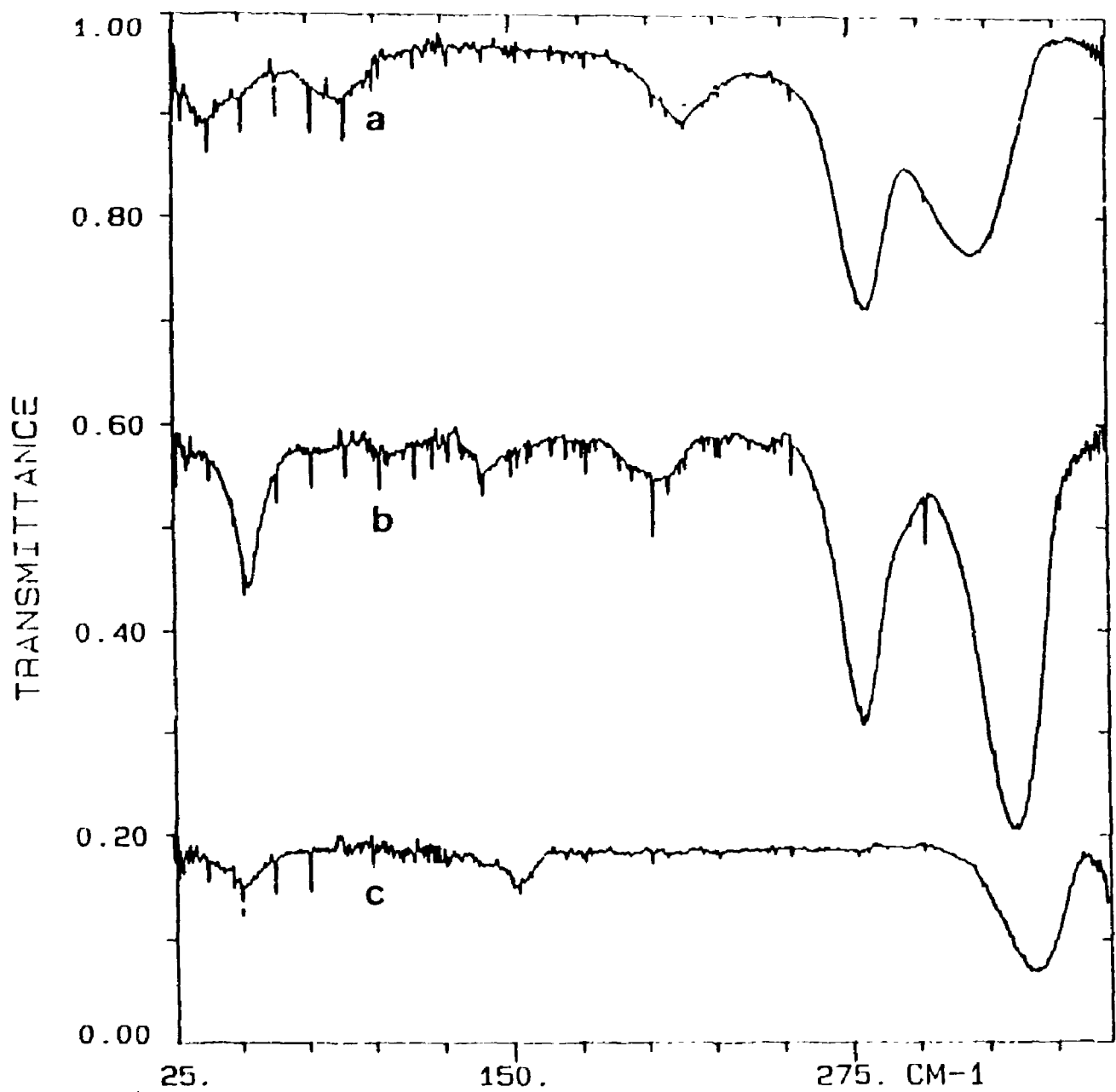


Figure 1. The infrared spectra (0.5 cm^{-1} resolution) of the vapours above (a) CrI_2 , (b) FeI_2 and (c) NiI_2 .

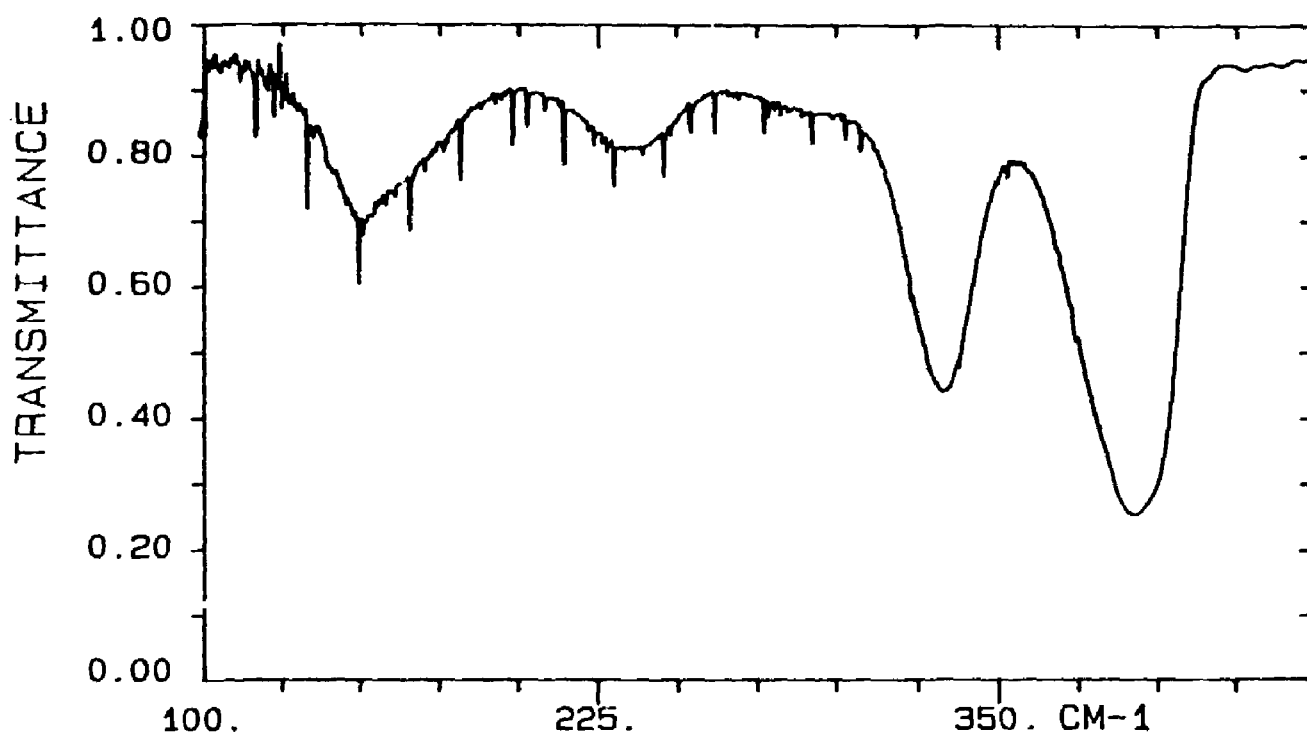


Figure 2. The infrared spectrum (0.5 cm^{-1} resolution) of the vapour above FeBr_2 .

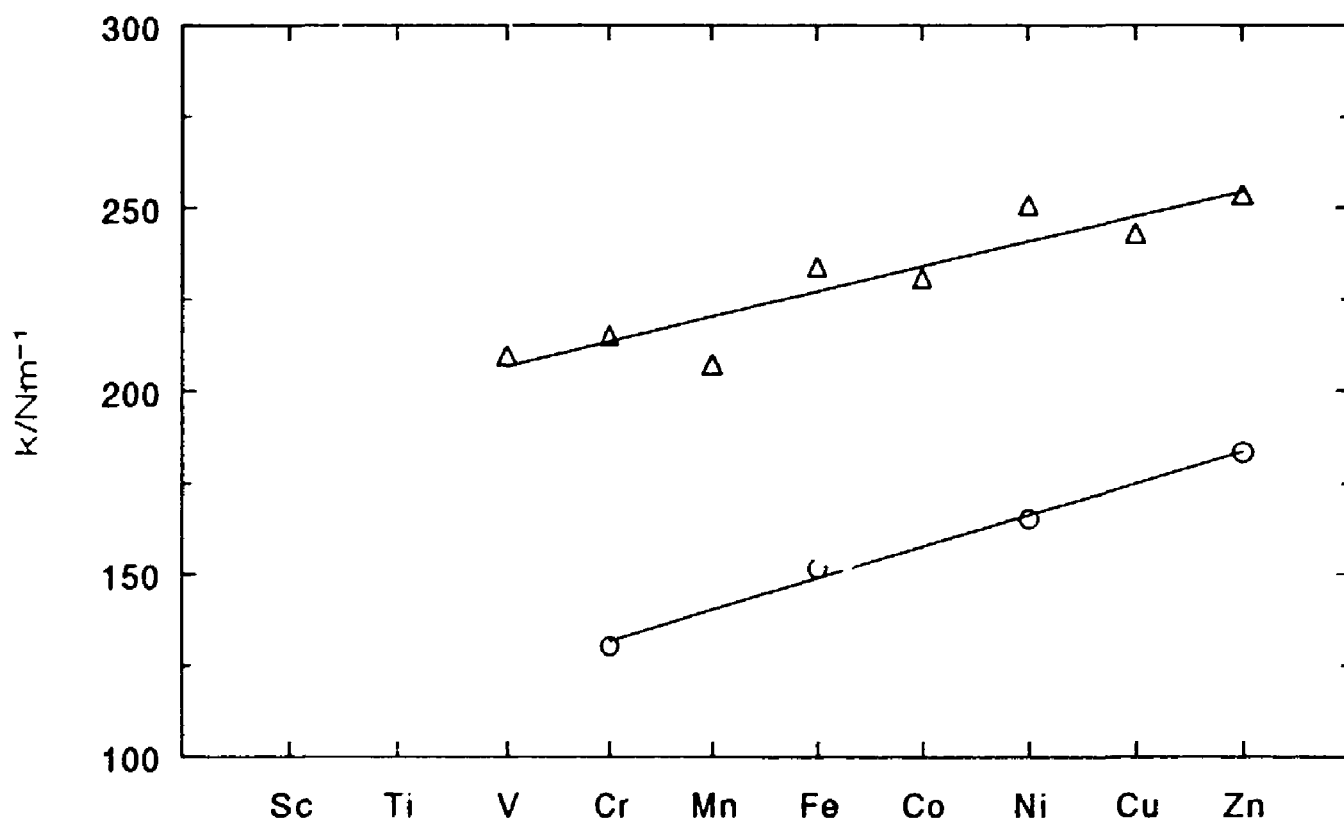


Figure 3. The variation of the stretching force constant k , in the first row transition metal dichlorides (Δ) and diiodides (\square).

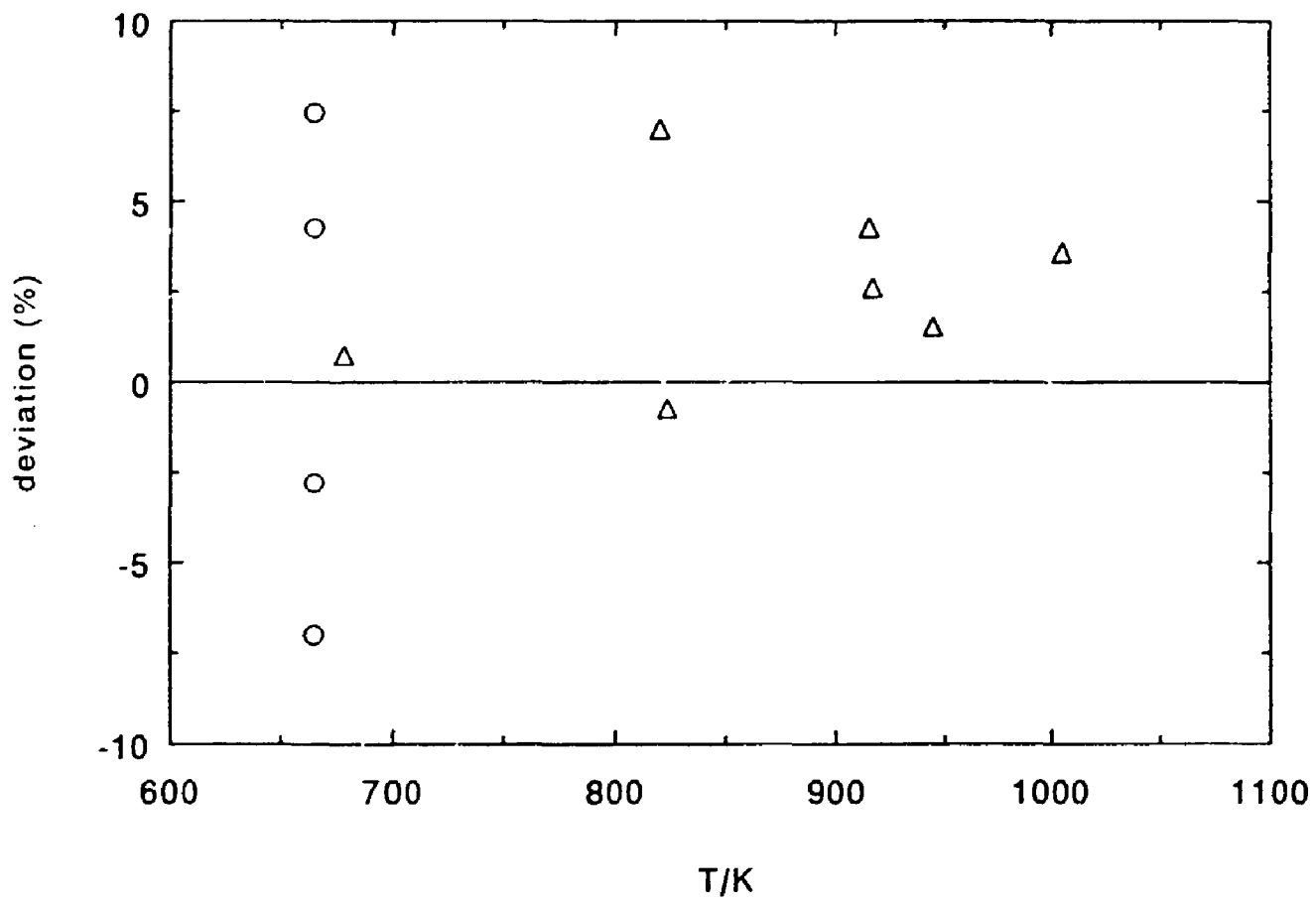


Figure 4. Deviation plot of the experimental entropy values (second law) of $\text{FeI}_2(\text{g})$; (O) mass spectrometry, (Δ) indirect techniques.

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