is more suppressed by increasing pressure than that of the antisymmetric mode regardless of the type of vibration (M–Cl, M–Br, M–N), central metal ion, molecular structure, or the relative position of the frequencies of the two modes. Although the most extensive work has been done on the M–Cl stretching modes, the M–Br and M–N we have investigated follow the same pattern and indicate the general applicability of the technique.

A recent publication indicates that for material in solution an increase in pressure may change a tetrahedral structure to square planar.[24] Since we observe similar changes in band intensities for square-planar structures as for the other structures, it is concluded that a change in structure does not occur.

Whether the observed effect is due to pressure alone or to a combination with sheer forces exerted by the anvils is difficult to determine and is immaterial for the purpose of distinguishing experimentally between symmetric and antisymmetric stretching modes. The observed effect cannot be explained by a phase transformation with varying amounts of low- and high-pressure phases (both phases present due to the pressure gradient across the anvils) as the pressure is changed for the following reasons. (1) Whenever two phases are present, they can be observed through a microscope.[15] The Beck line between the phases moves toward the edges of the anvils as the pressure is increased. This type of phenomenon has been looked for but not observed in any of the coordination compounds reported in this work. (2) Generally, the pressure range over which both high- and low-pressure phases can be detected spectrophotometrically is more limited than most of the pressure ranges reported in this work.[25] Further, the appearance of the high-pressure phase is marked by a discontinuous spectral change at a minimum pressure. All of the changes reported here are continuous from essentially atmospheric pressure. (3) If phase transformation is responsible, it seems unlikely that all of the compounds studied would have a similar high-pressure phase which would alter the intensity pattern in this identical way.

The intensity of an infrared band is related to the change in dipole moment during the vibration.[26] For the symmetric vibration a change in molecular volume occurs, while for the antisymmetric the volume remains essentially constant. A closer packing of molecules at high pressures may thus interfere more with the symmetric than with the antisymmetric vibration. It is not possible at this stage, however, to discuss quantitatively the effect of bulk pressure on intramolecular parameters.

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[24] A. E. Ewald and E. Sinn, *Inorg. Chem.*, **6**, 40 (1967).

[25] Unpublished results of lattice vibrations of alkali metal halides.

[26] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 241.

CONTRIBUTION NO. 2111 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
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A Spectrophotometric Study of the Equilibrium Formation of Gaseous Zinc(I) Chloride[1]

BY JOHN D. CORBETT AND RICHARD A. LYNDE

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The system $Zn(g)$–$ZnCl_2(g)$ has been studied at equilibrium over the range of 320–950° by means of its electronic spectrum. The absorbance of $ZnCl(g)$ was determined in the presence of various known concentrations of the reactants between 750 and 950° to give $\Delta H^\circ_{1125} = 43.9 \pm 0.5$ kcal for the reaction $ZnCl_2(g) + Zn(g) = 2ZnCl(g)$. With a statistical value for the entropy change ΔG°_{1125} is 33.4 kcal, and D°_0 is computed to be 2.37 ± 0.03 ev. No other product is detectable in either the electronic or the mass spectrum down to 300°. The latter results are in contrast with the substantial stability of gaseous Zn_2Cl_2 inferred from sublimation experiments.[2,3] Such a product is shown to give unreasonable thermodynamic data for the dimerization of $ZnCl(g)$ and for the vaporization of the presumed $Zn_2Cl_2(l)$ from liquid $ZnCl_2$. It is suggested that the sublimation properties of the mixed system are determined more by kinetic factors.

Introduction

In the zinc family the stability of M_2Cl_2 species in condensed halide systems increases markedly and reasonably uniformly from zinc to mercury. The principal evidence for $Zn_2Cl_2(l)$ is the Henry's law study of the small (~0.02 mole %) solubility of metal in $ZnCl_2(l)$ at 500°.[4] The compound $Cd_2Cl_2(l)$ has likewise been considered to be the probable product of the more substantial solution of metal in molten $CdCl_2$.[5]

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] D. H. Kerridge, *J. Chem. Soc.*, 1178 (1963).

[3] B. Gaiek and Fr. Proshek, *Russ. J. Inorg. Chem.*, **9**, 256 (1964).

[4] J. D. Van Norman, J. S. Bookless, and J. J. Egan, *J. Phys. Chem.*, **70**, 1276 (1966).

[5] L. E. Topol, *ibid.*, **67**, 2222 (1963); M. Okada, K. Yoshida, and Y. Hisamatsu, *J. Electrochem. Soc. Japan*, **32**, 99 (1964).

In neither system is there any evidence for a substantial amount of the paramagnetic monomer in the melt[6,7] or for a stable solid M_2Cl_2 analogous to Hg_2Cl_2, although a change in anions allows the isolation of $Cd_2(AlCl_4)_2$.[8]

On the other hand, the same gaseous M–MCl_2 systems contain somewhat different species. Present evidence is that Hg_2Cl_2(s) vaporizes by disproportionation to Hg(g) and $HgCl_2$(g), with only traces of HgCl(g) in equilibrium,[9] and the gaseous Cd–$CdCl_2$ system has also been shown to contain a small amount of CdCl(g).[10] The positive entropy of dissociation of M_2Cl_2(g) to the monomer is thought to be the principal reason for the absence of the dimer in the gas phase, in contrast to its predominance in the liquid or solid system. Recently, Kerridge[2] reported that gaseous $ZnCl_2$ is largely converted to the composition ZnCl when it is slowly sublimed over the less volatile metal at 295–350° and, because of the low stability expected for ZnCl(g) (based on $D°_0$ estimates), he concluded that the product is probably the dimeric Zn_2Cl_2(g). Gaiek and Proshek[3] subsequently confirmed this observation at higher temperatures (430–580°) and somewhat higher background pressures.

In the present study the equilibrium $ZnCl_2(g) + Zn(g) = 2ZnCl(g)$ has been studied directly at 750–950° utilizing the specific identification and high detection sensitivity of ZnCl afforded by the spectrophotometric observation of its electronic spectrum. Mass spectra of the system have also been obtained at 300–500°. These results and some reasonably predictable properties for the dimerization reaction offer a considerable contrast to the conclusions of the works just cited.

Experimental Section

Materials.—The $ZnCl_2$ was prepared by direct chlorination of the metal (Bunker Hill Electrolytic, 99.99%), typically with chlorine at 1 atm and metal at 500°. The product was sublimed twice under dynamic vacuum ($<10^{-5}$ torr) at 550°. Because of the extremely hygroscopic nature of the salt, all transfers were made in an argon-filled drybox, and both the salt storage ampoules and the spectral cells were sealed off under vacuum.

Apparatus.—A Cary Model 14 spectrophotometer was modified for use with reverse optics, that is, with the components in the order source, sample, monochromator, and detector. The normal sample and reference compartment was replaced by a specially constructed furnace and light-tight enclosure, the major features of which have been described earlier.[10] In the present case, one end of the enclosure bolted directly to the chopper compartment, with a special light source compartment mounted and aligned on the other. The furnace containing the Inconel cell holder could be placed in the beam without disturbing the position of the reference beam. Since the path length had been extended about 44 cm over the normal design, two fused-silica condensing lenses (Perkin-Elmer, 35-mm diameter, 55-mm focal length) were mounted in adjustable holders in each beam in order to bring the focal point near the entrance slit to the monochromator. The cylindrical, fused-silica cells (Pyrocell Mfg.) were of 22-mm diameter and 10.0- or 15.0-cm path length. The concentrations of the gaseous reactants were established from the weights (±10 μg or ≤0.3%) of metal and salt added to cells of known volume or from known vapor pressures. With the exception of runs I and II at 750° the components were entirely in the vapor phase at temperature. The cell holder was the same as described earlier[10] except that no provision was made for a side-arm heater. The furnace temperature was controlled with two Honeywell transistorized off–on controllers which gave a temperature variation of ±2° at 950°. The two 10-cm end units of the furnace were normally controlled 5° higher than the central 20-cm portion holding the cell block in order to compensate for heat loss and to prevent condensation on the cell windows; this made the windows 2–3° hotter than the body of the cell. Plugs of 12-mm Transite were placed at the end of the furnace in order to minimize heat losses, and holes drilled through these for the light beam were covered with 1-mm sheets of fused silica for the same purpose. Gradients across the thermal barriers provided by the cell wall and the silica protection tube about the thermocouple in the metal block were probably large compared with any within the block so that the resulting uncertainty in the actual cell temperature is thought to be ±3–5°.

Spectral Measurement.—The instrument base line was set at room temperature with no cell in the beam. The absorption of the gaseous system at the wavelength of the ZnCl transitions also includes contributions from the $ZnCl_2$ and the cell. The latter at temperature has an essentially constant absorption over the range of interest (270–330 mμ) with a slight temperature dependence. The ZnCl peaks were superimposed on the smoothly decreasing, low-energy tail of a large $ZnCl_2$ band ($\lambda_{max} < 200$ mμ) which reached $A = 2$ at 275–255 mμ for the concentrations and temperatures used here for quantitative observations of ZnCl. The total background absorbance was therefore determined by fitting a flexible draftman's spline to the smooth background across the region occupied by the ZnCl bands. This typically extended over a range of 24 mμ or 25 cm on the chart and was subject to relatively little uncertainty except in one run where the relatively high $ZnCl_2$ concentration required an extended interpolation. The stiffness of the spline then tended to cause a maximum background correction and hence to give minimum values for A(ZnCl).

Mass Spectra.—An EAI quadrupole mass spectrometer (Series QUAD 200) was used to obtain the mass spectrum of the vapor phase above Zn(s, l) plus $ZnCl_2$(s, l) over the range 300–525°. The 0.35-mm orifice of the Knudsen cell was 25 cm from the ionizing beam. The observation limit was about 1 part in 10^4.

Results

The Spectrum.—The spectrum of ZnCl was first observed qualitatively by Walter and Barratt[11] in absorption with gaseous mixtures of $ZnCl_2$ and Zn and was later defined more thoroughly in emission from a high-frequency discharge by Cornell.[12] The two sequences observed in the latter were attributed to the two components of a $^2\Sigma$–$^2\Pi$ transition. A qualitative description of the molecule would place the odd electron in a nonbonding σ orbital, with the first excitation to a degenerate pair of π orbitals, thereby giving rise to the doublet transition $^2\Pi_{1/2} \leftarrow {}^2\Sigma_{1/2}$ and $^2\Pi_{3/2} \leftarrow {}^2\Sigma_{1/2}$ in absorption. The typical spectrum obtained in this work, Figure 1, clearly shows these transitions, with accompanying vibrational fine structure, and an atomic transition of Zn at 307.2 mμ superimposed on the side of the $ZnCl_2$ band. The ZnCl bands found are centered at 34,110 and 33,840 cm^{-1}, or 293.1 and 295.4 mμ compared with 293.4 and 295.6 mμ reported earlier.[11] The

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[6] N. H. Nachtrieb, *J. Phys. Chem.*, **66**, 1163 (1962).

[7] J. D. Corbett, S. von Winbush, and F. C. Albers, *J. Am. Chem. Soc.*, **79**, 3020 (1957).

[8] J. D. Corbett, W. J. Burkhard, and L. F. Druding, *ibid.*, **83**, 76 (1961).

[9] K. Neumann, *Z. Physik. Chem.*, **A191**, 284 (1942); K. Wieland, *Helv. Phys. Acta*, **19**, 408 (1946).

[10] B. L. Bruner and J. D. Corbett, *J. Phys. Chem.*, **68**, 1115 (1964).

[11] J. M. Walter and S. Barratt, *Proc. Roy. Soc.* (London), **122**, 201 (1929).

[12] S. D. Cornell, *Phys. Rev.*, **54**, 341 (1938).

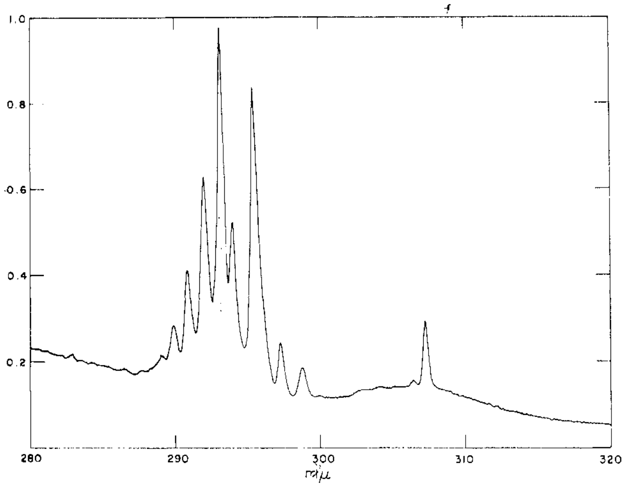

Figure 1.—The spectrum of the gaseous Zn–$ZnCl_2$ system in the region of the ZnCl bands; $[ZnCl_2] = 1.41 \times 10^{-3}$ *M*, $[Zn] = 1.51 \times 10^{-3}$ *M*, path length 15.03 cm, temperature 952°.

$ZnCl_2$ absorption is very large, and the maximum was not observed even at low concentrations ($\sim 3.5 \times 10^{-2}$ torr in a 10-cm cell). The $ZnCl_2$ absorbance in the region of ZnCl bands varied from about 0.2 to 0.6 with the range of the concentrations necessary to observe ZnCl. Attempts to correlate the absorbance of the nominally forbidden ${}^3P_1 \leftarrow {}^1S_0$ transition of Zn at 307.2 mμ with its concentration were not successful, presumably because of a substantial dependence of molar absorptivity on the pressure of the components, so all initial concentrations were calculated from the amounts of salt and metal added.

The character of the observed spectrum leaves no doubt that it arises from ZnCl, as opposed to the dimer Zn_2Cl_2 which should show a relatively broad and featureless band. No other identifiable absorptions were found out to 2.5 μ in the gaseous Zn–$ZnCl_2$ system at 750–850° or over the condensed solids down to 300°. The ZnCl(g) is detectable down to 650° with a 15-cm path length, and both reactants, down to 320°. If any other species is present, its spectrum is too weak to be detected, is masked by that of the other components, or lies outside of the range investigated.

Unlike CdCl,[10] the vibrational fine structure of ZnCl is complicated by the close proximity of the two band systems. The apparent 2–2 vibrational band of the lower energy system ($\Delta\Omega = 0$, presuming it is regular) lies under the 0–0 band for $\Delta\Omega = 1$. Similarly, the near coincidence of the 0–0 transition at 295.5 mμ ($\Delta\Omega = 0$) with the 0–1 and 1–2 transitions for $\Delta\Omega = 1$ add shoulders to the band center although they make a negligible contribution at the maximum. All absorbance values used in the thermodynamic calculations were therefore obtained from the latter transition. The half-widths of the two largest ZnCl absorptions were constant within experimental error for a wide range of conditions. Photodissociation was evidently not important as the same absorbance values were obtained on insertion of a Corex filter between the source and the sample.

A *very tentative* analysis of the vibrational bands yields approximate values of 381 and 507 cm^{-1} for ω_e'' and ω_e', respectively ($\Delta\Omega = 1$). These compare with 391 and 382 cm^{-1} reported for the same quantities *in emission* by Cornell,[12] who noted difficulties in the analysis from interference by N_2 bands as well as from the overlap of the two systems.

TABLE I

INITIAL CONCENTRATIONS OF Zn AND $ZnCl_2$ AND RESULTANT ZnCl ABSORBANCE

Run	Temp, °K	$[ZnCl_2]_0 \times 10^3$, *M*	$[Zn]_0 \times 10^3$, *M*	Absorbance of ZnCl (295.5 mμ, 15.03-cm path)
I[a]	1024.2	4.70	2.03	0.160
	1075.2		3.63	0.361
	1126.6		3.82	0.633
	1173.2			0.902
	1225.0			1.311
II[a]	1023.6	6.43	2.01	0.178
	1074.0		2.89	0.378
	1125.2			0.625
	1173.0			0.918
	1224.4			1.331
III	1023.6	13.47	1.63	0.339
	1174.2			0.562
	1125.4			0.917
	1173.2			1.152
IV	1023.2	1.41	1.51	0.119
	1075.6			0.203
	1127.0			0.331
	1173.6			0.487
	1225.2			0.717
V[b]	1023.2	1.38	1.48	0.107
	1075.8			0.135
	1126.8			0.217
	1173.2			0.327
	1224.6			0.487
VI	1025.6	3.94	1.10	0.172
	1075.0			0.283
	1127.4			0.453
	1174.0			0.680
	1225.6			0.979

[a] Measured in 10.02-cm cell. [b] Measured in 10.04-cm cell.

Thermodynamic Calculations.—The pertinent data for the initial concentrations of the components, the ZnCl absorbance, and temperature are collected in Table I for six separate experiments. These can be analyzed with the assumption that the absorbance of ZnCl at constant path length is proportional to concentration (*i.e.*, ε is constant) and that the amount of ZnCl formed is small so that the concentrations of the reactants are not substantially different from those added initially. In this case, the apparent equilibrium constant K_a for the reaction

$$Zn(g) + ZnCl_2(g) = 2ZnCl(g) \qquad (1)$$

is given by

$$K_a = A^2/[Zn]_0[ZnCl_2]_0$$

for constant path length. The logarithm of this *vs.* $1/T$ for all of the data is shown in Figure 2. The data are adequately described in this manner with no indication of a systematic irregularity outside of experimental error. The somewhat low points for run III

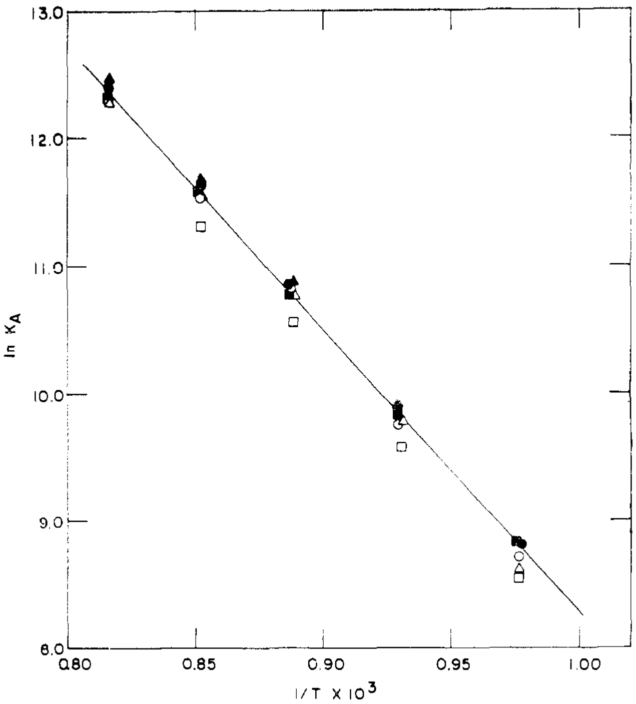

Figure 2.—Ln K_a *vs.* $1/T$: ○, run I; △, run II; □, run III; ●, run IV; ▲, run V; ■, run VI.

(see caption to Figure 2) pertain to an experiment with an unusually high $ZnCl_2$ concentration, where the background absorbance was determined with some difficulty because of both the width of the ZnCl absorption and the shift in scale of the recorder during the scan. The method used to establish the background (see Experimental Section) would probably give minimal values of A(ZnCl). The points for runs I and II at the lowest temperature (750°) seem to be slightly low; however, in these two cases, condensed zinc was present and the concentration of Zn(g) was determined from the measured temperature and known vapor pressure data.[13] The deviation appears to be within the uncertainty of these.

The linear least-squares description of the data in Figure 2 yields a $\Delta H°_{1125}$ value of 43.9 ± 0.5 kcal for reaction 1. With a calculated statistical value of 9.35 eu for $\Delta S°_{1125}$ of reaction 1[14–17] ($S°_{1125}$(ZnCl) = 69.9 eu), $\Delta G°_{1125}$ is 33.4 ± 0.5 kcal, K_{1125} is 3.3×10^{-7}, and ϵ is 2.4×10^4 l. mole^{-1} cm^{-1}. The intercept in Figure 2 is also quite consistent with these results. The initial assumption that the amount of ZnCl formed is relatively small is thus verified, as in no case was more than 0.1% of the lesser reactant converted to monochloride. The absence of other spectral features suggests no other species is formed; the consistency of the data shown in Figure 2 also requires that a substantial amount of an undetected product is not formed by a pressure-dependent equilibrium. This conclusion regarding the absence of other important species is also consistent with unpublished transpiration studies which showed that zinc is only slightly more volatile in $ZnCl_2$(g) at 600°.[18]

The present data may also be used to compute a better value for the dissociation energy of ZnCl than has been available previously. The $\Delta G°_{1125}$ quantity combined with $\Delta(G°_{1125} - H°_{298})$ of −12.5 kcal[17,19,20] gives $\Delta H°_{298}$ = 45.9 kcal for reaction 1. The enthalpies of formation of gaseous $ZnCl_2$, Zn, and Cl at 298°K[16,19,21] yield 55.3 kcal mole^{-1} for the atomization of ZnCl(g), and this together with a statistical value of $H°_{298} - H°_0$ of 2.28 kcal for ZnCl[14] and $H°_{298} - H°_0$ for the elements[19] gives 54.6 kcal mole^{-1} (2.3₇ ev) for $D°_0$ of ZnCl. This compares with estimates of 3.0[14] and 2.1 ± 0.2 ev[22] in the literature.

The mass spectrum of the vapor above the condensed reactants in a Knudsen cell was also examined between 300 and 500°. In addition to large amounts of parent ions from the components, only a small amount of $ZnCl^+$ was observed above 450°, with no evidence for heavier, reduced species such as $Zn_2Cl_2^+$.

Discussion

The gaseous monochlorides of the zinc family are all minor species in the gaseous MCl_2–M systems at moderate temperatures, with stability order CdCl > ZnCl > HgCl, or K_p for the disproportionation reaction of 1.6×10^5,[10] 2.6×10^7, and 9×10^9,[14,16,19,20] respectively, at 1000°K. The ordering follows directly from the relative enthalpies of formation of the gaseous di- and monochlorides since $\Delta S°_{1000}$ is nearly constant (9.9–10.4 eu). Although $\Delta H°_{298}$ for dissociation of CdCl to atoms is about 6 kcal less than for ZnCl, this is more than compensated by the 22 kcal lower stability of $CdCl_2$(g) (from the gaseous elements). On the other hand, HgCl(g) is much less stable, with $\Delta H°_{298}$ for dissociation to atoms of 24.6 kcal or about half that of ZnCl, while the formation of $HgCl_2$(g) is 33 kcal less exothermic than for $ZnCl_2$(g). The somewhat unique stability of Hg^0 (and, under different conditions, Hg_2^{2+}) is again apparent.[23]

According to the spectral studies, ZnCl is the only detectable new species in the gaseous Zn–$ZnCl_2$ system in the range of 700–950°. Of course, ZnCl will become relatively less important at lower temperatures, but there is no evidence in either the electronic or the mass spectrum for any other species down to 300°. The absence of solute absorption above 300 mμ for solutions of metal in $ZnCl_2$(l)[4] suggests that Zn_2Cl_2(g- may absorb at higher energies, but nothing was ob)

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[13] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963.

[14] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Princeton, N. J., 1950, p 579.

[15] D. P. Stevenson, *J. Chem. Phys.*, **8**, 898 (1940).

[16] L. Brewer, C. R. Somayajulu, and E. Brackett, *Chem. Rev.*, **63**, 111 (1963).

[17] D. Cubicciotti and H. Eding, *J. Chem. Phys.*, **40**, 978 (1964). The recommended revision of ν_2 for $ZnCl_2$ was used in the statistical calculations, giving $S°_{1125}$ of 85.36 eu.

[18] D. Cubicciotti and F. J. Keneshea, unpublished research.

[19] D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., 1956.

[20] K. K. Kelley, U. S. Bureau of Mines Bulletins 584, 592, U. S. Government Printing Office, Washington, D. C., 1960, 1961.

[21] F. J. Keneshea and D. Cubicciotti, *J. Chem. Phys.*, **40**, 191 (1964).

[22] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1953, p 233.

[23] J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).

served above the condensed components down to 200 mμ. The latter results are thus in direct conflict with more indirect evidence for $Zn_2Cl_2(g)$.[2,3] In addition, the data obtained here for ZnCl(g) may be combined with the implications of the earlier findings to require highly unreasonable thermodynamic data for (1) the dimerization reaction in the gas phase and (2) the vaporization of $Zn_2Cl_2(l)$ evidently present in the molten system.

First, it is necessary to describe more completely the nature of the earlier experiments. Kerridge[2] slowly sublimed $ZnCl_2$ from a reservoir at 295–350° over metal foil at close to the same temperature in a background pressure of 0.02 torr. In the work of Gaiek and Proshek,[3] either a molten mixture of the components was heated at 450 or 520° under a pressure of 5 torr or the salt was sublimed over separate metal at 580° and 5 torr or at 430–460° and 0.05 torr. The background gas in all experiments was apparently air from the pump. In all cases condensates of solid Zn and $ZnCl_2$ containing slightly less than 1 g-atom of zinc per chlorine were obtained outside of the furnace after a correction was made for the amount of zinc volatilization obtained in the absence of $ZnCl_2$. The enhanced metal vaporization was attributed to the formation of Zn_2Cl_2 since estimated data indicated that ZnCl would not be nearly this stable.

These sublimation experiments gave a direct measure of the equilibrium

$$Zn(g) + ZnCl_2(g) = Zn_2Cl_2(g) \qquad (2)$$

if it is assumed that equilibrium was attained and that diffusion was not important. (The vaporization of less than equilibrium amounts of $ZnCl_2$ is of no consequence since equilibrium 2 is pressure independent as long as zinc saturation is maintained.) With a corrected condensate composition of 0.97 Zn/Cl obtained[2] at 325°, $K_P = 0.94/0.06P^0_{Zn} = 2.36 \times 10^6$ for reaction 2. Combination of this with data for the reaction studied here then gives −70 kcal for ΔH°_{598} of the dimerization reaction $2ZnCl(g) = Zn_2Cl_2(g)$ if ΔS° is taken to be a plausible −24 eu. The enthalpy change is unexpectedly large, about twice that estimated for the corresponding cadmium reaction.[10] Neglecting any temperature dependence of ΔH° and ΔS°, such numbers require conversion of more than half the lesser reactant to $Zn_2Cl_2(g)$ even under the least favorable conditions represented in Table I. Only a much larger ΔS° and hence a larger temperature dependence would change this, such as is appropriate perhaps for a much greater degree of ZnCl polymerization, although we are still left with a species which has not been detected directly.

The formation of gaseous Zn_2Cl_2 with the indicated stability is also in considerable contrast with the behavior of the corresponding liquid system, where the solution composition at 500° corresponds to only 0.02 mole % Zn_2Cl_2 in $ZnCl_2$.[4,24,24a] If Zn_2Cl_2 is indeed the common product ΔG°_{773} for the vaporization of $Zn_2Cl_2(l)$ would be of the order of −10 kcal mole^{-1}, as summed from 13.1 kcal for the melt reaction (Raoultian behavior), 13.6 kcal for the gas reaction 2 with the reported[3] composition of 0.92 $Zn/ZnCl_2$, and corresponding data for the liquid–gas conversion of the reactants.[13,21] This in turn yields only about 5 ± 2 kcal for ΔH°_{773} of the vaporization of $Zn_2Cl_2(l)$ with entropy estimates of 3 ± 3 eu for the dissociation of liquid Zn_2Cl_2, 40.4 eu for the vaporization of 2 moles of ZnCl(l) based on that for CuCl,[25] and the assumed value of −24 eu for the gaseous dimerization. The remarkably small enthalpy of vaporization of Zn_2Cl_2 thus implied is in contrast with an approximate lower limit of 49 kcal mole^{-1} for the vaporization of liquid Cd_2Cl_2.[10] The principal assumption in the previous calculation has been the athermal solution of liquid Zn_2Cl_2 in $ZnCl_2$, and a very substantial, positive value for this would be required to give more plausible results.

The foregoing calculations indicate that the formation of Zn_2Cl_2 is not a reasonable interpretation for the observations that $ZnCl_2$ and Zn vaporize in nearly equal amounts at several combinations of temperature and pressure. Several factors suggest that this behavior may have resulted instead from a more physical process governed by kinetic effects in a nonequilibrium system. Even though the ratios of the equilibrium vapor pressure of $ZnCl_2$ (total) to zinc are between 8 and 10 over the temperature range covered, liquid $ZnCl_2$ is a well-known polymeric material[26] with an apparent activation energy for vaporization that is notably larger than for most molten salts. It is therefore conceivable that certain combinations of temperature and ambient pressure could be found empirically which would result in vaporization of the metal and salt in nearly equal amounts. The actual physical design of the experiment, the residual gas, and rate of heat transfer would also be important variables.[27] The relative rates of vaporization reported for the separate components[2] reflect the presence of a greater kinetic effect for the salt. In addition, the rate of vaporization of $ZnCl_2$ was reduced by an additional factor of about 2 by the restriction provided by the metal foil so that the apparent enhancement of the metal vaporization was actually somewhat less.

Perhaps equally important could be a change in the mechanism of metal transport when both components are present. The ambient pressure of 0.02 torr present in the first study exceeds the vapor pressure of metal[13] over the entire range studied so that the rate of volatilization of zinc alone that was subsequently used for

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[24] The directly determined value for the solubility of Zn in $ZnCl_2(l)$ at 500° is used in preference to the older indirect measurement.[7]

[24a] NOTE ADDED IN PROOF.—A still larger value (0.7% Zn at 500°) has recently been reported [D. H. Kerridge and S. A. Tarig, *J. Chem. Soc., Sect. A*, 1122 (1967)]. Use of an average of the three reported solubilities will raise subsequent ΔG° and ΔH° values by 4 kcal but will not substantially alter the conclusions regarding the vaporization of $Zn_2Cl_2(l)$.

[25] L. Brewer and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 3038 (1950).

[26] J. D. Mackenzie and W. K. Murphy, *J. Chem. Phys.*, **33**, 366 (1960).

[27] In one experiment of this sort we slowly sublimed $ZnCl_2$ through a coil of Zn foil at 325° under a static pressure of 0.02 torr of dry N_2. The 1.136 g of condensate obtained after 2 days had a gross $Zn/ZnCl_2$ molar ratio of 0.36.

correction of data obtained with $ZnCl_2$ present was probably determined mainly by the rate of diffusion. However, over the majority of the range (≥315°), the *equilibrium* pressure of $ZnCl_2$[21] exceeds 0.02 torr so that zinc would now be transported as well by $ZnCl_2(g)$ if anywhere near this $ZnCl_2$ pressure was attained. In actual fact, since a chloride pressure lower than equilibrium has already been anticipated, the sublimation results probably involved some combination of both a transport process and kinetic effects in the rates of evaporation. The evolution of gaseous impurities by the salt could also aid the metal removal.

Explanation of the results obtained at higher temperatures and pressures[3] is more difficult as numerical data for the control experiments with the pure components were not reported. The 5-torr background pressure exceeds the vapor pressure of the metal but not the salt over the majority of the range studied, but this does not apply at 0.05 torr.

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The Preparation and Characterization of Hydrothiophosphoryl Difluoride, SPF_2H, and Hydrophosphoryl Difluoride, OPF_2H

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Anhydrous hydrogen iodide reacts with dimethylaminophosphoryl difluoride and dimethylaminothiophosphoryl difluoride to form hydrophosphoryl difluoride and hydrothiophosphoryl difluoride in good yield. The compounds were characterized by nmr, infrared, and mass spectra and by vapor-pressure studies. Both are volatile liquids: the thiophosphoryl compound boils at 0.2° and is considerably more stable than the phosphoryl compound which boils at 55°. The results of hydrolytic and thermal decomposition studies are discussed.

Introduction

There have been few reports of halogenated phosphines or phosphoranes in which a hydrogen atom and a halogen atom are bound to the same phosphorus atom. The recent synthesis of difluorophosphine, PF_2H, by Rudolph and Parry[1] provides the only substantiated example of a halophosphine although inconclusive reports of the synthesis of chlorophosphines have appeared.[2] The fluorophosphoranes PF_4H and PF_3H_2, first reported by Blaser and Worms,[3] have recently been studied in greater detail[4,5] and an organofluorophosphorane, $C_6H_5PF_3H$, has also been reported.[6] We now report in detail[7] the direct synthesis and characterization of the pentavalent phosphoryl and thiophosphoryl hydrofluorides. One of these, hydrophosphoryl difluoride, has just recently been reported as a product of the reaction of HPF_4 with glass.[5]

Experimental Section

Standard vacuum techniques using Pyrex-glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon "N" grease. Infrared spectra were measured with Perkin-Elmer 421 (4000–200 cm^{-1}) or 337 (4000–400 cm^{-1}) instruments, mass spectra with an AEI MS-9 double-focusing mass spectrometer, and nuclear magnetic resonance spectra with Varian HA 100 (hydrogen) or HA 60 (fluorine and phosphorus) instruments. Fluorine spectra were measured at 56.4 Mcps (relative to CCl_3F standard) and phosphorus spectra at 24.1 Mcps. Hydrogen spectra were measured relative to tetramethylsilane (τ 10.0). Nmr spectra of the solid residues encountered in the study were obtained on dry acetonitrile or deuterioacetonitrile solutions.

Materials.—Commercial hydrogen iodide (Matheson) was purified by fractional distillation before use. The dialkylamino phosphoryl or thiophosphoryl difluorides were prepared from the corresponding dichloro compounds by fluorination with antimony trifluoride (catalyzed by antimony pentachloride when necessary) as described previously[8] followed by fractional distillation under vacuum before use.

Preparation of Hydrothiophosphoryl Difluoride.—In a typical reaction, dimethylaminothiophosphoryl difluoride (13.5 mmoles) was condensed with slightly more than a threefold molar ratio of anhydrous hydrogen iodide (41 mmoles) into a 1-l. glass reaction vessel fitted with a stopcock. The reaction vessel was allowed to warm to room temperatures whereupon reaction began and proceeded at a moderate rate for 1–2 hr. During the reaction the liquid dimethylaminothiophosphoryl difluoride slowly changed from a clear, colorless liquid to yellow then to dark red and finally to a dark red, crystalline mass. The volatile products were removed from the reaction vessel and fractionated; the SPF_2H passed a trap cooled to −81° and collected in a trap cooled to −131° giving yields up to 95% of theoretical (eq 1).

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(1) R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

(2) P. Royen and K. Hill, *Z. Anorg. Allgem. Chem.*, **229**, 112 (1936).

(3) B. Blaser and K. Worms, *Angew. Chem.*, **73**, 76 (1961).

(4) R. R. Holmes and R. N. Storey, *Inorg. Chem.*, **5**, 2146 (1966).

(5) P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Am. Chem. Soc.*, **89**, 2017 (1967).

(6) Zh. M. Ivanova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **31**, 3991 (1961).

(7) See T. L. Charlton and R. G. Cavell, *Chem. Commun.*, 763 (1966), for a preliminary account of the preparation of SPF_2H.

(8) R. G. Cavell, *Can. J. Chem.*, **45**, 1309 (1967); *ibid.*, in press, and references therein.