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VAPOR PRESSURES BY DIFFERENTIAL THERMAL ANALYSIS: APPLICATION TO SOME NICKEL CHELATES *

R.G. CHARLES

Westinghouse Research and Development Center, Pittsburgh, PA 15235 (U.S.A.)

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ABSTRACT

A simple and rapid DTA procedure is described for determining the vapor pressures of metal-organic compounds. We have applied the method to six volatile nickel β-ketoamine chelates which have proved useful, in previous work, for the chemical vapor deposition of nickel metal. The volatilities of these compounds are strongly influenced by the configuration (*cis* or *trans* planar) about the bonded metal atom and by the presence or absence of fluorine as part of the organic portion of the molecules. Some of the chelates have vapor pressures of several hundred torr at temperatures where thermal decomposition is not significant.

INTRODUCTION

A number of authors have pointed out the advantages of differential thermal analysis (DTA) and the related technique of differential scanning calorimetry (DSC) for determining vapor pressures of inorganic and organic materials [1—5]. These advantages include simplicity and rapidity of operation, small required sample size, and low sensitivity of the measurements to errors resulting from the formation of thermal decomposition products. Nevertheless, DTA and DSC approaches to vapor pressure measurement remain unfamiliar to many workers, and the techniques are not used to the extent that their value justifies [5]. In the present work we call attention to the usefulness of DTA for measuring the vapor pressures of metal-organic compounds and describe simple and inexpensive equipment for such measurements.

Considerable recent interest [6] in volatile metal-organic compounds derives from such applications as the gas chromatographic separation of metals [7], chemical vapor deposition of metals and oxides [8—11], and the laser-induced separation of metal isotopes in the vapor phase [12]. In previous investigations in this laboratory [11], we showed that nickel β-ketoamine chelates are useful for depositing nickel metal by hydrogen reduction of the compounds in the vapor state. In the present work, we have studied in

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more detail the volatility characteristics of some of these materials as a function of temperature.

EXPERIMENTAL

Apparatus and procedure

The DTA portion of the apparatus (Fig. 1) is similar to that described previously [13]. The sample and the inert reference substance (powdered fused quartz) were contained in the lower portions of identical quartz tubes, having bottom indentations for the two junctions of a chromel—alumel differential thermocouple. The output from this thermocouple was amplified five-fold and then fed to the Y-axis of an X—Y recorder at 5 mV full scale sensitivity. The hot junction of a second chromel—alumel thermocouple was also contained in the thermocouple well of the sample tube *. The potential of this thermocouple was used to measure the actual temperature of the sample. This output was fed through a cold-junction compensation circuit to the X-axis of the recorder. The recording arrangement is shown in Fig. 2.

The lower portions of the sample and reference tubes were held symmetrically within a stainless steel block which was heated at a linear rate of 12°C min^{-1} by means of a motor-driven Variac variable transformer and tube furnace. The upper portions of the quartz tubes were at room temperature.

Both sample and reference tubes were connected by means of rubber pressure tubing and greased standard-taper glass joints to a simple gas reservoir and manifold (kept at room temperature) equipped with a vacuum connection and inlet system for pure argon (Fig. 3). Gas pressure within the closed system was measured by means of a closed-tube mercury manometer at the lower pressures and by means of a Bourdon gauge at the higher pressures. Pressure readings were taken at intervals throughout each run since an increase in pressure within the system during a run is a sensitive indication of the formation of volatile thermal decomposition products [14]. (The vaporization of the sample itself does not give a measurable increase in the pressure within the system since the sample recondenses immediately on reaching the cool portion of the sample tube above the furnace.)

A 50 mg sample of the substance to be studied (which, in the present work, was always solid at room temperature but usually molten at the temperature of vaporization) was ground in a glass mortar with 250 mg of Thermal American Co. fused quartz powder and the mixture placed in the sample tube. The use of the mixture with fused quartz was necessitated by the observation that the samples, at temperatures where molten, often underwent severe "bumping" (sudden and violent evolution of vapor bubbles) at the boiling point, particularly at the lower pressures. This "bumping", which is analogous to that often encountered when vacuum distilling liquids, caused severe anomalies in the DTA curves. The use of fused quartz powder,

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* This approach differs from our previous work [13] where the temperature of the metal block surrounding the sample and reference tube was monitored.

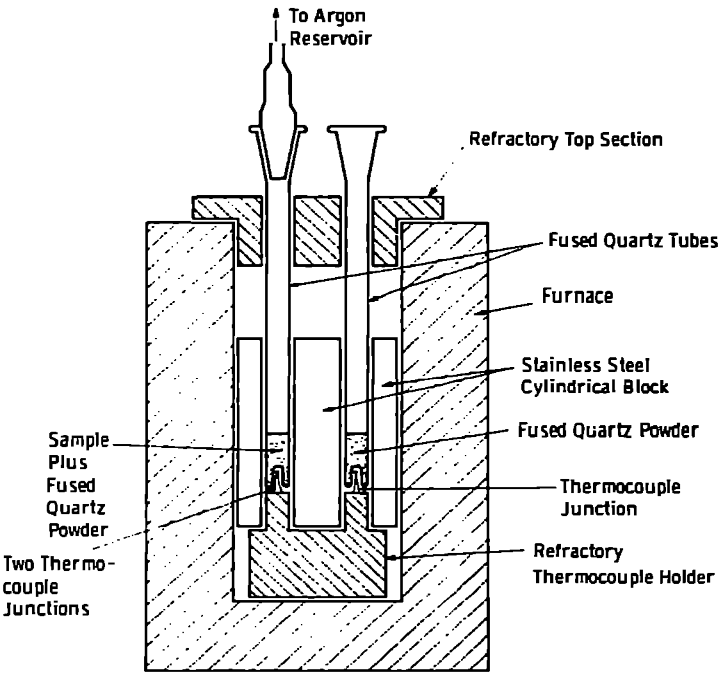

Fig. 1. Cross-section of DTA apparatus.

by providing innumerable nucleating points, removed this difficulty. The use of the quartz powder also provided flatter base lines for the DTA curves by making the thermal conductivity characteristics of sample and reference more nearly equal throughout the run.

Some ambiguity attaches to the interpretation of DTA-vaporization curves in that the endotherm corresponding to vaporization has significant width along the sample temperature axis and there is not universal agreement as to the most significant point on the endotherm. Although the point of initial departure from the base line has been used [1], in the present context we

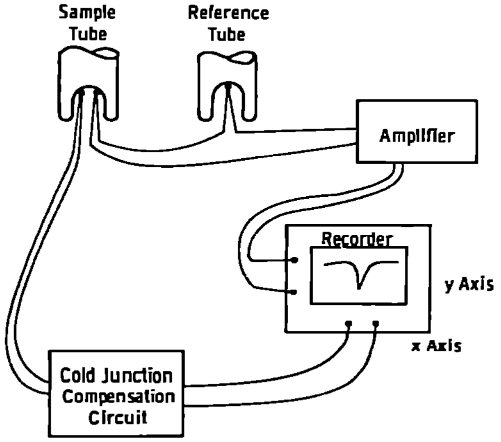

Fig. 2. Diagram of thermocouple placement and recording circuitry.

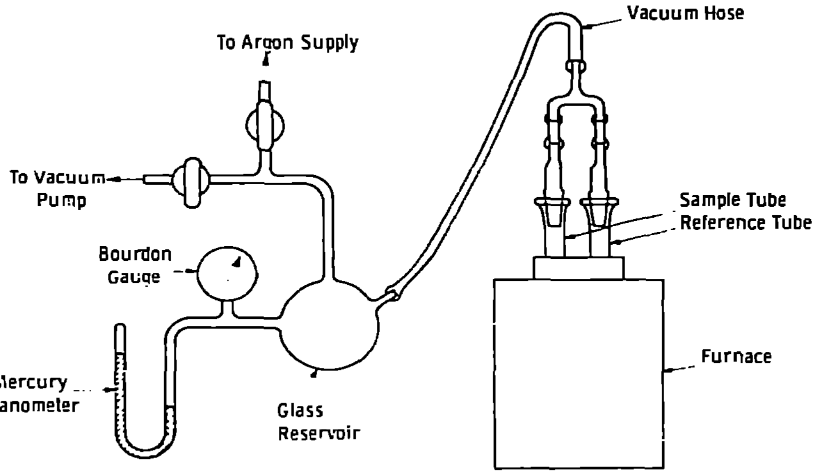

Fig. 3. Schematic of vapor pressure apparatus.

have chosen instead to employ the sample temperature at the endotherm peak as being more easily identified and reproducible. We have minimized any error this approach may entail by calibrating the apparatus with substances of known thermal properties. The calibration procedure is described in detail elsewhere [13].

Preparation of compounds

The following chelates were prepared and purified by the literature methods cited: nickel acetylacetone imide [15], nickel acetylacetone ethylenediimide [16], and nickel trifluoroacetylacetone ethylenediimide [17]. The other compounds were prepared as follows:

Nickel acetylacetone-1,2-propylenediimide

Propylenediamine (3.7 g, 0.05 mole) was added to 10.0 g (0.1 mole) acetylacetone in a flask. After the exothermic reaction had subsided, the mixture was dissolved in 200 ml water. A solution of 0.05 mole nickel acetate in 200 ml water was added, followed by 100 ml 1 M aqueous NH_4OH. Upon heating, the resulting red solution gradually deposited red crystals. After 5 min heating, the mixture was cooled, first to room temperature and then in the refrigerator. The compound was filtered off and air-dried to give 8.1 g product. Recrystallization was achieved by dissolving in 50 ml hot methanol, filtering hot and adding 100 ml water to the filtrate. Two successive recrystallizations gave 6.0 g (41%) of air-dried red crystals, m.p. 158—159°C (ref. 17, 157—157.5°C).

Nickel trifluoroacetylacetone imide

The following method for preparing trifluoroacetylacetone imide, though giving poor yields, was more convenient than the procedure cited in the literature [18]. Trifluoroacetylacetone (7.7 g, 0.05 mole) was dissolved in 10 ml absolute ethanol and 5 ml (an excess) concentrated aqueous NH_4OH was added. The solid which separated was redissolved by adding an additional 5 ml ethanol and heating briefly on the hot plate. After cooling, the mixture was taken to dryness in a stream of nitrogen. The residue was heated with 75 ml *n*-heptane to give partial solution. The hot liquid was filtered through filter paper to remove remaining solid. After cooling, the solution was reduced to half its volume in a stream of nitrogen and then cooled further in the refrigerator. The yellowish crystals were filtered off, washed with a little cold petroleum ether and air-dried. The yield was 1.2 g and the m.p. 85—87°C (ref. 18, 87—88°C). The identity of the product was established more definitively by the formation of the chelate below.

The above chelating agent (1.07 g, 7×10^{-3} moles) was dissolved in 10 ml absolute ethanol and added to a suspension of 0.87 g (3.5×10^{-3} moles) nickel acetate tetrahydrate in 25 ml ethanol. One ml (an excess) concentrated aqueous NH_4OH was added and the mixture was stirred and heated on the hot plate until all the solid had dissolved to give a deep green solution. On cooling, the solution turned brown and solid began to separate. The mixture was reduced to one third its volume in a stream of nitrogen and 25 ml water added. After standing overnight, the reddish-tan precipitate was filtered off, washed with water, and dried in a vacuum desiccator at about 10 torr. The yield was 0.92 g (72%) and the m.p. 198—199°C. To recrystallize, 0.9 g was dissolved in 25 ml hot absolute ethanol and reprecipitated with 25 ml water. The yield of vacuum-dried product was 600 mg. Calculated for $(C_5H_5F_3NO)_2Ni$: C, 33.1; H, 2.78; N, 7.72; F, 31.4%. Found: C, 34.0; H, 2.85; N, 7.73; F, 32.6%.

Nickel acetylacetone methyl imide

The method of Everett and Holm [19] was modified by employing tetrahydrofuran (rather than *tert*-butanol) as solvent and by using preformed potassium *tert*-butoxide (Alfa Inorganics) rather than potassium metal. The chelating agent was prepared by the method of Holtzclaw et al. [20]. The nickel compound was recrystallized from *n*-heptane. This chelate was found to decompose slowly on storage in a glass jar at room temperature, in contrast to the other chelates studied which appeared to be stable indefinitely.

RESULTS

Figures 4—9 give DTA curves for the six nickel chelates studied. Most of these curves show two endothermic peaks, corresponding, respectively, to melting and vaporization of the chelate. The two types of endotherm are readily distinguished by varying the pressure of inert gas above the sample. The position of the melting endotherm along the temperature axis is insensitive to pressure changes while the vaporization peak shifts to higher temperature values with increasing argon pressure. For nickel acetylacetone imide

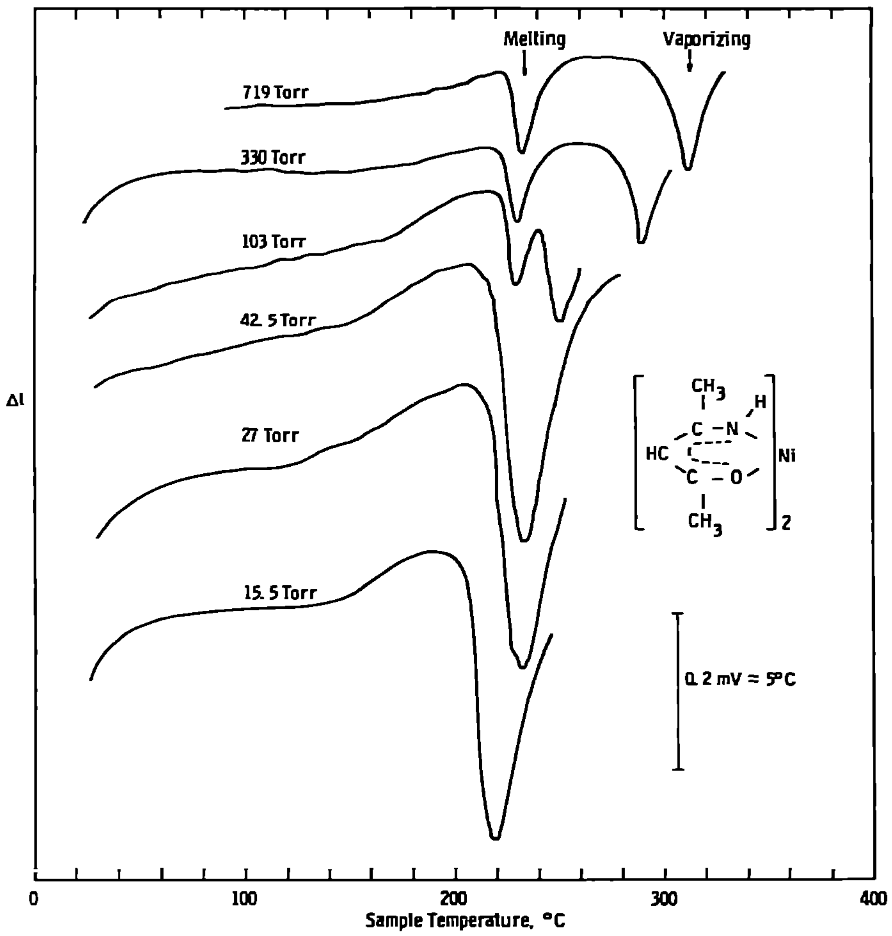

Fig. 4. DTA curves for Ni acetylacetone imide heated at the inert gas pressures indicated.

(Fig. 4) the melting and vaporization endotherms merge at the lower argon pressures. Further analysis of the data (vide infra, Fig. 10) shows that solid sublimation, as opposed to vaporization from the melt, occurs at the three lower external pressures for this compound. All the other chelates studied vaporize exclusively from the melt under the conditions employed here.

Vapor pressure—temperature curves for each of the six nickel chelates are plotted in Fig. 10 and the corresponding data listed in Table 1. As is true of many substances, the data of Table 1 can be represented, within the experimental error, by the equation

$$\log p = A - \frac{\Delta H_{\text{vap}}}{4.576\,T} \qquad (1)$$

where p is the vapor pressure in torr, ΔH_{vap} is the molar heat of vaporization, and A is a constant characteristic of the compound. Derived values of ΔH and A, for each compound, are included in Table 1.

Figure 10 shows nickel acetylacetone imide to be unique among the compounds examined in that two line segments are required to characterize its vaporization behavior over the temperature range studied. We interpret this

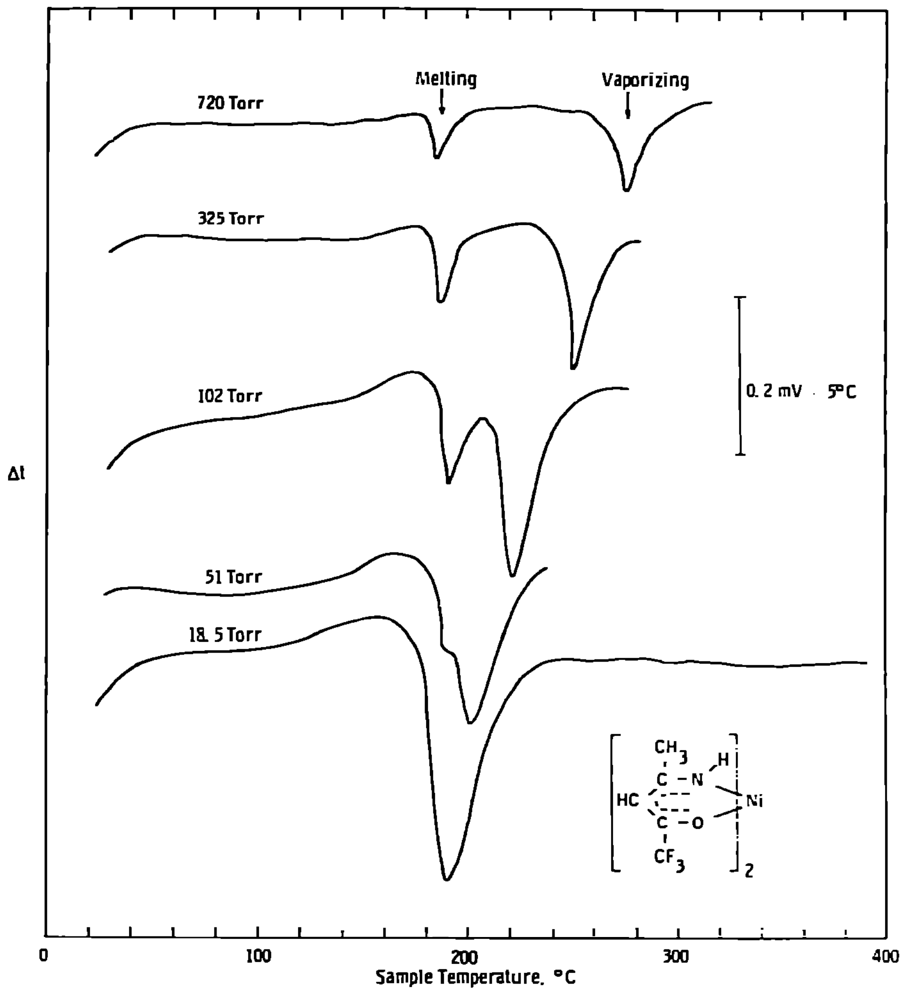

Fig. 5. DTA curves for Ni trifluoroacetylacetone imide heated at the inert gas pressures indicated.

behavior as due to sublimation from the solid chelate at the lower temperatures, as contrasted to volatilization from the melt at the upper *. A smaller heat of vaporization for the liquid (Table 1) results in a change of slope for the plot shown in Fig. 10 at the chelate melting point.

When determining vapor pressures of organic materials at elevated temperatures by almost any method, it is necessary to consider thermal decomposition as a potential source of error. In the present work, two lines of evidence indicate that thermal decomposition is not serious over the temperature ranges indicated in Fig. 10. These are the linearity of the curves when plotted as in Fig. 10, and the lack of significant pressure build-up in the closed system, which could be attributed to volatile decomposition products [14]. The short periods of time during which the samples are exposed to the higher temperatures with the DTA method allow one to obtain valid data at

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* See ref. 6 for further examples of chelates which behave in this manner.

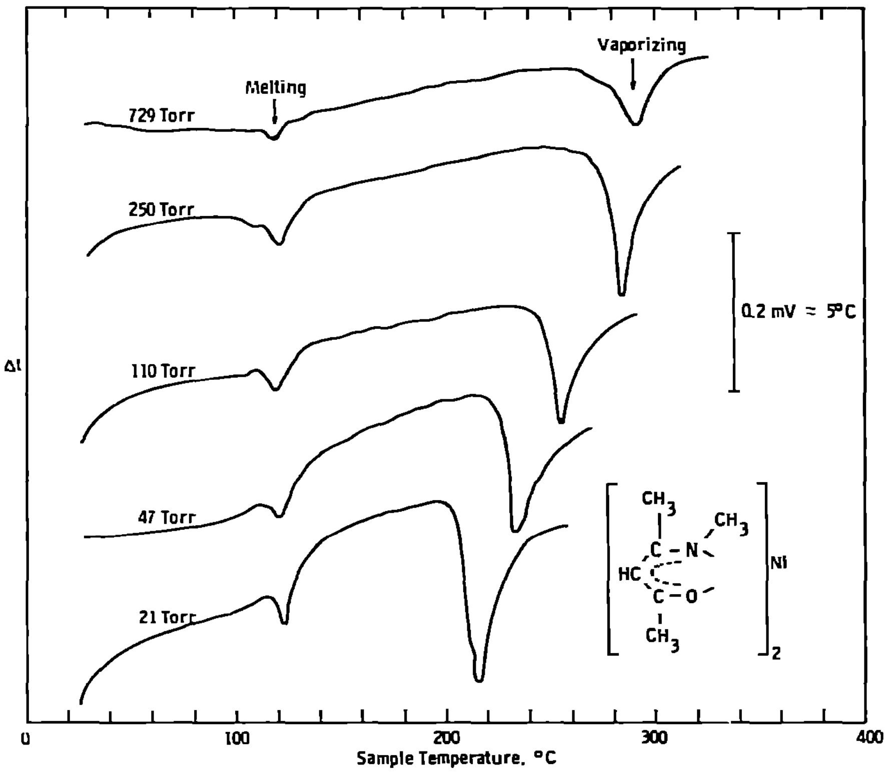


Fig. 6. DTA curves for Ni acetylacetone methyl imide heated at the inert gas pressures indicated.

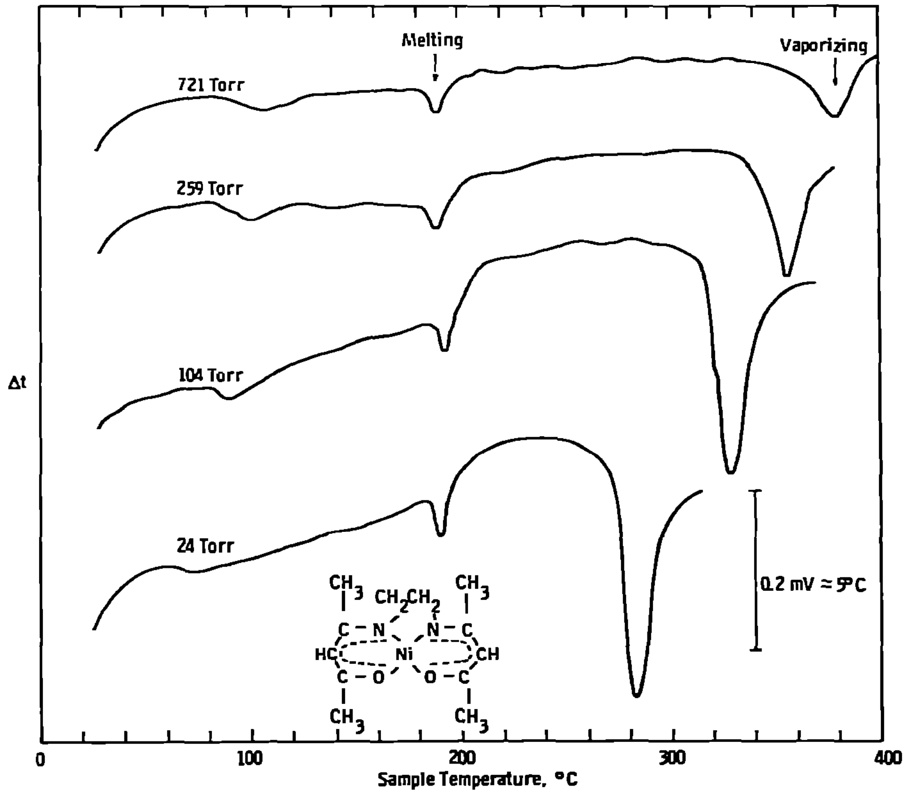


Fig. 7. DTA curves for Ni acetylacetone ethylenediimide heated at the inert gas pressures indicated.

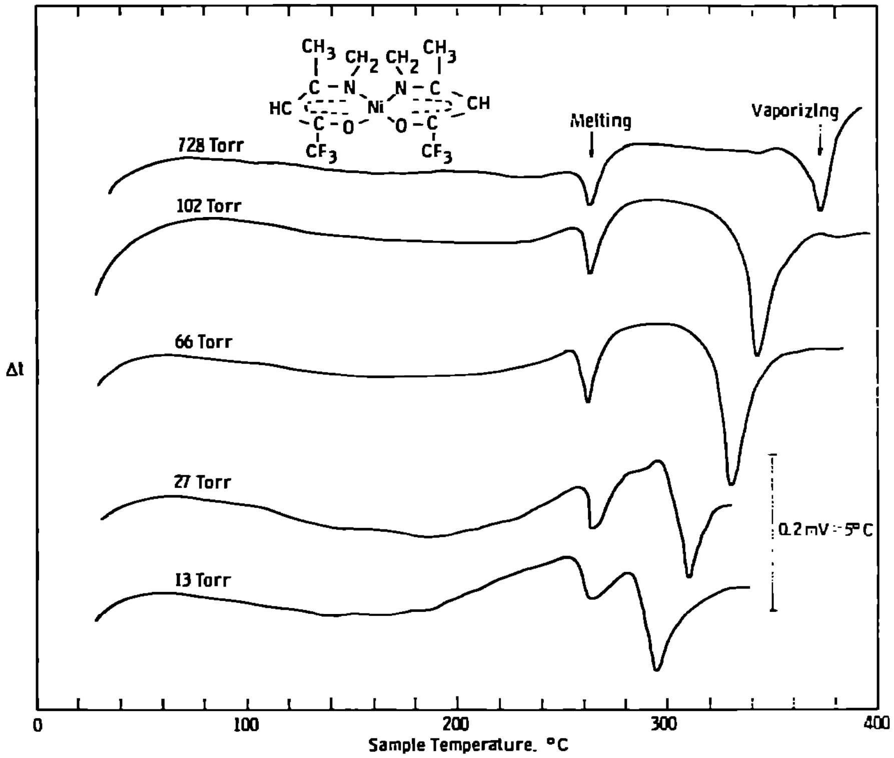


Fig. 8. DTA curves for Ni trifluoroacetylacetone ethylenediimide heated at the inert gas pressures indicated.

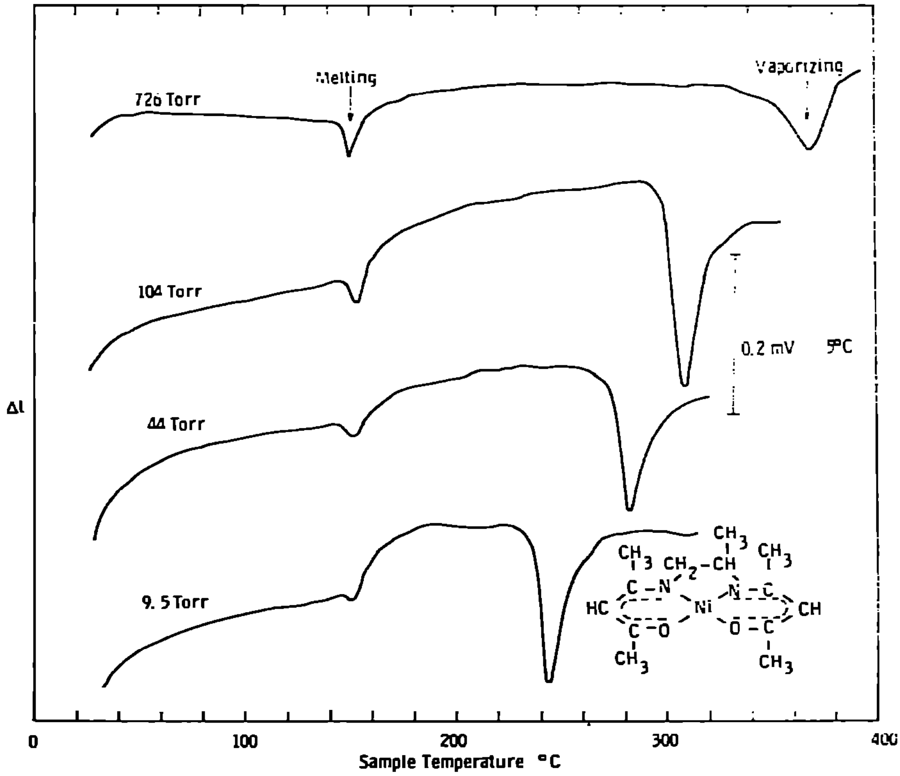


Fig. 9. DTA curves for Ni acetylacetone-1,2-propylenediimide heated at the inert gas pressures indicated.

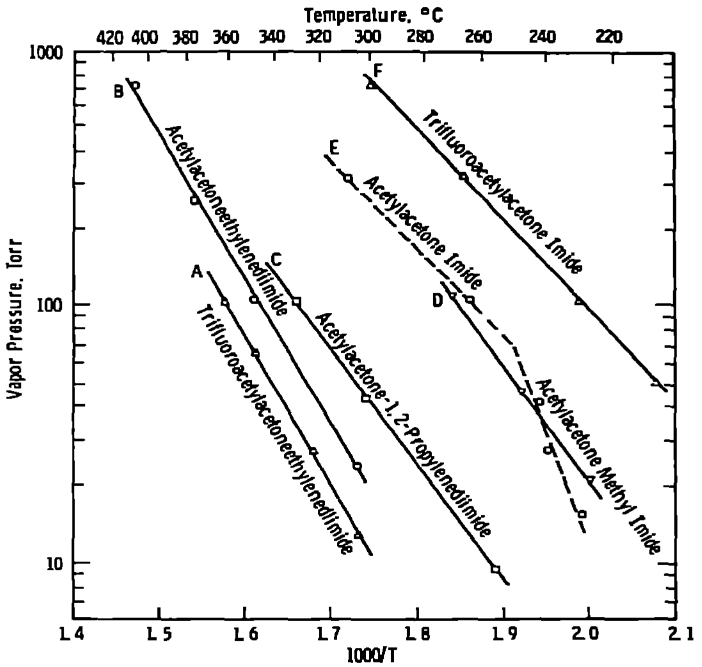


Fig. 10. Vapor pressure as a function of temperature for some nickel ketoamine chelates.

TABLE 1

Vapor pressure data for nickel β-ketoamine chelates

Nickel chelate	Temp. (°C)[a]	Vapor pressure (torr)	$-\Delta H_{vap}$ (kcal mole^{-1})[b]	A[b]
Acetylacetone imide, solid	229	15.5	33.2	15.78
	240	27		
	243	42.5		
liquid	265	103	15.6	8.36
	308	330		
Acetylacetone methyl imide	226	21	20.7	10.36
	247	47		
	270	110		
Trifluoroacetylacetone imide	208	51	16.1	9.04
	230	102		
	266	325		
	299	720		
Acetylacetone ethylenediimide	303	24	20.9	9.40
	350	104		
	377	259		
	406	721		
Trifluoroacetylacetone ethylenediimide	308	13	21.5	9.41
	322	27		
	348	66		
	362	102		
Acetylacetone-1,2-propylenediimide	257	9.5	16.8	8.08
	302	44		
	329	104		

[a] Corrected by means of a calibration curve as described in ref. 13.
[b] From eqn. (1).

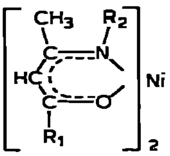
temperatures where long-term heating results in serious decomposition [16]. For four of the compounds, some evidence of decomposition was noted from the DTA runs carried out at atmospheric pressure. Although these DTA curves are included in Figs. 4—9, the corresponding data have been omitted from Fig. 10 and Table 1.

DISCUSSION

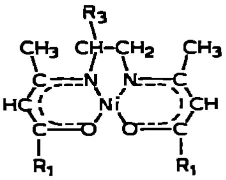
The volatilities of compounds can be compared in several different ways. Comparisons can be made on the basis of (a) heats of vaporization, (b) vapor pressures at a specific temperature, or (c) the temperatures corresponding to a specific value of vapor pressure. These three criteria do not necessarily lead to the same order of volatility when ranking a series of compounds.

Although heats of vaporization have been used [21] in making volatility comparisons, criteria (b) and (c) above would seem to be more closely related to the use of metal-organic compounds in vapor deposition work or in other practical applications such as metal separations in the vapor state. In the present work, it is sufficient to compare the relative positions of the vapor pressure—temperature curves of Fig. 10 along the temperature axis. This is equivalent to employing criterion (c), above, over much of the accessible pressure range.

The nickel chelates studied here can be represented by the generalized formulas I or II.



I

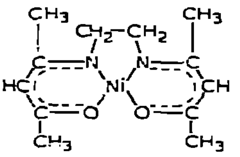


II

where $R_1 = CH_3$ or CF_3, $R_2 = H$ or CH_3, $R_3 = H$ or CH_3. Structural formulas for individual compounds are given in Figs. 4—9.

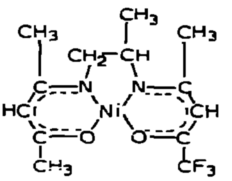
Structure II differs from I in that the planar *cis* configuration is enforced about the nickel atom by the bridge between the two nitrogens in II. Compounds of structure I, by contrast, can assume the sterically favored *trans* planar configuration. The following discussion will center on the volatility consequences of this difference in configuration as well as on volatility differences which result from changes in molecular structure at R_1, R_2, and R_3 in I and II.

Examination of Fig. 10 shows the three compounds which have structure II (curves A—C) to be significantly less volatile than the three chelates of structure I (curves D—F). This difference can be explained in terms of relative molecular polarities. Nickel chelates which have the *trans* planar configuration (structure I) are non-polar while compounds of structure II have large permanent electric dipole moments. Some of the dipole moment data [22,23] of Martell and his co-workers are given below, together with the respective structural formulas III—V. The polar nature of these chelates is expected to lead to increased intermolecular interactions and decreased volatility, in accordance with the results plotted in Fig. 10.



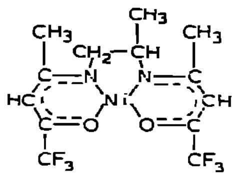
III

μ = 4.29 D.U.



IV

μ = 4.43 D.U.



V

μ = 9.30 D.U.

Within the two groups of compounds corresponding to formulas I and II, large changes in volatility result from substituting fluorine for hydrogen in the organic portion of the molecules. Substitution of trifluoromethyl for methyl (at R_1 in I) in nickel acetylacetone imide results in the significantly more volatile compound nickel trifluoroacetylacetone imide (curves E and F, Fig. 10). Similar enhancement of volatility by fluorine substitution has been reported [6] for other metal chelates and appears to be associated with decreased van der Waals forces between fluorinated molecules.

By contrast, substitution of fluorine for hydrogen in the *cis* compounds II results in *decreased* volatility (cf. curves A and B, Fig. 10). This result must be due to the very large increase in molecular polarity which results from fluorine substitution in the *cis* planar compounds (cf. IV and V, above). The increase in dipole moment apparently more than outweighs any decrease in van der Waals forces. Similar increases in dipole moment, upon fluorine substitution, do not occur for compounds of structure I since the moments associated with substituent groups cancel when in the *trans* configuration.

The final structural change investigated in the present work was the substitution of methyl for hydrogen at R_2 and R_3 in structures I and II. Exchange of methyl for hydrogen in nickel acetylacetone imide has relatively little effect on volatility (Fig. 10, curves D and E). However, methyl substitution in structure II results in a significantly more volatile compound (Fig. 10, curves B and C). Since the polarities of the two molecules do not differ greatly (cf. III and IV), the volatility difference may be the result of increased intermolecular screening of polar bonds by the additional methyl group. Other workers have noted the effect of bulky alkyl groups on increasing the volatilities of analogous β-diketone chelates [6].

A recent review [6] shows that most published chelate volatility work pertains to metal derivatives of β-diketones *. The work described here suggests

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* Metal derivatives of 8-hydroxyquinoline have also been shown to have significant volatility [24].

that the β-ketoamines may constitute an equally fruitful group of chelants for synthesizing volatile metal-organic compounds. Vapor pressures of several hundred torr are observed for some of the chelates studied here (Fig. 10). This order of volatility is not equalled by most of the metal β-diketone derivatives which have been studied [6].

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REFERENCES

1 M.M. Markowitz and D.A. Boryta, J. Phys. Chem., 66 (1962) 1477.
2 G.I. Novikov and O.G. Polyachenok, Russ. J. Inorg. Chem., 6 (1961) 996.
3 A.A. Krawetz and T. Tavrog, Rev. Sci. Instrum., 33 (1965) 1465.
4 G.P. Morie, T.A. Powers and C.A. Glover, Thermochim. Acta, 3 (1972) 259.
5 F. Noel and G.E. Cranton, Am. Lab., 11 (6) (1979) 27.
6 R.E. Sievers and J.E. Sadlowski, Science, 201 (1978) 217.
7 R.W. Moshier and R.E. Sievers, Gas Chromatography of Metal Chelates, Pergamon Press, New York, 1965.
8 R.G. Charles and P.G. Haverlack, J. Inorg. Nucl. Chem., 31 (1969) 995.
9 C.F. Powell, J.H. Oxley and J.M. Blocher, Jr. (Eds.), Vapor Deposition, Wiley, New York, 1966.
10 R.L. Van Hemert, L.B. Spendlove and R.E. Sievers, J. Electrochem. Soc., 112 (1965) 1123.
11 R.G. Charles and J.G. Cleary, U.S. Pat. 3,594,216 (1971).
12 D.M. Cox, R.B. Hall, J.A. Horseley, G.M. Kramer, P. Rabinowitz and A. Kaldor, Science, 205 (1979) 390.
13 R.G. Charles, Anal. Chim. Acta, 27 (1962) 474.
14 R.G. Charles, A. Perrotto and M.A. Dolan, J. Inorg. Nucl. Chem., 25 (1963) 45.
15 A.W. Struss and D.F. Martin, Inorg. Synth., 8 (1966) 232.
16 R.G. Charles, J. Phys. Chem., 65 (1961) 568.
17 R.J. McCarthy, R.J. Havey, K. Ueno and A.E. Martell, J. Am. Chem. Soc., 77 (1955) 5820.
18 S. Protnoy, J. Org. Chem., 30 (1965) 3377.
19 G.W. Everett and R.H. Holm, J. Am. Chem. Soc., 87 (1965) 2117.
20 H.F. Holtzclaw, J.P. Collman and R.M. Alire, J. Am. Chem. Soc., 80 (1958) 1100.
21 E.W. Berg and J.T. Trumper, J. Phys. Chem., 64 (1960) 487; Anal. Chim. Acta, 32 (1965) 245.
22 P.J. McCarthy and A.E. Martell, J. Am. Chem. Soc., 78 (1956) 2106.
23 R.J. Havey and A.E. Martell, J. Am. Chem. Soc., 82 (1960) 2697.
24 R.G. Charles and A. Langer, J. Phys. Chem., 63 (1959) 603.