Vapor Pressures, Mass Spectra, Magnetic Susceptibilities, and Thermodynamics of Some Phthalocyanine Compounds

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Vapor pressures of cobalt phthalocyanine (CoPc), tin phthalocyanine (SnPc), dichloro- and diphenyltin phthalocyanines (Cl_2SnPc and ϕ_2SnPc), hexadecachloro- and hexadecabromophthalocyanines ($Cl_{16}Pc$ and $Br_{16}Pc$), and tetraphenylporphine (TPP) were measured by the effusion method, and heats and entropies of sublimation obtained. A low evaporation coefficient, $\alpha = 0.007$, was found for CoPc; for ϕ_2SnPc, $\alpha \cong 1$. Mass spectra obtained with a time-of-flight mass spectrometer showed that CoPc, SnPc, and ϕ_2SnPc sublime without decomposition. Constants with least-squares standard deviations for the equation $\log P_{atm} = -A/T + B$ are

	A	B
CoPc	9591 ± 234	8.614 ± 0.333
SnPc	6452 ± 182	5.056 ± 0.290
Cl_2SnPc	11414 ± 315	10.254 ± 0.429
ϕ_2SnPc	9136 ± 324	8.347 ± 0.485
$Cl_{16}Pc$	7367 ± 299	11.886 ± 0.710
$Br_{16}Pc$	5702 ± 295	6.875 ± 0.637
TPP	5787 ± 87	4.124 ± 0.128

PHTHALOCYANINE compounds (Figure 1) are unusually thermally stable and are often purified by sublimation (*18*). However, the only quantitative vapor pressure data available are for copper phthalocyanine (CuPc), studied by Curry and Shaw (*8*). Mass spectra for CuPc and several chlorinated copper phthalocyanines have been reported by Hill and Reed (*11*) and Beynon, Saunders, and Williams (*2*), who vaporized samples into a mass spectrometer from a heated filament or a glass stage and were unable to measure the temperature of the vaporizing samples. They concluded that all the compounds sublimed as unchanged molecules up to some (unknown) temperature, but that thermal decomposition occurred beyond this point.

Using the effusion method, Curry and Shaw (*8*) found vapor pressures of CuPc ranging from 4×10^{-7} to 2×10^{-5} atm in the temperature range from 657° to 722° K. They reported that CuPc exhibits an evaporation coefficient $\alpha = 0.01$, as calculated by Equation 4 from data taken with five effusion cells. From the slope and intercept of a plot of corrected log p *vs.* $1/T$ they obtained for the sublimation of CuPc $\Delta H^\circ_{700^\circ K} = 63.6 \pm 1.2$ kcal per mole and $\Delta S^\circ_{700^\circ K} = 67.2$ eu. Curry and Shaw rationalized the low evaporation coefficient on the grounds of hindered sublimation of the large, flat molecules, which are oriented in perpendicular planes in the solid (*18*).

We have measured vapor pressures of six substituted phthalocyanines and one porphyrin by the effusion technique. Mass spectrometric studies were made for three of these.

For convenience, the formulas and molecular weights of the compounds studied are given in Figure 1.

MATERIALS

Dichlorotin Phthalocyanine (Cl_2SnPc) was prepared from $SnCl_2$ and phthalonitrile by the methods of Kinney (*13*) and Barrett, Dent, and Linstead (*1*). Tin phthalocyanine (SnPc) was also prepared from Cl_2SnPc by reaction with $SnCl_2$ according to a method given by Kinney (*13*).

Diphenyltin phthalocyanine (ϕ_2SnPc) was prepared for the first time by the following method. One hundredth mole (5.26 grams) of previously prepared dilithiophthalocyanine was placed in a Soxhlet thimble and extracted into 200 ml of refluxing (78°) absolute ethanol in a Soxhlet extractor protected from moisture with a calcium chloride trap. Diphenyltin dichloride (2.6 grams) was placed in a Soxhlet thimble and extracted into this solution. The resulting mixture was allowed to cool and the solid product was separated by centrifugation at 1000 rpm for 10 minutes. The blue precipitate was dried in a rotary evaporator by mixing with copper shot and immersing in a molten potassium isothiocyanate bath. The solid was placed in a vacuum sublimator and sublimed carefully at 4×10^{-6} mm of Hg and 450° C for 3 days. There resulted 60 mg of compound.

Cobalt phthalocyanine (CoPc) was prepared by reaction of dilithiophthalocyanine (*1*) and anhydrous cobaltous chloride in anhydrous acetone.

Hexadecabromophthalocyanine ($Br_{16}Pc$) and hexadecachlorophthalocyanine ($Cl_{16}Pc$) were prepared for the first time for use in these experiments by refluxing tetrabromo- and tetrachlorophthalic anhydrides with urea in 1-chloronaphthalene at 263° C in the presence of cobalt. The absence

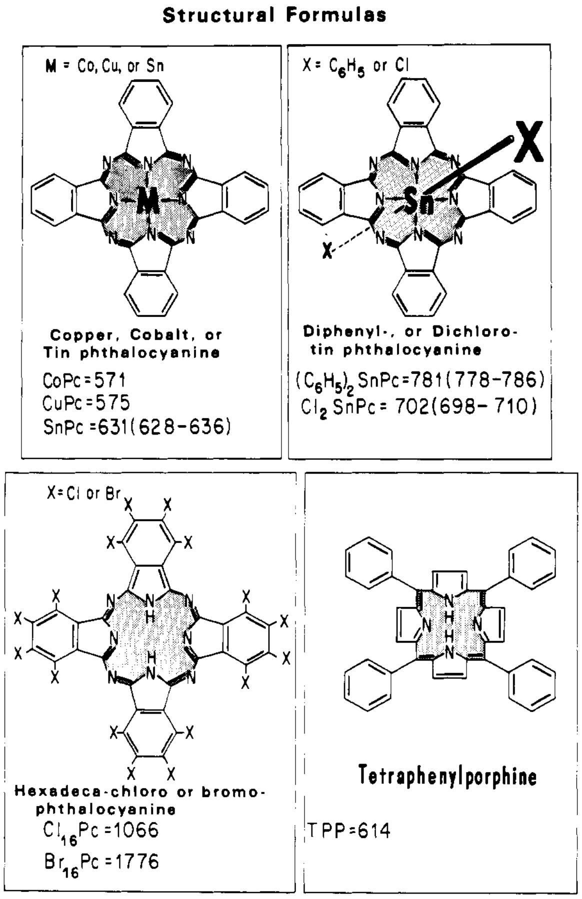

Figure 1. Structural formulas and molecular weights of compounds studied

Range of isotopic masses indicated for tin compounds

of cobalt in the products was shown by chemical analysis and by the fact that both products were diamagnetic when their susceptibilities were determined.

Tetraphenylporphine (TPP) was furnished to the authors by Krahn (*15*).

All these materials were subjected to elemental analysis by standard techniques. Results of the chemical analyses are given in Table I. It was necessary to precondition the combustion train used for C, H, and N determinations by burning a portion of the compound to be analyzed just prior to the actual analyses, in order to obtain reproducible analytical results.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The magnetic susceptibilities at room temperature of CoPc, SnPc, $Cl_{16}Pc$, and $Br_{16}Pc$ were measured by means of a Faraday balance constructed by Swanson (*21*). Analytical reagent grade sucrose (Fisher Scientific Co.) with an assumed gram susceptibility of $X_g = -0.566$ cgs unit was used as a standard. CoPc was found to be paramagnetic ($X_{\text{molar}} = 1484 \times 10^{-6}$ cgs), while SnPc was diamagnetic ($X_{\text{molar}} = -380 \times 10^{-6}$ cgs). Both $Cl_{16}Pc$ ($X_{\text{molar}} = -522 \times 10^{-6}$ cgs) and $Br_{16}Pc$ ($X_{\text{molar}} = -706 \times 10^{-6}$ cgs) were diamagnetic.

MASS SPECTROMETRIC OBSERVATIONS

Mass spectra of CoPc, SnPc, and ϕ_2SnPc were obtained by means of a Bendix Model 12-101 time-of-flight mass spectrometer in order to verify that they sublimed without decomposition and to confirm the molecular weight of ϕ_2SnPc, a compound not previously known. The instrument has usually been used (*6, 7*) for studying the sublimation of refractory inorganic compounds at high temperatures which are measured by means of an optical pyrometer.

Table I. Results of Chemical Analyses

SnPc	C	H	N	Sn
Calculated, %	60.89	2.55	17.75	18.88
Found, %	60.78	2.67	18.13	18.92
Cl_2SnPc	C	H	N	Sn
Calculated, %	54.60	2.28	15.98	16.83
Found, %	54.29	2.42	14.82	16.70
ϕ_2SnPc	C	H	N	
Calculated, %	67.27	3.33	14.26	
Found, %	67.59	3.48	14.07	
CoPc	C	H	N	Co
Calculated, %	67.26	3.20	19.61	10.34
Found, %	67.27	3.20	18.91	10.34
$Cl_{16}Pc$	C	H	N	
Calculated, %	36.06	0.19	10.51	
Found, %	35.80	0.12	8.58	
$Br_{16}Pc$	C		N	
Calculated, %	21.62		6.30	
Found, %	21.59		5.41	

The present samples were completely sublimed from a tungsten effusion cell, which was heated only by radiation from the filaments, rather than by the usual electron bombardment. The temperatures were increased slowly to a maximum of about 800° C, too low for use of the optical pyrometer.

The molecules effusing from the cell were ionized by means of electrons of 40-eV energy. Broad, asymmetric mass peaks were observed at high masses because the resolution of the time-of-flight instrument falls off as $1/(M)^{1/2}$, and because of the defocusing action of the thermal velocities of the effusing molecules. Thus, single mass peaks appeared broadened and ions differing because of loss of one or more protons by fragmentation could not be separated above $m/e = 200$. Typical widths at half height of the mass peaks near $m/e = 600$ were 10 to 15 mass units. However, the peaks fell at values of m/e readily identified with the parent phthalocyanine molecules and characteristic fragments of these. It appeared that the fragments observed resulted from electron impact rather than thermal decomposition, as also found by other workers (*2, 11*), who studied CuPc and chlorinated CuPc's at high resolution.

The mass spectrum of SnPc was analogous to that observed for CuPc by Hill and Reed (*11*). The parent ion $SnPc^+$ gave the most prominent peak; $SnPc^{2+}$ and $SnC_6H_4(CN)_2^+$ were also observed. The spectrum of CoPc differed; $CoPc^+$ was observed, but $CoPc^{2+}$ and $CoC_6H_4(CN)_2^+$ were absent. The most prominent fragment was Pc^+. In the mass spectrum of ϕ_2SnPc, the parent peak ϕ_2SnPc^+ and the fragments $\phi SnPc^+$ and $SnPc^+$ were observed. More sophisticated observations were not possible because of the low resolution at high masses and the high background of Pc^+ and its fragments which built up during successive experiments. Some small contamination of the samples by starting materials or side reaction products was detected, but the contaminants vaporized away rapidly.

Summary of Mass Spectral Observations. The mass spectra confirm the molecular formulas shown in Figure 1, because ions of the appropriate parent molecular weights were observed. They also support the conclusion that the three phthalocyanines studied sublime without thermal decomposition until some very high temperature is reached, as is also the case with other phthalocyanines (*2, 8, 11, 18*).

Thus one is justified in carrying out vapor pressure measurements by the Knudsen (effusion) method.

VAPOR PRESSURE MEASUREMENTS

Vapor pressures of all the compounds were determined as a function of temperature by the Knudsen effusion method (*5*, *14*), in which one measures the rate of effusion of the equilibrium vapor through a small orifice. The results are tabulated in Table II and plotted in Figures 2 and 3.

The Knudsen cells were constructed from tantalum spinnerets of 0.5-inch inner diameter and depth, to which lids were tightly spot-welded. The lids were fabricated from platinum foil 0.003 inch thick, into which orifices were drilled by sandwiching the foil between brass blocks and drilling through the sandwich. Orifice diameters were measured to ±0.001 cm by means of a Gaertner micrometer microscope.

The cells were suspended from one arm of an Ainsworth RV-AU-2 vacuum semimicrobalance into an evacuated quartz tube by means of two tungsten wires of 0.040-inch diameter, and 30-inch length and heated by means of a tube furnace surrounding the vacuum envelope. Weight losses were measured to ±0.01 mg by means of the strip chart record from the vacuum balance over appropriate times. Weight losses were corrected for the fraction of the total effusate which was intercepted by, and assumed to condense on, the suspension wires and quartz insulators slipped over them. This fraction amounted to 0.1150 in all cases. Temperatures of the cells were measured with platinum-platinum, 10% rhodium thermocouples spot-welded to their lids. The thermocouple wires were led from the hot zone along thin-walled quartz tubing, which was slipped over the tungsten suspension wires. The thermocouple circuit could be completed to a potentiometer by means of a rotating device inserted through the vacuum wall by a ball and socket joint and protruding between the suspension wires 30 cm above the cell. The thermocouples were not calibrated individually.

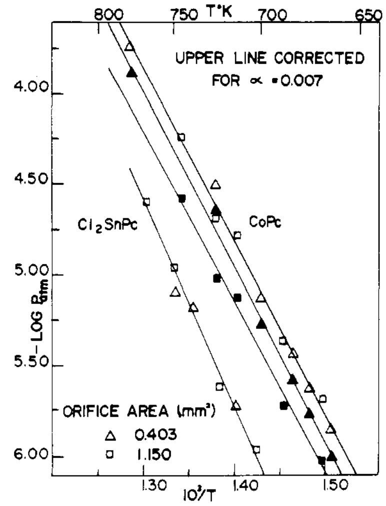

Figure 3. Vapor pressures of cobalt phthalocyanine and dichlorotin phthalocyanine determined with two orifice sizes

Cl_2SnPc. No difference observed, one least-squares line drawn through both sets of data

CoPc. Upper line and open data points correspond to data corrected for $\alpha = 0.0068$

For 0.403-mm² orifice, least-squares line given by $\log P_{obsd}(atm) = -(9694 \pm 276)T + (8.613 \pm 0.393)$

For 1.150-mm² orifice, equation is $\log P_{obsd}(atm) = -(9364 \pm 421)/T + 7.955 \pm 0.596$

The same procedure was used for effusion measurements on all the compounds. The pulverized compound was introduced through the orifice of the previously weighed effusion cell, which was then suspended from the vacuum balance, evacuated, and weighed. When the pressure fell below 1×10^{-6} torr, the furnace was heated slowly to a temperature in the range 400° to 600° K, where it was maintained until any initially high vaporization rate dropped off to a constant value, indicating that volatile

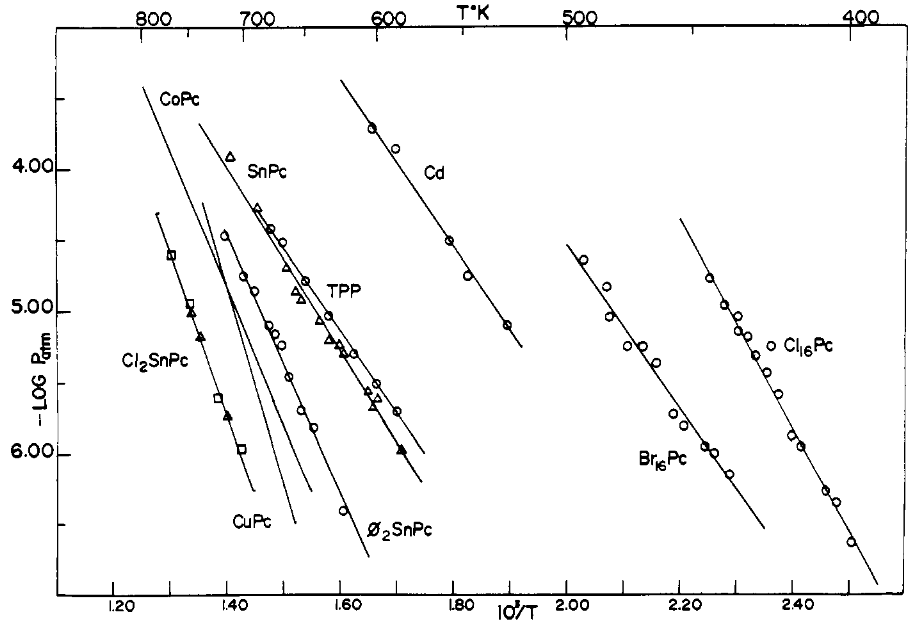

Figure 2. Vapor pressures of phthalocyanines, tetraphenylporphine, and cadmium

Experimental points shown

Cadmium line from Stull and Sinke (*20*)

Cobalt and copper phthalocyanine lines corrected for evaporation coefficients of 0.007 and 0.01, respectively

Copper phthalocyanine line from recalculation of Curry and Shaw's data (*8*)

Table II. Summary of Vapor Pressure Measurements

Least-squares constants A and B and their standard deviations correspond to equation log P(atm) = $-A/T + B$. Uncertainties listed for ΔH_T° and ΔS_T° are statistical standard deviations. A more realistic estimate of the accuracy in ΔH_T° and S_T° is 3 standard deviations, as listed below. Data for CoPc were corrected for evaporation coefficients of 0.0068 and 0.01, respectively. Curry and Shaw's data (*8*) for CuPc were treated by our least squares program after correction for $\alpha = 0.01$.

Compound	A	B	ΔH_T° Kcal/Mole	ΔS_T°, Cal/Deg-Mole	Orifice Area, Cm^2	Clausing Factor
CoPc	9591 ± 234	8.614 ± 0.333	43.9 ± 3.3	39.4 ± 4.5	4.03×10^{-3}	0.839
					1.15×10^{-2}	0.905
SnPc	6452 ± 182	5.056 ± 0.290	29.5 ± 2.4	23.1 ± 4.5	7.32×10^{-3}	0.884
CuPc	13661 ± 253	14.315 ± 0.367	62.5 ± 3.6	65.5 ± 5.1		
Cl_2SnPc	11414 ± 315	10.254 ± 0.429	52.2 ± 4.2	46.9 ± 6.0	1.15×10^{-3}	0.905
					4.03×10^{-3}	0.839
ϕ_2SnPc	9136 ± 324	8.347 ± 0.485	41.8 ± 4.5	38.2 ± 6.6	7.32×10^{-3}	0.884
$Cl_{16}Pc$	7367 ± 299	11.886 ± 0.710	33.7 ± 4.2	54.4 ± 9.9	7.32×10^{-3}	0.884
$Br_{16}Pc$	5702 ± 295	6.875 ± 0.637	26.1 ± 3.9	31.5 ± 8.7	7.32×10^{-3}	0.884
TPP	5787 ± 87	4.124 ± 0.128	26.5 ± 1.2	18.9 ± 1.8	1.15×10^{-2}	0.905

impurities in the sample had been eliminated. In most cases the initial weight loss was less than 2 mg. After each new temperature was set, the system was permitted to attain a constant rate of weight loss for 5 to 10 minutes before this was recorded. In the cases of SnPc above 720° K and TPP above 676° K, the rates of weight loss became unreproducible. This was taken to mean that thermal decomposition of the sample had occurred, and only data at lower temperatures were retained for calculation.

The vapor pressures were calculated from the well-known Knudsen equation (*5, 14*)

$$P = \frac{W}{Kat}(2\pi RT/M)^{1/2} = 0.02255\frac{W}{Kat}(T/M)^{1/2} \tag{1}$$

in which W is the weight loss in grams through an orifice of area a (cm^2) in time t (seconds), at a temperature of T° K, M is the molecular weight of the effusing molecules, R is the ideal gas constant, and K is the Clausing factor (*4, 9*) which corrects for the finite thickness of the orifice. Results for each compound are given in Table II, which lists constants A and B for the vapor pressure equations

$$\log P_{\text{atm}} = -A/T + B \tag{2}$$

obtained from least-squares fits to the data. Also listed are the heats and entropies of sublimation at the mean temperatures of measurement, obtained by rewriting Equation 2 in the familiar form

$$\log P_{\text{atm}} = -(\Delta H_T^\circ/2.303R)/T + \Delta S_T^\circ/2.303R \tag{3}$$

Standard deviations are listed for A and B, while the uncertainties listed for ΔH and ΔS are ± three standard deviations.

Figures 2 and 3 show the vapor pressure plots. The special cases of CoPc, SnPc, and Cl_2SnPc are discussed below.

The vapor pressure of cadmium metal was measured at five temperatures from 528° to 603° K as a check of the apparatus, technique, and temperature scale. The pressures obtained were in good agreement with the literature (*12, 20*) available when the work was completed. This is shown in Figure 2, in which the line corresponding to the literature data (*12, 20*) passes nicely through the experimental points. A least-squares treatment of log P *vs.* $1/T$ gives a pressure and its standard deviation at the mid-temperature, 565° K, of $(4.27 \pm 0.25) \times 10^{-5}$ atm, compared with 4.4×10^{-5} atm obtained from the tabulations of Hultgren (*12*) or Stull and Sinke (*20*). The least-squares slope and intercept yield $\Delta H_{565}^\circ = 28.1 \pm 1.3$ kcal per mole and $\Delta S_{565}^\circ = 29.8 \pm 1.7$ cal/mole-deg. These values are higher than but within two standard deviations of the literature enthalpy (*12*), $\Delta H_{565}^\circ = 26.4$ kcal per mole, and the absolute entropy change (*12*), $\Delta S_{565}^\circ = 26.8$ cal/mole-deg. A recent redetermination of the vapor pressure of cadmium by McCreary and Thorn (*17*) by mass effusion and torsion effusion techniques gives values, respectively, 15 and 22% higher than the older tabulations. However, their heats of sublimation from both techniques and from an analysis of the earlier literature are in agreement within 0.1 kcal. Because only five data were taken by us on cadmium, we feel that the enthalpy and entropy changes obtained are satisfactory, and we have selected three standard deviations as a realistic estimate of the absolute uncertainties of the heats and entropies of sublimation of the phthalocyanines. A temperature error of ±3° would yield a fractional error in the pressure of cadmium of ±13%, as can be seen from the relationship $d\ln P/dT = \Delta H/RT^2$. This appears to be an appropriate estimate of the accuracy of our temperature scale.

EVAPORATION COEFFICIENTS OF CoPc, Cl_2SnPc, AND SnPc

Consideration of the various molecular fluxes within an effusion cell with no pressure gradient, but with a vaporizing sample of gross area A and nonunity evaporation coefficient α, leads to the equation

$$P_{\text{eq}} = P_{\text{obsd}}(1 + Ka/A\alpha) \tag{4}$$

where, P_{obsd} is the observed pressure calculated by Equation 1 from effusion measurements, while P_{eq} is the equilibrium vapor pressure. Equation 4 is also a special case for the ratio of length to radius of the effusion cell used here, of the equation derived by Motzfeldt (*19*) and by Whitman (*24*), who attempted to account for pressure gradients within the cell. Equation 4 is often used in conjunction with effusion measurements with two or more orifices to calculate P_{eq} and α.

Carlson *et al.* (*3, 4*) have discussed the inconsistencies and approximations involved in deriving Equation 4, and have shown that it applies rigorously only to the case of a spherical cell with negligible rate of effusion. Ward and Fraser (*23*) have shown by Monte Carlo simulation of the real effusion process that, despite the inconsistencies, Equation 4 should give P_{obsd} correct within 1% for cells of the present geometry and α's on the order of 0.01. Carlson *et al.* (*3, 4*) have also observed that α's obtained via Equation 4 may be spurious, because nonequilibrium effects such as temperature gradients and surface depletion may result from the use of large orifices.

Curry and Shaw (*8*) found $\alpha = 0.01$ by this method. It is of interest to treat the data for CoPc and Cl_2SnPc, each taken with two orifices, by this approach, for comparison with Curry and Shaw's results.

CoPc. This compound has the same crystal and molecular geometries as CuPc (*18*). Effusion measurements were made with CoPc in effusion cells of orifice areas 4.03×10^{-3} and 1.15×10^{-2} cm^2, with Clausing factors of 0.839 and 0.905. The values of P_{obsd} which resulted are plotted as filled symbols in Figure 3, in which a systematic difference in P_{obsd} for the two cells is easily seen. Least-squares lines through each of the two sets of data are drawn in Figure 3. The value $\alpha = 0.0068$ was obtained by using the two least-squares equations to calculate a value of P_{obsd} for each orifice at 720° K: $(1.42 \pm 0.09) \times 10^{-5}$ and $(0.89 \pm 0.07) \times 10^{-5}$ atm, for the smaller and larger orifices, respectively. Then Equation 4 was solved simultaneously for α and P_{eq}. The area of the bottom of the effusion cells (1.267 cm^2) was used for area A of the sample. The result is $\alpha = 0.0068$.

If one assigns uncertainties of ±20% to P_{obsd}, a propagation of errors via Equation 4 gives a corresponding uncertainty in α of only ±0.002. The individual data were then recalculated with $\alpha = 0.068$ in Equation 4 to obtain P_{eq}. The recalculated points are plotted as log P_{eq} *vs.* $1/T$ as open symbols in Figures 2 and 3. A least-squares analysis of these "corrected" data yielded the equation listed in Table II.

Cl_2SnPc. Vapor pressures were measured with the same two orifices used for CoPc. The plot of log P *vs.* $1/T$ shown in Figure 3 discloses no systematic difference between the data taken with the two orifices, within the experimental precision. (The line drawn in Figure 3 is the least-squares line for the combined data.) It thus appears that the evaporation coefficient of Cl_2SnPc is near unity. The good agreement of data taken with the two orifices here is taken as evidence that the nonequilibrium effects mentioned earlier were absent from both the CoPc and Cl_2SnPc measurements.

SnPc. One would expect this compound, which is isostructural with CoPc and CuPc, to exhibit a low evaporation coefficient, just as they do. However, because of lack of time, only one orifice, with $a = 7.32 \times 10^{-3}$ cm^2, $K = 0.884$, was used. If one surmises that $\alpha = 0.01$ for SnPc, the experimental vapor pressures are lower by the factor 1.51 than the equilibrium values.

DISCUSSION

The most volatile compound studied was $Cl_{16}Pc$, which has roughly ten times the vapor pressure of $Br_{16}Pc$. Attempts to synthesize $F_{16}Pc$ for further comparison were unsuccessful. These compounds, though the most volatile studied, had the highest molecular weights.

The observed vapor pressure of CoPc is comparable with that reported by Curry and Shaw (*8*) for CuPc. However, in the same temperature range SnPc is approximately 10 times as volatile. More surprising are the large differences in heats and particularly the entropies of sublimation, which show the progression CuPc > CoPc > SnPc. Because the compounds have the same molecular structure and similar packing in the solids, one would expect similar vibrational contributions to the crystals and gaseous molecules. One presumes the observed differences to be due largely to electronic and/or magnetic effects involved with the intermolecular bonding in the crystals. Semiconductor behavior has been observed in some metal phthalocyanines (*18*), although not the ones studied here. Because enthalpic and entropic effects are functionally related, it is not surprising that the progressions are similar for ΔH and ΔS. Indeed, a plot of ΔH°_T *vs.* ΔS°_T for CuPc, CoPc, SnPc, ϕ_2SnPc, and Cl_2SnPc is linear with little scatter about the line, while the data for $Cl_{16}Pc$ and $Br_{16}Pc$ lie well below the line. Apparently the former group with their centrally coordinated metal ions constitute a set with "sufficiently equivalent significant configurations" in the sense discussed by Thorn (*22*). Such a "compensatory effect" is not uncommon in many organic systems (*16*).

A propagation of random errors based on Equation 3, with assumed uncertainties in W of ±0.03 mg, in T of ±2° K, and in t of ±2 seconds, yields estimated standard deviations in P of 5 to 12% for the various experimental points. These values agree satisfactorily with the scatter of data shown in Figure 2. In view of the good agreement between the measured vapor pressure of cadmium and the literature values, we believe that large systematic errors are absent. However, the vapor pressure equations for Cl_2SnPc, $Cl_{16}Pc$, $Br_{16}Pc$, and TPP must be considered lower limits because of the possibility of low vaporization coefficients.

In a very recent paper on the absorption spectra of phthalocyanines in the vapor phase Edwards and Gouterman (*10*) have reported heats of sublimation of CoPc, Cl_2SnPc, and CuPc, based on the change of absorption with temperature. Their results agree with ours within their quoted errors, which were stated to be ±15% of the observed heats of sublimation: CoPc, 49 ± 7; Cl_2SnPc, 47 ± 7; and CuPc, 64 ± 10 kcal per mole.

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