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VAPOR PRESSURE STUDIES ON METAL CHELATES

THESIS

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VAPOR PRESSURE STUDIES ON METAL CHELATES

THESIS

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Walter A. Frankhauser

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Abstract

The vapor pressures of several metal chelates of acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone were measured in the temperature range 40° to 140°C by the effusion and isoteniscope methods. The results showed large differences from the literature values, where available, and a qualitative discussion is offered to illustrate the major sources of error in the experiments.

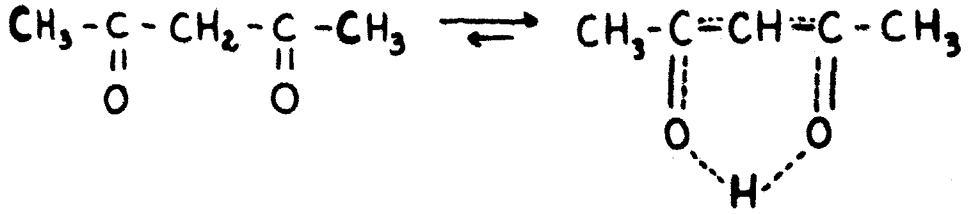
A comparison between the experimental vapor pressure trends among the chelates and the observations made with regard to the order of elution of the chelates in gas chromatography showed that for the chelates of a given metal atom, the volatility increased with increasing fluorination of the ligand and the time for elution from the chromatographic column decreased.

I. Introduction

Metal coordination compounds with organic ligands are of great interest in physico-chemical research because of their unusual properties. While they contain central metal atoms and have comparatively high molecular weights, they nevertheless behave in a manner similar to organic compounds. With the special class of chelates in the present study, where the charge on the ligand cancels the charge on the metal, insolubility in water, and solubility in non polar solvents are characteristic. In addition, these chelates are surprisingly volatile.

The purpose of this thesis is to report the vapor pressures of several metal chelates measured by the effusion and isoteniscope methods, and to correlate the results with the experimental observations made by Sievers, et.al.$^{(1)}$ on the behavior of the complexes in gas-liquid chromatography columns.

The ligands in all the chelates studied are acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone. Acetylacetone is a β-diketone having the structure:



(keto form) (enol form)

Equilibrium favors the enol form since it has a stabilization energy 3.9 kilocalories per mole higher than the keto form$^{(2)}$. Acetylacetone and its fluorinated derivatives are bidentate ligands; these ligands are bonded to the metal atom through the two oxygen atoms, thereby forming a chelate ring. Sterochemically, the bivalent metals generally react with two molecules of ligand to form square planar or tetrahedral complexes. Some of the bivalent metals form octahedral complexes with attached neutral groups at the polar positions. The trivalent metals react with three ligand molecules to form octahedral complexes.

Many theories to describe and account for the bonding in these complexes have been advanced and following is one of the simpler descriptions. Atomic chromium has the electronic structure:

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^4$$

When the chromium(III) ion reacts with the ligand, it replaces the hydrogen on one oxygen to form a covalent bond. The remaining pair of unshared electrons on the other oxygen goes into the 3d orbital. Since three ligand molecules react with one chromium(III) ion, the total number of electrons supplied by the ligand is twelve, six of which form three covalent bonds, and the other six complete the 3d orbital of the chromium atom. The chelates are called inner complexes if the charge on the metal ion is exactly matched by the sum of the charges on the ligands so as to form a neutral species.

Associated with the chelates are several problems involved with the determination of their vapor pressures. One of these problems is outgassing of the sample. If a static method such as the isoteniscope is used and the sample is improperly outgassed, the apparent vapor pressure values obtained will be higher than the true vapor pressures. Another problem is the possibility of reaction of the chelate with its surroundings. In the effusion method, there is the possibility of the chelate reacting with the walls of the effusion cell. For the isoteniscope, there is the possibility of reaction with the confining liquid, especially mercury.

The effusion method was chosen because of its apparent simplicity. The isoteniscope method was chosen not only for its apparent simplicity but also because values for the vapor pressures of β-diketone chelates in literature sources were obtained by this method. In addition, neither method requires elaborate and complex apparatus.

The vapor pressures of five chelates were measured by effusion, and of one chelate by the isoteniscope method. Benzoic acid was used as a standard for both methods.

Knudsen Effusion Method. The Knudsen effusion method(3) has been used extensively for the measurement of vapor pressures of metals. Egerton(5) used the method to determine the vapor pressure of cadmium and mercury, Pilling(6) for calcium, and Langmuir(7,8,9) for electrically heated filaments. The method has also been used for the vapor pressures of organic crystals by Swan and Mack(10), in reaction studies such as the thermal decomposition of sodium carbonate by Motzfeldt(11), and in the observation of reactions occurring on thoriated cathodes by Hoch and Johnston(12).

Basically, the effusion method is straightforward. The compound to be observed is placed in a cell covered with a cap which contains a small hole of known area and wall thickness. During operation, the cell is placed in a vacuum system and the section containing the cell is maintained at constant temperature. With a knowledge of the temperature of the effusing vapors and the time for a known amount of material to effuse out of the cell, the vapor pressure can be calculated.

Isoteniscope Method. The isoteniscope was first used by Smith and Menzies(13) and later modified by Booth and Halbedel(14). The isoteniscope has generally been used for measurement of the vapor pressures of liquids but the method can be modified for solid compounds providing that a non-reacting manometric fluid with a low vapor pressure can be found. On one side of a suitable confining liquid, the sample is vaporized at a known temperature. Enough air or other gas is allowed into the system on the other side of the confining liquid to null out the difference in levels. The pressure is then read on an external manometer connected to the vacuum system. If mercury is used as the confining liquid, small differences in the mercury levels can be read directly with a cathetometer. In the present study, mercury is used as the confining liquid because of the difficulty in finding an oil in which the chelates are not soluble.

Research on β-diketone Chelates. Metal chelates of β-diketones were known as early as 1887 when Combes(15) synthesized several metal acetylacetonates. In addition, Morgan and Moss(16), Charles and Pawlikowski(17), and many others, synthesized numerous chelates of acetylacetone and postulated models for their molecular structure based on the properties they observed.

Not until recently had any extensive research been done to measure the vapor pressures of the chelates. In 1959 Berg and Truemper(18) reported the vapor pressures of aluminum, cobalt, copper and other β-diketone chelates with various groups substituted onto and in place of the methyl carbons on the ligand, in a study of the volatile characteristics of these complexes. The vapor pressures were measured with the isoteniscope. Wood and Jones(2) used the isoteniscope to measure the vapor pressures of several tervalent transition metal acetylacetonates in order to evaluate the coordinate bond energies and inner orbital splitting in the chelates.

Other research includes the evaluation of the heats of combustion and bond energies of several β-diketonates of iron(III) by Farrar and Jones(19). Sievers, et.al.(20) reported the infrared spectra of metal chelate compounds of hexafluoroacetylacetone. Sievers and others(1) have also done extensive work in the field of gas-liquid chromatography (GLC) of metal chelates. They showed that the order of elution of the chelates of a given metal atom was hexafluoro (hfa), trifluoro (tfa), and acetylacetonate (acac), respectively. Sievers also demonstrated the feasibility of separating complex mixtures of metals with similar properties by chelating the mixture with H(hfa) and separating the chelates by chromatography. As an example, several mixtures of metal trifluoroacetylacetonates were separated; furthermore, the separation of mixtures of the rare earths was postulated. Also, it was shown that mixtures of cis and trans isomers of a metal chelate could also be separated by GLC. Sensitivity of detection by the electron capture detector has been demonstrated to be of the order parts per billion(32,33,34).

II. Theory

Effusion Method. From the amount of material, G (grams), which effuses out of a hole of known area, A (cm^2) in time t (sec), the vapor pressure of the material can be calculated from the equation (3):

$$P_1 - P_2 = \frac{G}{t}(W_1 + W_2)/\sqrt{D} \tag{1}$$

where P_1 is the pressure of the saturated vapor in the cell, P_2 is the pressure in the vacuum system above the effusion orifice, and D is the density of the vapor at the temperature of the experiment and at a pressure of one dyne per square centimeter. W_1 and W_2 are the resistances to flow of the effusion orifice and the tube T (see Figure 1). Since the cross sectional area of the tube T is much larger than the area of the effusion orifice, W_2 is negligible with respect to W_1, which is given by:

$$W_1 = \sqrt{2\pi}/A \tag{2}$$

Using the ideal gas law, one obtains the following expression for D:

$$D = RT/M \tag{3}$$

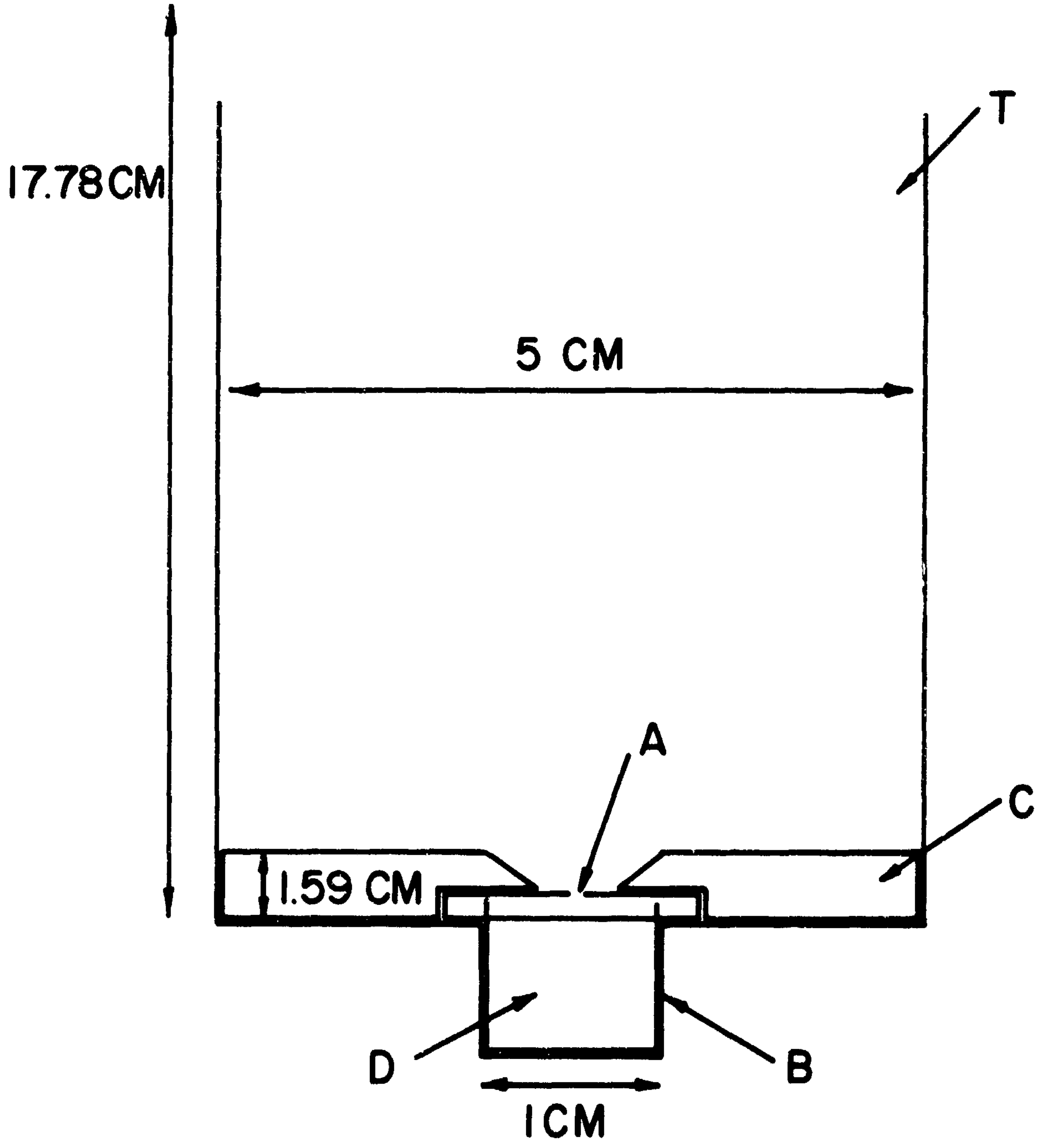
where R is the gas constant in ergs, T is the absolute temperature in degrees Kelvin, and M is the molecular weight of the effusing species.

If the system pressure is negligible with respect to the vapor pressure of the material, substituting Eq (2) and Eq (3) into Eq (1) yields the Langmuir equation.

$$P_1 = \frac{G}{At}\sqrt{2\pi RT/M} \tag{4}$$

Figure 1

EFFUSION APPARATUS



It is noted that in addition to the assumptions mentioned above, Eq (4) is strictly applicable only to an "ideal" system. The equation does not consider the possible resistance to evaporation represented by a low accommodation (evaporation) coefficient for the evaporating surface or the resistance exerted on the effusing gases by the main body of the cell. Also, the equation does not consider the possible reflection of molecules back into the hole from the walls of the vacuum system. This effect is made negligible by having the walls of the system remote from the effusion orifice. Eq (4) neglects the possible reflection of molecules back into the cell from the walls of the orifice; that is, the equation is strictly applicable only to a hole of infinitesimal thickness. Clausing(21) studied the vapor transport through right circular cylindrical channels and calculated values for a factor to be multiplied by the observed channel area to form an effective area. The Clausing factor is a function of the length-to-radius ratio of the channel. Clausing showed that if this ratio were small, the fraction of the molecules entering the channel that is reflected back would be negligible. Whitman(22) and Motzfeldt(11) extended Clausing's studies to effusion cells and orifices and developed a correction factor to account for the re-emission of effusing material from orifice and cell walls back to the vapor source. Carlson(23) re-examined the degree of vapor saturation within the cell using a model similar to that of Clausing, but did not make the restrictive assumption of a linear pressure gradient in the cell as did Clausing. Carlson found that if the orifice area is small relative to the cross sectional area of the cell and if the vaporization coefficient of the evaporating material is near unity, the vapor in the cell could be considered as saturated.

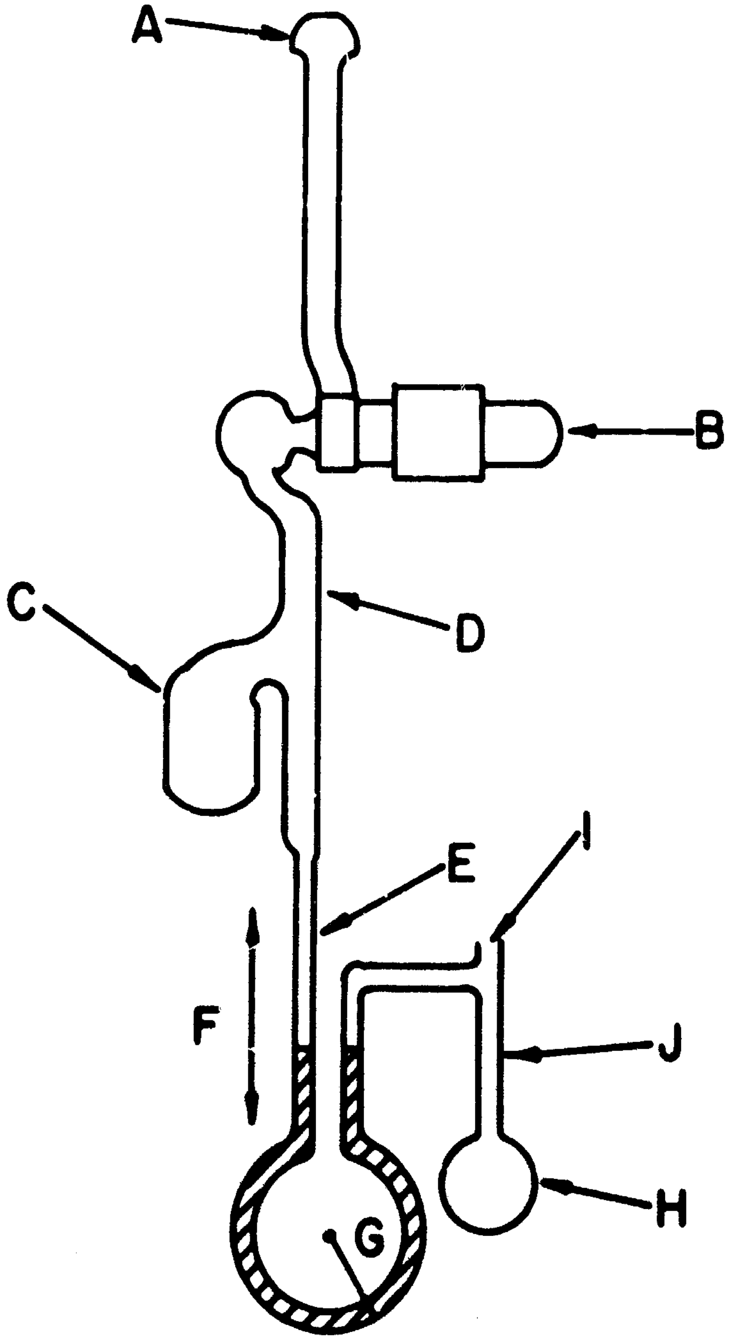
Winterbottom and Hirth(24) questioned the assumption Clausing made that a molecule striking a site, on the cell wall, for example, would be reflected from the same site. They postulated that there is a high probability of adsorption and surface diffusion such that re-emission of the molecule occurs at a site removed from the point of impingement. This results in a model in which transport of material through the orifice occurs both in the vapor and solid states. They developed expressions for calculating the contribution to the total flow observed made by surface diffusion. The true vapor pressure is then calculated from the net vapor phase effusion flux. It was shown that the contribution to the total flux by surface diffusion becomes more important for small orifice radii. Finally, Eq (4) and the above calculations and correction factors are used when free molecular conditions exist within the cell orifice. This means that there are no intermolecular collisions in the orifice and interactions are limited to collisions with the orifice walls. According to Knudsen's criterion, such conditions exist if the mean free path of the vapor molecules is of the order ten times the orifice diameter.

Isoteniscope Method. The Smith-Menzies isoteniscope(13), later modified by Booth and Halbedel(14) by the addition of the tear shaped receptacle C and the stopcock B is shown in Figure (2). If the apparent pressure on the sample side is P_a and the apparent pressure on the system side is P_b then the observed pressure difference in the manometer is given by:

$$P_{obs} = P_a - P_b \qquad (5)$$

Figure 2

ISOTENISCOPE METHOD APPARATUS



The observed deflection corrected to 20°C is given by:

$$P_{corr} = P_{obs}\, d_{Hg}^{T} / d_{Hg}^{20} \qquad (6)$$

where d_{Hg}^{T} and d_{Hg}^{20} are the densities of mercury at temperature T°C and 20°C, respectively. The observed reading must be corrected for the vapor pressure of mercury trapped on the sample side of the manometer. In addition, if a "zero point deflection", i.e.: a deflection in mercury levels at room temperature is noted, the observed deflection at elevated temperatures must be corrected for this also. This "zero point deflection" can be caused by several factors, neglecting for the present time the possibility of decomposition of the chelate. If the deflection is due to a trapped non-condensable gas, then a correction must be made for expansion of the gas at higher temperatures. If the trapped gas is a high vapor pressure impurity, re-purification of the sample must be made by sublimation or another technique.

The final expression for the equilibrium vapor pressure at temperature T°C is given by:

$$(P_{eq})_T = P_{obs}\, d_{Hg}^{T} / d_{Hg}^{20} - (P_{Hg})_T \pm P_0 \qquad (7)$$

where $(P_{Hg})_T$ is the vapor pressure of mercury at temperature T°C and P_0 is the "zero point deflection" at room temperature. The plus sign is used if the mercury level on the sample side is initially higher than the level on the vacuum side.

The basic assumption made is that no reaction occurs between the chelate and the mercury in the vapor phase or at the mercury surface. This is not necessarily a safe assumption because at least two possible reactions can be postulated. The first reaction is a mercury catalyzed decomposition of the chelate to form the free metal or metal oxide and gaseous organic products. This reaction would obviously give high apparent vapor pressures. A second reaction is the simple replacement of the metal by mercury to form the mercury chelate and free metal. Either irreproducible results or the appearance of foreign matter at the surface of the mercury or elsewhere in the chamber can be regarded as evidence that some reaction is occurring.

III. Experimental and Results

The vapor pressures of $Al(acac)_3$, $Al(tfa)_3$, $Al(hfa)_3$, $Cr(acac)_3$, and $Cu(tfa)_2$ were measured by the effusion method. The vapor pressure of $Cr(acac)_3$ was also measured by the isoteniscope method (see Table 2).

Sources of β-diketone Chelates.

1. Aluminum acetylacetonate was prepared by R. E. Sievers according to the method of Young(28) and purified by the author according to the same reference by recrystallization from benzene by the addition of hexane. The observed melting point was 194-195°C (lit. 193-194°C(31)).
2. Aluminum trifluoroacetylacetonate was prepared and purified by a modification of the method of Morris, et.al.(29), for the preparation of aluminum hexafluoroacetylacetonate. The compound was recrystallized in the same manner as above. The observed melting point was 120-122°C (lit. 117°C(31)).
3. Aluminum hexafluoroacetylacetonate was prepared and purified according to the method of Morris, et.al.(29). The observed melting point was 72-74°C (lit. 73-74°C(20)).
4. Chromium acetylacetonate was synthesized by R. E. Sievers and recrystallized by the author according to the method of Fernelius and Blanch(30). The observed melting point was 215-216°C (lit. 216°C(30)).
5. Copper trifluoroacetylacetonate was prepared and purified according to the method of Staniforth(31) by the addition of an aqueous solution of cupric chloride to an aqueous solution of trifluoroacetylacetone neutralized with ammonium hydroxide. The chelate was recrystallized from hot benzene solution by the addition of hexane. The observed melting point was 196.5-197.5°C (lit. 200°C(18)).

Effusion Method. The apparatus used for the effusion method is shown in Figure (1). The tubes T and B and the solid cylindrical cover C are constructed of brass. The tube T is 5 cm in diameter and tube B is wide and deep enough so that the effusion cell D fits snugly into it. The brass cover C was used to insure that the cap of the effusion cell was at the same temperature as the rest of the cell and the receptacle B was designed to improve the heat conduction into the effusion cell. The effusion cell was constructed of one-sixteenth inch aluminum 1 cm in diameter and height. A hole of approximately 4 mm diameter was drilled into the aluminum cap and a piece of platinum foil 0.5 mils thick and 1 cm square containing the effusion orifice was affixed to the cap with epoxy resin. The orifice was positioned concentrically with the hole in the cap. Effusion orifices of three different diameters were constructed. The diameters and areas of these orifices are given in Table (1). The diameters were measured with a traveling microscope, accurate to ± 1×10^{-3} mm. The number in parenthesis next to the value for the diameter is the number of observations made of the diameter.

After a period of operation the epoxy resin began to discolor. The platinum foils were removed from the caps with a razor blade and resealed with General Electric RTV-102 silicone rubber, which did not discolor. The orifices were drilled with a micropress and polished with 200 mesh alumina to eliminate any burrs in the walls of the orifice.

The brass tube T is connected to the glass vacuum system by an O-ring coupling. Connected to the glass system are a diffusion pump and conventional oil pump. The glass system is joined to the diffusion

Table 1

Effusion Orifice Dimensions

Orifice No.	Orifice Diameter (mm)	Orifice Area (cm^2)
1	0.410 ± 0.002(9)	$(1.317 \pm 0.011) \times 10^{-3}$
2	0.266 ± 0.001(9)	$(5.560 \pm 0.021) \times 10^{-4}$
3	0.313 ± 0.001(9)	$(7.709 \pm 0.003) \times 10^{-4}$

pump through a large trap cooled with liquid nitrogen. The trap serves to lower the pressure in the system as well as to keep vapors from contaminating the diffusion pump.

At the start of each experiment, the cap and cell containing the sample were weighed on a pan balance accurate to one-tenth milligram. The can was placed into the receptacle B, covered with the solid brass cylinder C and the tube T was connected to the vacuum system. With the system at atmospheric pressure the sample was equilibrated at bath temperature for at least forty five minutes. A forepump was used to bring the system pressure to about 10^{-4} mm in approximately 90 seconds. This pressure was arbitrarily chosen as being negligible with respect to the vapor pressure of the chelate in the cell D. The diffusion pump circuit was opened to the system and liquid nitrogen was introduced into the cold trap; the pressure decreased rapidly to 10^{-5} or 10^{-6} mm of Hg. At the end of the experiment, the cell was removed from the vacuum system and allowed to cool to room temperature before weighing again to eliminate any error in weight loss measurement due to bouyancy effects of the cell or gases originally adsorbed on the cell and sample. The vapor pressure was then calculated from Eq (1).

Temperatures were controlled with a Brookstat constant temperature regulator. A spatula type heater immersed in a well-agitated mineral oil bath was used. Reported temperatures are corrected for emergent stem. Table (2) shows the common, IUPAC, and abbreviated names for the chelates measured. Tables (3) through (8) show the vapor pressure of benzoic acid, which was used as a standard, and the chelates, with literature comparisons where available.

Data obtained with the effusion method were treated in the following manner. According to the Clausius-Clapeyron equation(25), if the heat of vaporization of a substance is assumed independent of temperature, a plot of the logarithm of the vapor pressure versus reciprocal absolute temperature yields a straight line. The form of the equation is:

$$\ln P(mm) = -\Delta H_{vp}/RT + P_{\infty} \qquad (8)$$

where ΔH_{vp} is the molar heat of vaporization and P_{∞} is the logarithm of the theoretical pressure at infinite temperature. The vapor pressure data obtained were treated in a least squares computer program to determine the empirical equation (8) and the molar heats of vaporization. The literature values shown were obtained with the same procedure as described above and back-calculation of the vapor pressures from the resultant empirical equation at the author's experimental temperatures. The procedure of comparing experimental values with calculated values from literature sources is justified if the original literature measurements were made in the same temperature range and with no phase change.

The limits of error given with the experimental values for the vapor pressures were computed from four sources. These are: (1) the error in measurement of the change in weight of the cell before and after the experiment, (2) the uncertainty in the temperature of the bath, (3) the error in measurement of the orifice diameter, and (4) the error in run-time for the system pressure to become negligible with respect to the pressure of the sample in the cell, arbitrarily chosen as ±90 seconds. No account is made for the error in time for the system to return to atmospheric pressure as this time was less than

Table 2

β-diketone Chelates Observed by Effusion

Common Name	IUPAC Name	Abbreviated Name
Aluminum Acetylacetonate	tris(2,4-pentanediono)aluminum(III)	$Al(acac)_3$
Aluminum Trifluoroacetylacetonate	tris(1,1,1-trifluoro-2,4-pentanediono)aluminum(III)	$Al(tfa)_3$
Aluminum Hexafluoroacetylacetonate	tris(1,1,1,5,5,5-hexafluoro-2,4-pentanediono) aluminum(III)	$Al(hfa)_3$
Chromium Acetylacetonate	tris(2,4-pentanediono)chromium(III)	$Cr(acac)_3$
Copper Trifluoroacetylacetonate	bis(1,1,1-trifluoro-2,4-pentanediono)copper(II)	$Cu(tfa)_2$

Table 3

Vapor Pressure of Benzoic Acid by Effusion

Orifice No.	Temp °C	vp(mm)	vp(mm) (Ref 27)*
1	60.22 ± 0.20	0.045 ± 0.001	0.054**
1	70.36 ± 0.20	0.126 ± 0.002	0.132**
1	75.43 ± 0.20	0.196 ± 0.004	0.203**
1	80.31 ± 0.20	0.283 ± 0.007	0.304**
1	85.40 ± 0.20	0.421 ± 0.015	0.457**

$\ln p(\text{mm}) = 28.7235 - 10{,}195.524/_T$

$\Delta H_{vp} = 21.0522$ Kcal/mole

$\ln p(\text{mm})$ (Ref 27) $= 27.5347 - 10{,}153.927/_T$

$\Delta H_{vp} = 20.1748$ Kcal/mole

* measured by the method of Menzies (35)

** calculated values

Table 4

Vapor Pressure of $Al(acac)_3$

Orifice No.	Temp °C	vp(mm)	vp(mm) (Ref 18) (isoteniscope)
1	60.23 ± 0.20	$<$0.0010	0.705*
1	100.55 ± 0.20	0.0086 ± 0.0002	1.603*
1	110.20 ± 1.00	0.0159 ± 0.0003	1.918*
1	120.61 ± 1.00	0.0441 ± 0.0008	2.272*
1	130.74 ± 1.00	0.0934 ± 0.0019	2.669*
1	140.93 ± 1.00	0.2206 ± 0.0052	3.110*

$\ln p(mm) = 28.8904 - 12{,}611.5800/_T$

$\Delta H_{vp} = 25.0579$ Kcal/mole

$\ln p(mm)$ (Ref 18) $= 7.3116 - 2551.0036/_T$

$\Delta H_{vp} = 5.0686$ Kcal/mole

* calculated values

Table 5

Vapor Pressure of $Al(tfa)_3$

Orifice No.	Temp °C	vp(mm)	vp(mm) (Ref 18) (isoteniscope)
1	80.27 ± 1.00	0.0422 ± 0.0009	0.9105*
1	85.24 ± 1.00	0.0718 ± 0.0015	1.091*
1	90.30 ± 1.00	0.1251 ± 0.0019	1.300*
1	100.51 ± 1.00	0.3208 ± 0.0090	1.823*

$\ln p(\mathrm{mm}) = 34.3475 - 13,252.9250/_T$

$\Delta H_{vp} = 26.3322$ Kcal/mole

$\ln p(\mathrm{mm})$ (Ref 18) $= 12.8552 - 4571.0136/_T$

$\Delta H_{vp} = 9.0821$ Kcal/mole

* calculated values

Table 6

Vapor Pressure of $Al(hfa)_3$

Orifice No.	Temp °C	vp(mm)
2	45.07 ± 0.20	0.5787 ± 0.0087
2	50.12 ± 0.20	1.0356 ± 0.0354
2	55.08 ± 0.20	1.7078 ± 0.0581

$\ln p(\mathrm{mm}) = 34.9700 - 11{,}299.7310/_T$

$\Delta H_{vp} = 22.4514$ Kcal/mole

Table 7

Vapor Pressure of $Cr(acac)_3$

Orifice No.	Temp °C	vp(mm)	vp(mm) (Ref 2) (isoteniscope)
1	100.92 ± 0.20	0.0017 ± 0.0001	0.157*
1	120.64 ± 1.00	0.0072 ± 0.0002	0.236*
1	130.89 ± 1.00	0.0134 ± 0.0003	0.285*
1	140.86 ± 1.00	0.0306 ± 0.0006	0.341*

$\ln p(\text{mm}) = 23.0354 - 11{,}011.9200/_T$

$\Delta H_{vp} = 21.8796$ Kcal/mole

$\ln p(\text{mm})$ (Ref 2) $= 6.1647 - 2990.6977/_T$

$\Delta H_{vp} = 5.9422$ Kcal/mole

* calculated values

Table 8

Vapor Pressure of $Cu(tfa)_2$

Orifice No.	Temp °C	vp(mm)	vp(mm) (Ref 36) (isoteniscope)
1	80.41 ± 0.20	0.0058 ± 0.0003	0.15*
1	85.50 ± 0.20	0.0078 ± 0.0002	0.175*

* approximate values read from a graph

ten seconds.

With higher temperatures and correspondingly higher volatilities, smaller orifices and shorter run times were used so that all of the chelate sample in the cell would not be lost to effusion. The total error reported ranges from less than two percent up to five percent.

Isoteniscope Method. The modified isoteniscope is shown in Figure (2). The part A was connected to the vacuum system with a ground glass ball-and-socket joint. The glass tubing D was constructed of 14 mm outer diameter pyrex tubing, and the tear shaped bulb C was large enough to hold slightly more mercury than is required for the manometer G (about 20 cc). The glass tubing E was constructed of 5 mm inner diameter heavy walled pyrex for extra support of the mercury receptacle. The straight vertical portions of the manometer F are about 50 mm long and the sample tube J was constructed of 20 mm outer diameter pyrex tubing. The location B is a teflon stopcock fitted with Viton O-rings. The curved portion of the manometer is circular with a radius of 35 mm.

Before each experiment, the glass was cleaned first with nitric acid, then chromic acid solution, washed with tap water and finally distilled water. The apparatus was dried and pumped on to remove water vapor. A rubber stopper, previously boiled in sodium hydroxide solution, was in place at I during this procedure. Sufficient clean mercury was decanted through B, with the stopcock bore removed, into the receptacle C. The mercury was distilled into the manometer G under vacuum, by gentle heating.

The mercury was decanted back into C and the sample was introduced at I into the bulb H through a paper funnel which was used to prevent the sample from being deposited on the glass at I with subsequent decomposition when the tubing is sealed off.

After the tubing at I was sealed off, the isoteniscope was immersed in a silicone oil bath to a sufficient depth to cover the point I. With the mercury in C, the system was pumped on to outgass the glass and sample. The temperature selected for the bath depended on the volatility of the chelate being observed.

After outgassing the sample for approximately thirty minutes, the mercury was redecanted into G until the mercury levels were half way along the vertical portions of the manometer. If the mercury levels were not equal at room temperature, the above procedure for outgassing the sample was repeated until the levels were the same.

At each temperature of observation, the system was allowed to equilibrate for at least one hour. Many observations of the difference in mercury levels at each temperature were made with a cathetometer accurate to ±0.01 mm. The third decimal place in the vapor pressure is estimated. After several observations the isoteniscope was gently shaken to move the mercury levels in the manometer. This procedure insured uniform meniscuses on the mercury. A thermistor controlled spatula type heater was used to control the bath temperature to ±0.5°C, and the bath was vigorously stirred.

Benzoic acid was used as a standard. The vapor pressure results are shown in Table (9), and the number in parenthesis next to the value is the number of observations made of the difference in mercury levels.

The vapor pressure of chromium acetylacetonate is reported in Table (10). This was the only chelate examined by the isoteniscope method in the present work.

Table 9

Vapor Pressure of Benzoic Acid by the Isoteniscope Method

Temp °C	vp(mm) (Corrected)	vp(mm) (Ref 27)*	vp(mm) (Ref 18)*	vp(mm) (Ref 2)*
70.36 ± 0.50	0.148 ± 0.041 (7)	0.132	0.247	0.127
80.31 ± 0.50	0.359 ± 0.054 (12)	0.304	0.437	0.285
90.60 ± 0.50	0.561 ± 0.078 (8)	0.688	0.741	0.627

* calculated values

Table 11

Apparent Vapor Pressure Results for Varying Run Times by Effusion for Benzoic Acid at 85°C

Run Time (hr)	Cell No. 1 (0.410 mm diameter)	Cell No. 2 (0.266 mm diameter)	$\frac{\text{Cell No. 2}}{\text{Cell No. 1}}$
1	0.4946 mm	0.8210 mm	1.66
1.5	0.4962	0.8346	1.68
2.0	0.4814	0.7435	1.54

literature value (27) for 85°C is 0.457 mm.

Knudsen's criterion states that the mean free path of the molecules be of the order ten times the effusion orifice dimensions for molecular flow conditions to exist. The mean free path of benzoic acid vapor molecules was calculated at 80°C. It was found that Knudsen's criterion was not satisfied. Anomalously, even though the flow was viscous, the experimental results for the vapor pressure of benzoic acid from orifice number 1 agreed closely with the literature values. One cannot correct for the effects of viscous flow through the orifice since data on the viscosities of the effusing vapors are not available. Furthermore, it was calculated that at temperatures 60°C and lower, free molecular flow conditions existed for benzoic acid; however, there was still a large increase in apparent vapor pressure in going from the larger to smaller orifices.

The assumption made in the heat transfer calculation that a steady state temperature distribution exists in the solid sample is questioned. The larger the effusion orifice, the greater is the possibility that the material evaporates at such a rate from the surface of the substance that heat cannot be supplied at a sufficiently fast rate to maintain the substance at or near the bath temperature. This means that saturation would not occur and the effusion rate would not be a constant as a function of time even though the ideal heat transfer transient period was passed. The fact that organic compounds are notoriously poor conductors of heat lends some weight to the above supposition.

In summary, the phenomena of surface diffusion and self-cooling vary inversely in their effects on the apparent vapor pressure when the effusion orifice size is varied. It is believed that these are the chief contributors to the actual errors in the effusion method. At best, then, the data given from the effusion method must be considered approximate and the associated indications of precision are not representative of the true experimental limits. The fact that orifice number 1 (diameter = 0.410 mm) gave values for the vapor pressure which most closely agreed with the literature values is not sound justification that all results with this orifice are accurate. However, one might expect that data obtained with this orifice are more accurate than results obtained with orifices of smaller diameters. This assumption is based on the evidence that even at relatively low temperatures, where effusion rates were of the order 10^{-6} grams per second, the discrepancy in the apparent vapor pressures for different orifice diameters still existed. Table (12) shows the results of this experiment.

Table 12

Apparent Vapor Pressure of Benzoic Acid under Molecular Flow Conditions

Orifice diameter (mm)	Orifice No.	Run time (hr)	Temp °C	vp(mm)
0.410	1	4	60.22	0.0535
0.266	2	4	60.22	0.0729

$$\frac{\text{vp(mm) orifice No. 2}}{\text{vp(mm) orifice No. 1}} = 1.36$$

literature value (27) for 60°C is 0.057 mm.

Isoteniscope Method. During the runs on benzoic acid, the surface of the mercury became discolored on the sample side. Whether this was due to outgassing of the sample or condensation of the vapor on the mercury, or impurities in the acid itself, is not known, but the effect was to suppress the meniscus. Gentle shaking of the isoteniscope removed the discoloration. Considerable difficulty was encountered with the outgassing of the $Cr(acac)_3$ sample, and the procedure for outgassing described in the experimental section was used several times until reproducible results were obtained.

Difficulty was also encountered in consistently observing the difference in levels of the mercury with the cathetometer. This was due to the problem of adequately backlighting the meniscuses because of the refractive effects of the bath oil. Also, some error is introduced due to differences in shape and height of the meniscuses. No correction is made for meniscus effect and the shaking technique described in the experimental section usually eliminated the effect.

The literature values are on the average two to three times higher than the experimental values. One reason that the experimental values may be low is due to the difficulty in reading the difference in levels of the mercury consistently. This is coupled with the fact that the chief contribution to the observed difference in levels is made by the vapor pressure of the mercury, resulting in errors of the same order of magnitude as the vapor pressure of the chelate. A second explanation deals with the outgassing of the sample. Truemper(18) reported in his work that sometimes the mercury levels were different at room temperature. It seems likely that this is due to improper outgassing of the sample, but Truemper simply subtracted this "zero point reading" from the observed differences at higher temperatures. If the "zero point reading" was due to a trapped non-condensible gas, then apparently no correction was made for the expansion of the gas at higher temperatures. In the present work, data were rejected and outgassing was repeated until the "zero point reading" was negligible. Wood and Jones(2) reportedly used the same procedure as Truemper. If the sample is not properly outgassed, the apparent vapor pressures could easily be two or three times the true vapor pressure.

Several times in this work, the difference in mercury levels was considerable at room temperature. The sample was equilibrated at some higher temperature and the outgassing technique previously described was used. When the original "zero reading" was subtracted from the observed difference in mercury levels after thorough outgassing, the result was a negative value for the apparent vapor pressure of the chelate. Obviously, the practice of subtracting a "zero point reading" cannot be justified.

It is also noted that although the outgassing technique was successful for the less volatile chromium chelate, if such a technique were used for the more volatile chelates, considerable sample loss would probably occur. A better method for outgassing the sample is to sublime the chelate into the top of the sample tube at I (see Figure 2), or to sublime the sample into a break-seal ampule and introduce the sealed ampule into the sample tube.

V. Conclusions and Future Work

From the discussion of theory on the effusion method it is readily realized that the method is not quite as straightforward as Eq (1) leads one to believe. Because of the considerations and restrictions mentioned, the effusion method is only strictly applicable to the determination of the vapor pressures of metals, for which heat conduction and other problems are negligible.

Even though the absolute vapor pressures in the present work must be considered as approximate, the trends in the vapor pressure in going from non-fluorinated to more extensively fluorinated ligands on a given metal atom parallel the orders of elution of the chelates in gas chromatography; that is, the higher the vapor pressure, the shorter is the elution time (see Table 13). It is concluded that the overall effect on the elution times of the chelates in the chromatograph is probably due to the volatility of the chelate rather than any large variations in the extent of interaction with the substrate in the column. The possibility of a reaction occurring between the chelate and the mercury must be considered in the isoteniscope method. In addition, the use of mercury, a high density liquid, as confining liquid obviates the greatest advantage of the method for the determination of small vapor pressures.

Research in measuring the vapor pressures of β-diketone chelates is presently being conducted in two main areas at the Institute of Technology. These are: (1) the refinement of the isoteniscope method. A survey of the solubility characteristics of the chelates in various low viscosity, low vapor pressure oils is being undertaken to find a

Table 13

Comparison of Vapor Pressures by Effusion with Elution Times in Gas Chromatography

Chelate	Temp °C	vp(mm)	(Ref 37) Column Temp °C	Elution Time (min)
$Al(acac)_3$	100.55	1.603	165	1*
$Al(tfa)_3$	100.51	1.823	106	4.25*
$Al(hfa)_3$	55.08	1.708	50	4.4**

* column length of one foot

** column length of five feet
estimated equivalent one foot column length elution time is 0.9 minutes.

more suitable manometric fluid than mercury. The oil would give a larger apparent reading at each temperature, and the lower surface tension of the oil on glass would eliminate errors associated with the mercury meniscus. Also, the possibility of reaction with the oil would be much less likely. The survey showed that $Cr(acac)_3$ was partially soluble in all the oils but was apparently least soluble in Apiezon C oil at room temperature. Repeated attempts to reproduce values for the vapor pressure of $Cr(acac)_3$ at 120°C failed with the use of Apiezon C oil as confining liquid. This was due to the fact that the lighter fractions in the oil were distilling out on the vacuum side as a function of time. This resulted in a region of higher density oil on the vacuum side than on the sample side of the manometer; (2) the investigation of other methods of measuring vapor pressure. Under consideration are two null techniques. With one technique the deflection of a thin metal membrane caused by the pressure of the chelate is nulled by the admission of air to the vacuum side and the pressure is read on a manometer connected to the vacuum system. The null sensing device is a capacitance-inductance bridge circuit connected to the membrane. The second technique utilizes the aneroid manometer designed by Stewardson(26). The principles involved are basically the same as those described for the metal membrane only the sensing device is a mirror-knife edge arrangement mounted on the glass membrane. This device has the important advantage that the metal chelate comes in contact only with glass surfaces.

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