Vapor Pressure of Iron(III) Chloride

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The absorbance of unsaturated iron(III) chloride vapor (between 300 and 600 °C) and of vapor in equilibrium with $FeCl_3(s)$ (between 150 and 210 °C) has been measured in the UV-visible range of the spectrum. Effects of added chlorine, HCl, and $FeCl_2(s)$, respectively, and of change in container surface area have been examined. The molar absorptivity previously assigned to $Fe_2Cl_6(g)$ at 360 nm has been confirmed. Vapor pressures derived from absorbance data are compared with manometric, transpiration, and effusion measurements reported by others. With an estimated $\Delta C_P°$ equation, the relationship $\ln P_{Fe_2Cl_6(g)}$ (atm) = $29.69 \ln T - 0.06472T + (1.85 \times 10^{-5})T^2 - 12453T^{-1} - 136.34$ is derived for the equilibrium $2FeCl_3(s) = Fe_2Cl_6(g)$. At 500 K this result gives $\Delta H° = 31278$ cal mol^{-1} and $\Delta S° = 53.66$ cal mol^{-1} deg^{-1} (standard deviations 125 and 0.25, respectively). A comparison is made with values derived from heat capacity, spectroscopic, and calorimetric data.

A recent study of the heat capacity of iron(III) chloride by Stuve, Ferrante, Richardson, and Brown (*1*) reveals a substantial λ transition at 8.4 K which increases the standard entropy of the solid at room temperature and above by 1.31 cal mol^{-1} deg^{-1} over previously adopted values (*2*). This brings into question recommended thermodynamic constants for the vaporization of iron(III) chloride, based in part on third-law treatments which did not include the entropy contribution from this transition. A discrepancy has also been noted between values of the molar absorptivity of $Fe_2Cl_6(g)$ derived from saturated-vapor adsorbances and calculated vapor pressures (*2*), and those based on the absorbances of unsaturated vapors and analytically determined amounts of iron in the cells (*3–5*). These questions have led us to make a new absorbance study and to reexamine vapor pressure data reported by others (*6–15*). An equation for the temperature dependence of $Fe_2Cl_6(g)$ partial pressures in equilibrium with $FeCl_3(s)$ over the temperature range 150–305 °C has been derived by a van't Hoff treatment of combined absorbance and vapor pressure data. The result is found compatible with the newly determined entropy of $FeCl_3(s)$ and estimates for $Fe_2Cl_6(g)$ from spectroscopic data.

General Considerations

It is well established that below 300 °C the dominant molecular species in the vapor in equilibrium with $FeCl_3(s)$ is $Fe_2Cl_6(g)$. Several investigators have studied the dimer dissociation equilibrium 1 at higher temperatures (*12*, *16*, *17*). At

$$Fe_2Cl_6(g) = 2FeCl_3(g) \qquad (1)$$

500 K, constants given in the JANAF tables (*2*) lead to eq 2,

$$K_D = P_M^2/P_D = \exp(-17388T^{-1} + 17.081) \qquad (2)$$

where P_M and P_D represent the partial pressures of the monomer ($FeCl_3$) and dimer (Fe_2Cl_6), respectively. P_M/P_D ratios predicted for the saturated vapor between 120 and 300 °C are very small, 0.001–0.002. Alternatively, if the entropy calculated for $FeCl_3(g)$ by Givan and Loewenschuss (*18*, *19*), incorporating results of a matrix isolation Raman study, is used with the JANAF entropy of $Fe_2Cl_6(g)$ and the van't Hoff enthalpy change from ref *16* or *17*, eq 3 results, which gives K_D values smaller

$$K_D = \exp(-17564T^{-1} + 15.440) \qquad (3)$$

by a factor around 7. In either case, in the temperature range of interest here, the monomer contribution to the total pressure or to the absorbance is predicted to be so low as to be in the range of experimental error. Mass spectra of the saturated vapor have generally indicated only the presence of dimer and monomer (*20–22*); one study reports traces of $Fe_3Cl_8^+$ and $Fe_3Cl_7^+$, which suggests the presence of traces of higher polymers (*23*).

To derive Fe_2Cl_6 partial pressures from manometric measurements of the total pressure, one must also consider the decomposition reaction 4. Reaction 4 at lower temperatures

$$Fe_2Cl_6(g) = 2FeCl_2(s) + Cl_2(g) \qquad (4)$$

is slow to equilibrate (*10*, *24*), and equilibrium constants derived by various investigators are not in close agreement (*10*, *14*, *25*, *26*). We have used eq 5, based on thermodynamic con-

$$K_{Cl_2} = P_{Cl_2}/P_D = \exp(3115T^{-1} - 8.369) \qquad (5)$$

stants at 500 K given in the JANAF tables (*2*, *27*), to predict the contribution of chlorine when both $FeCl_2(s)$ and $FeCl_3(s)$ are present. In view of the lack of agreement of the various investigators, the chlorine pressures must be considered to have a relatively large uncertainty.

As described in the following paragraphs, values of P_D have been calculated from data reported by the various investigators. The correlation covers a substantial temperature range and eq 6 has been assumed to characterize reaction 7. The heat

$$\Delta C_P° = 58.99 - 0.2571T + (2.205 \times 10^{-4})T^2 \text{ cal deg}^{-1} \qquad (6)$$

$$2FeCl_3(s) = Fe_2Cl_6(g) \qquad (7)$$

capacity constants were selected to fit the JANAF estimated values of $\Delta C_P°$ at 400, 500, and 600 K (*2*). The various sets of data were then correlated by using eq 8, where $\Delta H^\bullet$ and

$$Y = \ln P_D - 29.69 \ln T + 0.6472T - (1.85 \times 10^{-5})T^2 = -\Delta H^\bullet/RT + \Delta S^\bullet/R \qquad (8)$$

$\Delta S^\bullet$ are enthalpy- and entropy-related integration constants. A calculation using the second virial coefficient estimated for Al_2Cl_6 in the JANAF tables (*28*) indicates that appreciable deviation from perfect gas behavior is not expected at the temperatures and pressures of concern here.

Absorbance Measurements

Experimental procedures have been described previously (*3–5*) and only a brief summary of the present study is now given.

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Table I. Iron(III) Chloride Absorbance Samples

	cell		10^4(concn), mol L^{-1}		
sample	path length,[a] cm	vol, cm^3	C_{Fe}	C_{Cl_2}	C_{HCl}
A	1	4.33	1.71 ± 0.08 (1.76 ± 0.06)	12.6 ± 0.7	65.6 ± 0.5
B1	2	ca. 7	33[b]	1.8 ± 0.2	0.27 ± 0.03[c]
B2	2	ca. 7	33[b]	0	<0.1[d]
C	10	ca. 29	nd[e]	0.12 ± 0.03	nd[e]
D	2	7.00	1.72 ± 0.06 (1.75 ± 0.04)	1.04 ± 0.15	1.6 ± 0.1[c]
E[f]	1	3.40	6.11 ± 0.08	0	nd[e]
F[g]	1	3.32	3.38 ± 0.05	0	nd[e]
G[h]	1	3.49	7.7 ± 0.1	0	nd[e]

[a] ±0.001 cm, certified by Pyrocell Manufacturing Co., Westwood, NJ. [b] Based on weight of the piece of iron wire converted to $FeCl_3$. [c] Measured spectrophotometrically; not added initially, generated in situ. [d] Below detection limit. [e] Not determined. [f] Mixture of $FeCl_3$ and $FeCl_2$ (mole fraction 0.3). [g] Mixture of $FeCl_3$ and $FeCl_2$ (mole fraction 0.2). [h] Mixture of $FeCl_3$ and $FeCl_2$ (composition not determined).

Iron(III) chloride was prepared by reaction of iron wire (Allied Chemical, 99.90%) and chlorine in all-quartz or quartz–Pyrex systems. Chlorine was generated by heating copper(II) chloride. Iron(III) chloride samples were sublimed into and sealed in quartz absorption cells (1.9-cm i.d., 1–10-cm path length), in some cases along with chlorine and/or HCl. The cells were heated and spectra recorded with a Cary 14H spectrophotometer. Temperatures of various sections of the cells were measured with chromel–alumel thermocouples, calibrated at the boiling point of water and the melting point of tin. $FeCl_3$(s) condensed in the tip of the side arm of the cell (at T_3), which was kept below the temperature of the cell body (at T_1) and the windows (at T_2) to prevent condensation on the windows.

When an excess of chlorine was added, the chlorine concentration was determined spectrophotometrically from the absorbance at room temperature at 330 nm. A manometrically measured amount of HCl was added to one sample through a Pyrex vacuum break-seal. The HCl concentration in other cells was determined spectrophotometrically at 190 nm with a Cary 219 spectrophotometer.

The absorbances of two unsaturated vapor samples were studied for comparison with results reported earlier (*3*, *5*). Amounts of iron(III) chloride were determined following the absorbance measurements using an inductively coupled plasma spectrometer (Model 955 Plasma Atomcomp). To avoid significant error from photolysis (*24*) at temperatures below 300 °C, we exposed samples to the light beam for only the few seconds needed to record the absorbance at a selected wavelength, 360 nm, very near an absorption peak maximum. Concentrations of iron(III) chloride in the cells, total amount expressed as C_{Fe}, the concentration equivalent as number of moles of Fe per liter, of Cl_2 added, and of HCl for the various samples are listed in Table I.

Above 250 °C the iron(III) chloride was fully vaporized in samples A and D. The calculated amount of iron present, based on the measured absorbances at 360 nm between 300 and 600 °C and values of the molar absorptivities for $FeCl_3$(g) and Fe_2Cl_6(g) reported previously (*5*), are shown in parentheses after the value determined analytically; the two are seen to agree well. HCl was not added to samples used in the earlier study; the large amount added to sample A had no observable effect on the calculated molar absorptivity, in contrast to the result reported recently for iron(II) chloride (*4*). In sample D the area of the quartz surface was substantially increased by packing a section of the side arm with 35 mg of fine quartz wool. The amount of HCl generated in this cell, presumably by reaction of iron(III) chloride with H_2O or OH groups bound to the quartz, was larger than observed with sample B1. The iron-containing product of this reaction appears not to contribute to the vapor absorbance or to be soluble in 2% HNO_3 as the calculated and analytically determined values of the molar absorptivity are in agreement (contrary to the behavior observed with $FeCl_2$) (*4*). The agreement also indicates that appreciable amounts of iron(III) chloride are not adsorbed on the quartz surface.

Table II. Absorbances at 360 nm[a]

sample	T_1, K	T_3, K	A	sample	T_1, K	T_3, K	A
E	489.7	473.2	0.497	B2	436.5	430.0	0.0175
F	467.2	456.7	0.155	B2	436.5	434.6	0.0245
F	477.2	464.2	0.268	B2	447.8	445.4	0.0605
F	488.2	472.5	0.483	B2	468.8	468.8	0.370
F	500.2	484.4	1.058	B2	478.7	475.3	0.581
G	449.2	437.4	0.036	B2	480.6	478.8	0.794
G	459.8	450.7	0.096	B2	458.6	456.7	0.146
G	472.2	464.0	0.268		Unsaturated Vapor		
G	483.4	474.4	0.558	A	575.2		0.911
C	445.9	429.3	0.0158	A	678.2		0.870
C	445.5	426.5	0.0123	A	791.2		0.918
C	445.9	425.3	0.0105	A	884.2		0.953
C	445.7	434.4	0.0247	D	632.8		0.8845
C	452.1	440.8	0.0418	D	737.4		0.8805
C	458.0	447.1	0.0703	D	683.2		0.8575
C	470.2	458.2	0.169				
C	463.6	452.2	0.107				
C	432.1	421.7	0.0085				

[a] Samples are identified in Table I. Absorbances (A) have been divided by cell path length. T_1 is the cell body temperature; T_3 is the side-arm tip temperature. For the unsaturated vapor samples, T_1 and T_3 were approximately equal.

Only saturated-vapor absorbances were measured for samples B, C, and E–G. Results are shown in Table II. After an initial series of measurements with sample B (B1), the $FeCl_3$ was sublimed into the cell body and the HCl and Cl_2 present were frozen into the tip by immersion in liquid nitrogen. The tip was then sealed off. Saturation vapor absorbance measurements were then repeated (B2) and found to duplicate the results for B1. No HCl could be detected in B2 after the series of measurements. Samples E–G, mixtures of $FeCl_2$ and $FeCl_3$, gave results indistinguishable from each other or from those of B1 and C in which a sufficient concentration of chlorine was added to prevent formation of $FeCl_2$. At low temperatures the saturated-vapor absorbances of samples A and D were in good agreement with those of sample B in which a large excess of $FeCl_3$(s) was present; thus no significant dependence on crystallite size was apparent.

Equation 2, together with the relationship $ART_1 = E_MP_M + E_DP_D$, where A is the observed absorbance divided by the path length and E_M and E_D are the molar absorptivities of the monomer and dimer, respectively, at the selected wavelength (*5*), was used to derive monomer (P_M) and dimer (P_D) partial pressures. The dimer partial pressures in the saturated vapor were then correlated with T_3, the temperature of the condensed $FeCl_3$ phase, and, along with those reported earlier by Shieh and Gregory (*3*), are shown graphically in Figure 1B.

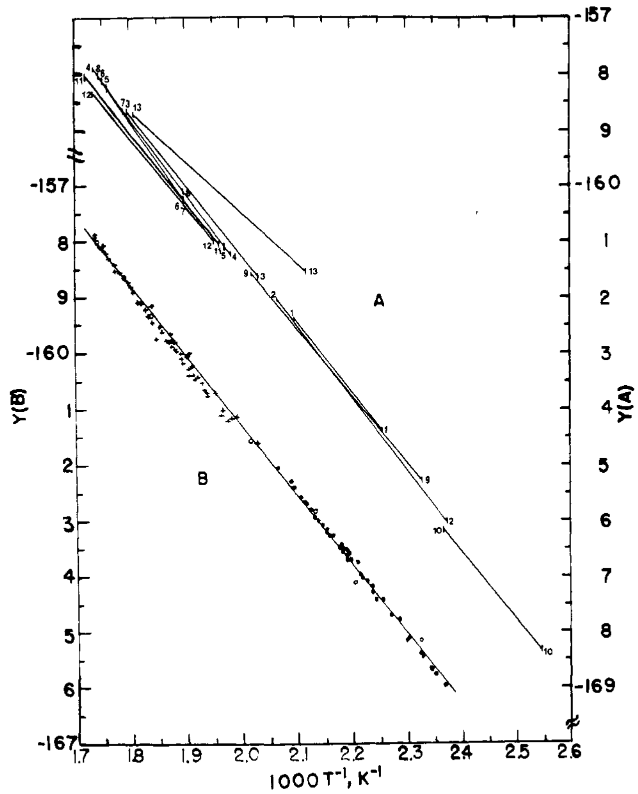

Figure 1. 1. Plot of the function Y (see Table III) vs. reciprocal of temperature. (A) Least-squares lines for the results of the independent investigators; see Table III for number identification. (B) The 126 set (see Table III): absorbance (●), transpiration (O), manometric (+); the solid line corresponds to result 19, Table III.

Summary of Results of Other Workers

Manometric Measurements. A number of authors report the total pressure of vapors in equilibrium with $FeCl_3(s)$ under such conditions that the chlorine pressure is fixed by the presence of both $FeCl_3(s)$ and $FeCl_2(s)$. We assume $P_{total} = P_D + P_{Cl_2} + P_M$, from which, with eq 2 and 5, each partial pressure may be derived. In other cases a known partial pressure of chlorine, sufficient to prevent formation of $FeCl_2(s)$, has been added. Then $P_{total} - P_{Cl_2} = P_D + P_M$, and only eq 2 is needed to derive values of P_D and P_M. Arbitrarily we have decided not to include total pressures below 10 torr because of the larger relative uncertainty.

Maier (*6*), Stirnemann (*7*), Sano (*8*), Johnstone et al. (*9*), and Wilson (*10*) used static methods. Maier heated $FeCl_3$ in a Pyrex tube, connected to an external mercury manometer by a capillary of negligible volume. Plugging of the capillary was prevented by addition of a known pressure of nitrogen which was subtracted from the total pressure. To minimize reaction with chlorine produced by the decomposition reaction, he covered the mercury surface with 98% H_2SO_4. Johnstone et al. also used Maier's method. Stirnemann measured pressures developed by $FeCl_3(s)$ in a sealed curved quartz manometer. Wilson studied four samples in Pyrex diaphragm gauges: an initially pure sample of $FeCl_3(s)$, two mixtures of $FeCl_3(s)$ and $FeCl_2(s)$, mole fractions of $FeCl_3$ of 0.93 and 0.30, and $FeCl_3(s)$ to which a known pressure of Cl_2 (0.17 atm at 232 °C) had been added. Hammer (*12*) also measured total pressures generated by a mixture of chlorine (at 0.18 atm at 229 °C) and $FeCl_3(s)$ in a quartz diaphragm gauge.

Transpiration Measurements. Jellinek and Koop (*14*) used a gas flow method to study the reduction of a series of metal halides by hydrogen; they observed transport of iron(III) chloride vapor and report four values calculated for the vapor pressure, based on an extrapolation to zero flow rate. Ringwald (*15*) used nitrogen as a carrier gas (flow rate 0.01 mol h^{-1}) and calculated vapor pressures of the dimer, $P_{D,R}$, from the measured weight of iron(III) chloride condensed in a water-cooled trap. In the present correlation we have made the small correction for the presence of monomer, assuming $2P_{D,R} = 2P_D + P_M$ and eq 2.

Wilson (*10*) used argon and argon with chlorine as carrier gases (over $FeCl_3(s)$ and mixtures of $FeCl_3(s)$ and $FeCl_2(s)$) with flow rates between 2.5 and 140 cm^3 min^{-1}. We have reexamined the flow rate dependence reported by Wilson and selected P_D values at four representative temperatures predicted for flow rates of 5 cm^3 min^{-1}.

Effusion Measurements. Hammer (*12*) found steady-state pressures developed by $FeCl_3(s)$ in effusion cells to depend on orifice diameter. We have used the four values of P_D as derived in ref *12* for comparison with other results.

Results and Discussion

Least-squares solutions for the independent sets of data are shown as separate lines, terminated at points which define the temperature range studied by the investigator, in Figure 1A. The equation used and derived thermodynamic constants are listed in Table III. Whereas a general overall correlation is seen, substantial differences, beyond anticipated experimental error, are noted, particularly when the results of independent studies in different temperature intervals are extrapolated for comparison. This difficulty was especially apparent when predicted vapor pressures based on manometric data were extrapolated for use with absorbance data to derive values of the molar absorptivity of Fe_2Cl_6.

As noted by others (*2*, *9*, *10*), the results of Jellinek and Koop differ widely from the rest and have been excluded in treatments of combined sets of data. A least-squares treatment including all the remaining 159 observations gives result 14, shown in Table III. We suggest, however, that certain of these sets also should be excluded. The results of Maier (*6*) and Sano (*8*) lie appreciably below those of other workers, particularly at high temperatures. Maier used a nonuniform temperature system and the work was regarded by him as "hurried" rather than careful. The effusion experiments gave steady-state pressures which were different for different orifice areas; the pressures represented in Figure 1A were derived by extrapolation to zero orifice area but still appear low relative to the others and one must question whether they represent equilibrium values. For the remaining 126 observations (49 absorbance, 69 manometric, 8 transpiration), a combined least-squares treatment gives result 15, Table III.

For 75 of the 126 observations the evaluation of the dimer partial pressure does not require the use of eq 5, with its attendant uncertainty. The least-squares result for this set, result 17, Table III, which includes absorbance and transpiration data and those manomeric measurements in which an excess of chlorine was added, gives slightly higher values for the enthalpy and entropy of sublimation. The presence of chlorine in excess also reduces the possibility that solid solutions between $FeCl_3$ and $FeCl_2$ might be formed. However, it should be noted that, for those samples without added chlorine, the calculated chlorine contribution to the total pressure is only between 5% and 10%, and in some cases even complete disregard of the chlorine contribution still gives a dimer pressure below the least-squares line for the combined set. Also, Wilson (*10*) could find no evidence that the presence of $FeCl_2$ appreciably changed the saturation vapor pressure, and, as indicated above, our absorbance studies have led to the same conclusion.

In Figure 1A, lines 3-8 are observed to converge at higher temperatures. An average value of Y was derived at 570 K from the independent least-squares lines for these six sets of data. Similarly lines 1, 2, and 9 agree well at lower tempera-

Table III. Least-Squares Constants Derived for the Equilibrium $2FeCl_3(s) = Fe_2Cl_6(g)$[a]

method (ref)	no. of observations	ΔH^* (SD, %)	ΔS^* (SD, %)	$\Delta H°$(500 K)	$\Delta S°$(500 K)
1. absorbance (*3*)	24	24 463 (2.08)	−271.43 (0.41)	30 995	53.14
2. absorbance (this work)	25	25 633 (0.64)	−269.04 (0.14)	32 165	55.52
3. d gauge, added Cl_2 (*12*)	7	25 142 (1.92)	−270.13 (0.34)	31 674	54.44
4. d gauge, added Cl_2 (*10*)	11	26 535 (1.18)	−267.76 (0.22)	33 067	56.81
5. d gauge (*10*)	30	27 197 (0.68)	−266.64 (0.13)	33 729	57.93
6. quartz manometer (*7*)	16	28 246 (2.18)	−264.82 (0.42)	34 779	59.75
7. capillary manometer (*9*)	5	28 307 (2.74)	−264.67 (0.54)	34 840	59.90
8. transpiration (*15*)	4	26 516 (2.37)	−267.81 (0.43)	33 048	56.76
9. transpiration (*10*)	4	23 652 (8.36)	−273.36 (1.57)	30 184	51.20
10. effusion (*12*)	4	24 197 (0.86)	−272.96 (0.19)	30 730	51.61
11. capillary manometer (*6*)	10	25 008 (1.48)	−271.05 (0.25)	31 541	53.52
12. static method (*8*)	19	24 522 (1.12)	−272.11 (0.18)	31 055	52.46
13. transpiration (*14*)	4	18 109 (2.38)	−282.65 (0.30)	24 641	41.91
Various Combinations					
14. all except ref *14*	159	24 280 (0.49)	−272.11 (0.09)	30 812	52.46
15. all except ref *6, 8, 12, 14*	126	24 480 (0.40)	−271.59 (0.07)	31 013	52.98
16. exclud abs data from 126 set	77	25 236 (0.96)	−270.22 (0.17)	31 768	54.35
17. exclud dep on calcd P_{Cl_2}	75	24 833 (0.41)	−270.78 (0.08)	31 366	53.78
18. 126 set, assuming $\Delta C_P = 0$	126	31 036 (0.30)	52.98 (0.35)	31 036	52.98
19. constants fitted at 570 and 435 K	126	24 745 (0.50)	−270.91 (0.09)	31 278	53.66

[a] Y vs. $1/T$, with T taken as T_3 (K). $Y = \ln P_D(\text{atm}) - 29.69 \ln T + 0.06472T - (1.85 \times 10^{-5})T^2 = -\Delta H^*/RT + \Delta S^*/R$. $\Delta H°(T) = \Delta H^* + 58.99T - 0.1286T^2 + (7.35 \times 10^{-5})T^3$ cal mol^{-1}. $\Delta S°(T) = \Delta S^* + 58.99(1 + \ln T) - 0.2572T + (1.103 \times 10^{-4})T^2$ cal mol^{-1} deg^{-1}.

tures and were used to derive an average value of Y at 435 K. These two values of Y were used to assign values to ΔH^* and ΔS^* and gave result 19, Table III. Inasmuch as this result, which is also in close agreement with result 17, reproduces these points of common agreement, we suggest that eq 9 be used for prediction of dimer pressures in equilibrium with

$$\ln P_{Fe_2Cl_6}(\text{atm}) = 29.69 \ln T - 0.06472T + (1.85 \times 10^{-5})T^2 - 12453T^{-1} - 136.34 \quad (9)$$

$FeCl_3(s)$ in the temperature range 422–575 K.

It will be noted that the $\Delta C_P°$ terms contribute the largest part of the value of the function Y; however, as shown in Table III, result 18, a least-squares treatment with $\Delta C_P°$ taken as zero gives values of $\Delta H°$ and $\Delta S°$ for sublimation of dimer which are essentially the same as those derived from the above equation at 500 K, near the mean temperature of the observations.

From the equation for ln P_D, $\Delta S°$(500 K) for reaction 7 is found to be 53.66 ± 0.25 cal mol^{-1} deg^{-1}. For $FeCl_3(s)$, $S°$(300 K), as determined by Stuve et al. (*1*), is 35.47; the difference $S°$(500 K) − $S°$(300 K), as recommended by the JANAF tables (*2*), is 12.97, which, taken together, gives a value of $S°$(500 K) for $FeCl_3(s)$ of 48.44 cal mol^{-1} deg^{-1}. From the standard entropy of sublimation one then obtains 150.54 cal mol^{-1} deg^{-1} as the standard entropy of $Fe_2Cl_6(g)$ at 500 K. The estimate of this value in the JANAF tables is 150.22 (*2*). Frey, Werder, and Günthard (*29*), using vibrational frequencies assigned from a matrix isolation study, derive a value of 148.6; they suggest that approximately 1 unit should be added for the gas molecule. It is seen that the value based on the vapor pressure data is only slightly higher than those estimated by statistical thermodynamic methods.

The values of $\Delta S°$ and $\Delta H°$ of sublimation derived above are smaller by ca. 2.4 cal mol^{-1} deg^{-1} and 1.5 kcal mol^{-1}, respectively, than those based largely on manometric data alone (*2*, *10*). Considered independently, the least-squares lines for the absorbance data and the manometric data, Figure 1B, are displaced and roughly parallel when extrapolated to a common temperature range. Both have somewhat larger slopes, as reflected by values of $\Delta H°$ listed in Table III, than the slope of the line based on the equation for the combined data sets. The molar absorptivity derived from saturated vapor absorbances and predicted vapor concentrations based on sublimation constants from the 1965 JANAF tables (*2*), e.g., at 200 °C, E_D (360 nm) = 15 × 10^3 cm^{-1} mol^{-1} L, is considerably larger than that given by the absorbance of the unsaturated vapor and the amount of iron found in the cell, 10.5 × 10^3, the discrepancy noted earlier (*3*–*5*). The difference is somewhat less for the data selected in Figure 1B. For the 77 observations remaining in the set of 126 after the 49 absorbance values are excluded, a combined least-squares treatment, result 16, Table III, predicts concentrations which, together with the observed absorbances, give a mean value of the molar absorptivity of 12.8 × 10^3. In the present experiments we have found no indication that the absorptivity based on the unsaturated vapor absorbance and the amount of iron in the cell is in error. No substantial effect on the absorbance was detected after addition of chlorine, HCl and/or $FeCl_2$, or after changing the surface area of the quartz. In view of the agreement between values of the entropy derived from the van't Hoff treatment of the combined data set and the entropy projected from third-law considerations, we conclude that the differences in slope must reflect some systematic error, the effect of which is largely eliminated when the data are combined. It is also noted that the enthalpy of sublimation derived agrees within experimental error with the calorimetric observation of Mapes (*30*), 30.6 ± 1 kcal mol^{-1} at 550 K.

It appears fortuitous that the increase in the third-law entropy of $FeCl_3(s)$ contributed by the transition discovered by Stuve et al. (*1*) approximately compensates the reduction in the derived entropy of sublimation when the manometric and absorbance vapor pressure are combined, with the result that the projected entropy of $Fe_2Cl_6(g)$ is changed very little.

Registry No. $FeCl_3$, 7705-08-0; Fe_2Cl_6, 12371-17-4.

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Binary Gaseous Diffusion Coefficients. Air with Methylfuran Derivatives

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Binary gaseous diffusion coefficients at 1-atm pressure of air with methylfuran derivatives were measured at three temperatures by the capillary tube method of Stefan–Winkelmann: 2-methylfuran (49, 56.5, 61 °C), 2,5-dimethylfuran (49, 65, 80 °C), 2-methyltetrahydrofuran (49, 61, 71.7 °C), and 2,5-dimethyltetrahydrofuran (49, 65, 80 °C). Experimental results are compared with those predicted by the Chen–Othmer and Slattery–Bird equations. Some regularities in the behavior of furan and tetrahydrofuran homologous series are observed.

Furan derivatives have been used as solvents and as starting materials for polymer compounds. An effective design of separation and reaction processes involving an organic compound in the gas phase requires reliable data on the gaseous diffusivities. There are equations and correlations available that predict diffusion coefficients with a reasonable accuracy but, under certain conditions or for complex molecules, experimental data are indispensable.

Using the Stefan–Winkelmann technique, we measured binary gaseous diffusion coefficients at 1 atm and three temperatures for the following systems: air-2-methylfuran, air-2,5-dimethylfuran, air-2-methyltetrahydrofuran, and air-2,5-dimethyltetrahydrofuran.

Experimental Section

The experimental technique was identical with that described in previous works (*1*–*3*). There are several sources of error in any experimental measurement of diffusivities based on the Stefan–Winkelmann technique (*4*, *5*) which are worthy of consideration in relation to the apparatus used in this work.

1. Cooling effect at the liquid–gas interface. This effect is due to the evaporation of the liquid in the capillary tube. It may be considered negligible given the cell used (0.3-cm i.d. × 20-cm length), there being in all the experiments an initial diffusion length of at least 9 cm.

2. Turbulence at the cell top. Mixing effects at the cell top may disturb the concentration profile inside the capillary cell and, therefore, invalidate the stagnant-film assumption. It was shown experimentally that, by use of airflows between 100 and 450 cm^3/min, a good reproductivity of data was obtained. In all the experiments in this work an airflow of 250 cm^3/min was used.

Table I. Critical Constants and Boiling Temperatures Used in Calculations of Vapor Pressures To Determine Diffusion Coefficients

substance	T_c, K	P_c, atm	V_c, cm^3 g-mol^{-1}	T_b, °C	ref
air	132	37.2	90.5		*8*
2-methylfuran	528	46.6	246	63.8	*8*
2-methyltetrahydrofuran	537	37.1	267	80	*8*
2,5-dimethylfuran	559	41.1	304	93	*a*
2,5-dimetiltetrahydrofuran	552	36.1	339	91	*a*

[a] Estimated values.

Table II. Experimental and Calculated Diffusion Coefficients D_{AB} (cm^2 s^{-1}) for Air–Methylfuran Derivatives at 760 mmHg

T, °C	$D_{AB,exptl}$	$D_{AB,calcd}$ (*10*)	$D_{AB,calcd}$ (*11*)	n
		Air–2-Methylfuran		
49	0.0981	0.1025	0.1061	
56.5	0.1027	0.1069	0.1106	1.99
61	0.1055	0.1096	0.1134	
		Air–2-Methyltetrahydrofuran		
49	0.0992	0.0977	0.0969	
61	0.1067	0.1044	0.1036	1.93
71.7	0.1131	0.1106	0.1097	
		Air–2,5-Dimethylfuran		
49	0.0825	0.0900	0.0970	
65	0.0912	0.0983	0.1060	1.93
80	0.0985	0.1063	0.1147	
		Air–2,5-Dimethyltetrahydrofuran		
49	0.0666	0.0850	0.0930	
65	0.0734	0.0928	0.1016	1.99
80	0.0800	0.1004	0.1100	

3. Surface tension effect at the liquid–gas interface. The liquid meniscus may cause a decrease in the vapor pressure at the interface in accordance with Kelvin's equation. For the systems measured in this work this effect was negligible.

4. Free convection inside the cell. This effect can arise because of the difference in density between the vapors produced from the liquid inside the cell and the inert sweeping gas. In our case this effect is not relevant as the vapor density is higher than the air density at the operating conditions.

An important advantage of the apparatus used is that thermal gradients inside the diffusion cell are kept to a minimum. This is achieved by using condensing vapors as heat-transfer media.

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