COMPRESSION AND PHASE TRANSITIONS OF SOLID

HCl, HBr, SiH$_4$, AND SF$_6$[*]

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Abstract

Isothermal PV curves for solid HCl, HBr, SiH$_4$, and SF$_6$ have been determined by the direct piston displacement method up to pressures of 20,000 kg/cm^2 at various temperatures between 50°K and 190°K. Relative volume changes (and in some cases molar volumes) and compressibilities have been calculated for each substance. Phase transitions have been observed as discontinuities in the piston motion. First order transitions have been observed in solid HCl, SiH$_4$, and SF$_6$. Phase diagrams are included. The expected second order transition in solid HBr was not noted, probably because of impurities in the samples. The approximate volume changes accompanying the observed transitions have been determined. Their consistency with other data has been checked by means of the Clausius-Clapeyron equation.

I.   Introduction

Previously described[1, 2] techniques have been utilized to apply
high pressure to samples of solid HCl, HBr, SiH_4, and SF_6. PV isotherms
and phase transition parameters to 20,000 kg/cm^2 have been observed for
various low temperatures. The piston displacement technique[1] was em-
ployed throughout. Samples of each gas were condensed directly into the
sample holder, and uniaxial compression applied with a piston. The validity
of the PVT data thus obtained depends upon the plasticity of the solid.
The samples must exhibit plastic behavior, as opposed to brittleness,
and must have low shear strength. These conditions appear to be met for
these four solids in the temperature ranges considered here. The present
results are apparently the first high pressure data which have been ob-
tained for these substances in their solid states.

The HCl, HBr, and SF_6, obtained from Matheson lecture bottles,
were of unknown relatively high purity. The silane was from a sample
supplied to the author through the kindness of Dr. R. M. Joyce of the
duPont Experimental Station, Wilmington, Delaware. HCl and HBr appeared
to be of special interest on account of the phase transitions which occur
at atmospheric pressure. Very little work of any kind had previously been
done with solid SiH_4 and SF_6. These four substances bring to twenty-two
the total number of solidified gases for which compressibility and phase
transition data have been determined by the present techniques[1,2,3,4,5].

The apparatus used in the current investigation was that pre-
viously employed[2] for similar studies of solid NH_3, SiF_4, H_2S, and CF_4.
The details of the experimental manipulation and reduction of data were
similar. A search was made for solid-solid transitions in each of the

substances investigated. HCl, SiH_4, and SF_6 each showed one first order transition, while none was found in solid HBr. The volume changes of the first order transitions were measured and correlated with the experimentally observed slopes of the transition lines. This correlation proves to be quite inaccurate because the inevitable friction and the low but finite concentration of impurities in the solid samples tend to smear out the transitions over a wide pressure range. It is believed that the pressure at which such a transition runs in thermodynamic equilibrium at a given temperature can be determined by the present technique to within 5 to 10 per cent. The accuracy of $\Delta (\Delta V/V_o)$ at transitions is considerably poorer than this.

II. Experimental Technique and Calculations

A detailed description of the experimental methods[1,2] will not be repeated here. In brief, the procedure was as follows. After initial compaction of the loosely frozen solid, the change of length of the sample was observed as a function of monotonically increasing and decreasing pressure. Weights were added to and removed from the pan of the dead weight gauge in sequence, and the piston position observed each time. The values of $\Delta V/V_o$ were determined by the method originally proposed and used by Bridgman[6]. Correction had to be made for the appreciable distortion of the press members and the small dilation of the sample holder under internal pressure[2].

Transitions appeared as finite breaks in the volume versus pressure curves. In the present investigation only first order transitions

were observed. The difference in the apparent pressures at which a transformation runs with monotonically increasing and decreasing pressure is equal to twice the sum of the effective friction in the apparatus and the overpressure ("region of indifference") which must be applied to induce the transition to run. The latter is increased in width by impurity in the sample. Thus, the greater the contamination, the less accurately can one determine the actual transition pressure and the accompanying volume change.

The sample temperature was adjusted to the desired value and maintained constant in a variable temperature cryostat of the type designed by Swenson[7]. Liquid nitrogen was the coolant for 77° K $<$ T $<$ 200°K, while liquid helium was used for the single run on SiH_4 at 54°K. The temperature was measured and monitored by means of a resistance coil of extruded 99.999% pure indium[8] wire mounted in close thermal contact with the outside of the pressure cylinder[9]. By manual adjustment of the flow rate of the coolant by means of a valve, the temperature could be held constant to within about one degree Kelvin for periods of four hours or longer.

After the total compression of a sample, $- \Delta V/V_o$, had been obtained as a function of pressure, fit was made to a Murnaghan[10] relation of the form

$$P = \frac{3}{2\beta_o} \left[y^7 - y^5 \right] \left[1 - \xi (y^2 - 1) \right] \qquad (1)$$

β_o is the compressibility at zero pressure, $y^3 = V_o/V$ with V_o the volume at zero (atmospheric) pressure and V the volume at pressure P. ξ is an

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adjustable constant whose value depends upon the relative importance in the compressional energy of strain terms higher than quadratic. The fit was in all cases at least as good as the experimental accuracy of the $\Delta V/V_o$ data - roughly $\pm$ 5 per cent. Equation (1) is useful only for pressures between atmospheric and that of a transition. At a transition ξ and β_o assume different values in a manner which is difficult to interpret. A new fit can be made for the pressure range above a transition, but this is not particularly meaningful.

The "instantaneous" compressibilities, $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ were determined by analytic differentiation of (1). This yields

$$ K = \frac{1}{\beta} = \frac{1}{2} K_o y^5 \left[-9\xi y^4 + (7 + 14\xi) y^2 - (5 + 5\xi) \right] \tag{2} $$

where K is the instantaneous bulk modulus. This gives smoothed values of the compressibility which are more accurate than one can obtain graphically from the original data.

As yet there is no basis for comparison between the experimental data for these substances and a theoretically calculated PVT surface. So far such detailed calculations are possible only for the simplest solids, such as the solidified rare gases[11] and the alkali metals[12]. The theoretical calculation of pressure as a function of temperature for solid-solid transitions represents an even more difficult problem. No final solution based upon microscopic theory has been found for any substance.

III. Detailed Results and Discussion

In Table I is presented a summary of the PVT results at one selected temperature for each of the four substances under consideration. Detailed discussion of each follows.

HCl

This has been investigated over the temperature range 77°K - 152°K. Twenty-four separate determinations of volume as a function of pressure were made at different temperatures and in three sizes of sample holder. In general, three to five runs were made with each sample. Where direct comparison could be made, reproducibility of $\Delta V/V_o$ was within 5%.

HCl gas was condensed into the steel sample holder with liquid nitrogen. A current of approximately 3 amperes was passed through the 0.031" i.d. stainless steel filling capillary to prevent blockage by solid. Little difficulty was experienced in filling the sample holders.

It is well known that solid HCl exhibits a first order transition at 98.4°K at atmospheric pressure[13]. The latent heat of the transition is 284 calories per mole[13] (7.8 calories per gram). We have observed this same transition under pressure at temperatures between 101°K and 125°K. The transition always was quite sharp, appearing equally clearly under increasing and decreasing pressure. All but two of the observed points lie closer than experimental error to the smoothed PT curve (Fig. 1). This curve extrapolates very nearly to 98.4°K at P = 0; the lowest transition pressure observed was 1,630 kg/cm^2.

At 105°K the observed $\Delta (\Delta V/V_o)$ for the transition is 0.7%, so $\Delta V = 0.18$ cm^3/mole. We observe dP/dT = 430 kg/cm^2 $^{\circ}$K, and from the

Clausius-Clapeyron equation $dP/dT = L/T\Delta V$, one finds that $L_{105} = 190$ calories per mole. This is to be compared with Giauque's value[13] of 284 calories per mole at $98°K$. On account of the smearing out of the transition there is no doubt that our value of $\Delta(\Delta V/V_o)$ is too small. If we neglect the (small) change of L between $98°K$ and $105°K$ and use Giauque's[13] value, we obtain a calculated $\Delta(\Delta V/V_o)$ of 1.0%. Actually this is consistent with the current experimental data. The uncertainty is great enough so that one could easily draw the original V vs P curve with a relative discontinuity of 0.010 in $\Delta V/V_o$, instead of 0.007. Except for the most plastic of the solidified gases, friction and non-hydrostatic stress components are too great for precise measurement of volume discontinuities to be possible. Sample purity is also a factor. The relative accuracy of the overall volume changes at high pressure is considerably greater.

The value of the density of solid HCl, 1.469 gram/cm^3 ($107°K$) used in the above calculation and upon which was based the determination of the molar volumes in Table I, was obtained by means of a pycnometer by Simon and Simson[14]. This is the only reliable measurement of the density above the transition temperature. There has been no satisfactory direct measurement of the density change of the solid at the transition at atmospheric pressure. The various density measurements which have been reported[15,16,17] at different temperatures are not wholly self-consistent.

The crystal structures of the two modifications of HCl have been determined by X-ray diffraction[14,15,17] and confirmed by infra-red

spectrum[18] and nuclear magnetic resonance[19] studies. The current consensus of opinion[20] is that the high temperature phase I is face-centered cubic (isotropic) and the low temperature phase II is face-centered orthorhombic (anisotropic). It is now definitely known that this is not a rotational transformation of the methane type[5]. The current high pressure data are of no assistance in determining the crystal structure. It can be stated that there is apparently only this one transition in the pressure-temperature domain bounded by $77^{\circ}K$, $152^{\circ}K$, atmospheric pressure, and approximately $17,000 \ kg/cm^2$. Because of friction, transitions occurring just below the upper limit of $20,000 \ kg/cm^2$ cannot be ruled out.

<div align="center">HBr</div>

This substance might be expected to be analogous to HCl. However, its behavior at atmospheric pressure was observed by Giauque and Wiebe[21] to be quite different. Instead of a single first order transition as in HCl, three apparently second order transitions were observed, at $89.7^{\circ}K$, $113.6^{\circ}K$, and $116.9^{\circ}K$. Later work has confirmed this multiplicity. The phase diagram of solid HBr is thus quite complicated. In the case of DBr[22], the two upper transitions coalesce into one, which is still second order. Giauque[21] and Alpert[19] report that the HBr transitions show much more temperature hysteresis than does the HCl transition.

Somewhat surprisingly, in the present investigation no transitions of any kind were observed in solid HBr. On account of the fact that the transitions are second order, one would not expect a volume discontinuity such as is observed in HCl. However, differing compressibilities of the two phases should be revealed by a break in the slope of

the volume vs pressure curves[5]. It is extremely unlikely that all four
of the expected phases of HBr would have the same compressibility. Some
of the modifications might have a limited domain of existence in the PT
plane. No such break was observed in fourteen runs covering a tempera-
ture range of $89^{\circ}K$ - $178^{\circ}K$, and the pressure range 1 - 20,000 kg/cm^2.

The probable explanation of this negative result is that it was
never possible to fill a sample holder more than one-third full of solid
HBr. Condensation always stopped prematurely, and no amount of manipu-
lation of the sample holder temperature could induce more gas to condense.
When the sample holder was warmed above the melting point of HBr the
entire contents invariably evaporated. This difficulty at first appeared
to be similar to that experienced earlier with H_2S[2]. The use of a large
bore capillary in the cold region, coupled with electrical heating and
the use of a silica gel drying tube (measures which had solved the prob-
lem for H_2S) unfortunately proved to be of no benefit in the case of HBr.
Furthermore, to remove possible traces of Br_2, the HBr gas was also
passed over finely divided silver. There was little tarnishing of the
silver, so that this contaminant could not have been present in any great
degree. In addition, the cylinder of HBr was immersed in a dry-ice
acetone mixture in order to freeze out possible non-volatile impurities.
The nature of the impurity responsible for the apparent blocking of the
filling line is not known. Possibly it is a strongly bonded hydrate
such as $HBr \cdot H_2O$ with a freezing point below room temperature, but consi-
derably above that of HBr.

The shortness of the samples impaired the relative accuracy of the compressibility data. In these cases, the distortion correction for the press and cylinder amounted to over 60% of the total effect observed. This correction must be subtracted from the raw data. Thus the HBr $\Delta V/V_o$ data in Table I are certainly less accurate than those for HCl. Had it been possible to obtain samples of normal size, it is conceivable that the expected transitions would have been observed. However, relatively large hysteresis is to be expected in view of the observations of Giauque[21] and Alpert[19] mentioned earlier, while the effects being sought are probably small compared to that in HCl.

The value of the density of solid HBr at 150^oK, 2.55 ± 0.1 gram/cm^3 used in calculating the molar volumes in Table I is based upon interpolation between several rather uncertain experimental values[17,23,24]. There have apparently been no more recent determinations.

Evidently[25], the crystal structures of the highest and lowest temperature modifications of solid HBr are similar to those of the two HCl phases. On the other hand, the details of the transition mechanism from one to the other must be quite different.

SiH_4

This substance offers an interesting comparison with CH_4. However, as occurs frequently when compounds containing analogous elements in the periodic table are compared, the phase transitions are found to be qualitatively different. Clusius[26] observed a first order

transition at 63.5°K with a latent heat of 147 calories per mole (4.58 calories per gram). This is completely unlike the methane transition[5] (20.5°K) which is unmistakably second order.

At high pressure (nine determinations) we have observed a single first order transition. This could be traced only to 4,000 kg/cm^2 (Fig. 2), at which pressure the transition occurs well above the melting point at atmospheric pressure. Attempts to follow the transition to higher pressure failed because of loss of the samples. The observed transition curve is linear, and extrapolates closely to 63.5°K at atmospheric pressure. dP/dT is found to be 91 kg/cm^2 $^{\circ}$K, and the $\Delta (\Delta V/V_o)$ for the transition (80°K) is 2.4%. The transition is sharp and the hysteresis slight. Thus the experimental value of $\Delta (\Delta V/V_o)$ should not be too small as it may be for broad transitions.

There appears to have been no reliable determination of the density of solid silane. One, therefore, cannot check consistency of the transition data by means of the Clausius-Clapeyron equation. However, if we assume the same value of $\Delta (\Delta V/V_o)$ at atmospheric pressure as observed at 1,500 kg/cm^2, we can calculate the density at 63.5°K, ρ_o, to be 0.71 gram/cm^3. This appears to be a bit low. There is one observation[27] of the density of liquid silane at the melting point - 0.68 gram/cm^3. Thus one might expect the density of the solid at the transition temperature to be in the neighborhood of 0.75 to 0.80 gram/cm^3. It is possible that either the latent heat or our $\Delta (\Delta V/V_o)$ could have a 10% error. The agreement between the observed and calculated $\Delta (\Delta V/V_o)$ is much closer for SiH$_4$ than for HCl, where the hysteresis effects are greater.

The preparation of adequately large samples of solid SiH_4 offered no fundamental difficulty. The only problem was that, since silane ignites spontaneously in the atmosphere to form a "snowstorm" of fine particles of silica, traces of air in the filling system led to clogging of the valve seats. After each run it was necessary to remove the valve stems and purge the system with dry nitrogen. On each occasion clouds of silica were seen to emerge. Particles of inert SiO_2 embedded in the solid SiH_4 samples should not cause smearing out of the transitions.

The nine runs which were made covered the ranges $54°K - 108°K$ and $1 - 20,000$ kg/cm^2. For the runs above the melting point ($88.5°K$) it was not possible to lower the pressure to zero lest the sample escape. In all cases with this substance friction was unusually small. It appeared to be quite plastic.

The crystal structures of the two phases of solid SiH_4 have apparently never been determined. Clusius[26] observed that phase I (between $63.5°K$ and the melting point) is weakly doubly refracting, while the low temperature phase II was found to be strongly birefringent, showing considerable anisotropy. The transition appears to be of the ordinary crystallographic type. No evidence has been found for the existence of rotational transformations analogous to those in solid CH_4 and CD_4.

$\underline{SF_6}$

We have made a total of sixteen runs with solid SF_6, covering the ranges $81^\circ K$ - $190^\circ K$ and 1 - 20,000 kg/cm^2. A single first order transition was observed at twelve different pressures (Fig. 3). The transition is apparently linear in the PT plane. Our transition line extrapolated to atmospheric pressure gives excellent agreement with the transition studied at $94^\circ K$ by Eucken and Schroder[28]. They concluded that the transition was first order, with a latent heat of 384 calories per mole (2.63 calories per gram).

The observed value of $\Delta (\Delta V/V_o)$ for this transition is 2.6% at $182^\circ K$ and 7,300 kg/cm^2. Hysteresis and friction were small, so that this is a relatively accurate value. The transition occurred rapidly for both increasing and decreasing pressure and so could be located quite precisely. As is the case with Figures 1 and 2, the error bars on the points in Figure 3 correspond to the size of the pressure increments used.

The density of solid SF_6 has been measured at very low temperature and at the melting point by Klemm and Henkel[29]. At $182^\circ K$ the value 2.55 grams/cm^3 has been obtained by interpolation, with account taken of the discontinuous density change at the transition. This value was used to determine the molar volumes in Table I.

If we use the observed dP/dT (82.8 kg/cm^2 $^\circ K$) and L at $94^\circ K$, we find from the Clapeyron equation $\Delta V = 2.10$ cm^3/mole. The interpolated density[30] at $94^\circ K$ is 2.70 gram/cm^3, giving a molar volume of 54.1 cm^3.

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Thus $\Delta (\Delta V/V_o)_{94}$ = 3.9%, which agrees reasonably well with the value of 2.6% observed in the current investigation at $182^{\circ}K$. Inasmuch as the latent heat of transformation might be expect to vary considerably over a large range of temperature, there is no basis for a direct comparison at $182^{\circ}K$ and 7,300 kg/cm^2. If L and dP/dT both remained the same between $94^{\circ}K$ and $182^{\circ}K$, then at the latter temperature $\Delta (\Delta V/V_o)$ would be only 2.0% which is definitely smaller than indicated by the current observations.

No data appear to be available on the crystal structure of solid SF_6. The transition has all the characteristics of an ordinary crystallographic one.

Because of blockage of the filling capillary, it was impossible to obtain large samples of solid SF_6. After it was found that it had no observable effect, the use of the silica gel drier in the line was discontinued. On account of the lack of friction and the sharpness of the observed transition, it is believed that the blockage was by solid SF_6 itself rather than by impurities. SF_6 has a high triple point pressure, 1,700 mm Hg, so that the gas must be continuously supplied at a pressure above 19 psig in order to permit condensation to the liquid rather than sublimation to the solid. Under these conditions blockage readily occurs. It is not felt that the shortness of the SF_6 samples significantly affected the accuracy of the results.

IV. Acknowledgments

The author wishes to acknowledge the assistance of Mr. Phillip Sommer who constructed much of the apparatus. He is grateful to Messrs. James N. Boyd and Charles D. Smith who helped with the manipulation of the multikilogram weights for the dead weight gauge, and with some of the calculations.

TABLE I. COMPRESSION OF SOLID HCl, HBr, SiH$_4$, AND SF$_6$

Pressure Kg/cm²	HCl M.P. 159°K, T = 130°K			HBr M.P. 186°K, T = 150°K			SiH$_4$ M.P. 88.5°K, T = 80°K		SF$_6$ S.P. 210°K, T = 182°K		
	Molar Vol. cm³	$-\frac{\Delta V}{V_o}$	$\beta \times 10^{-5}$ cm²/kg	Molar Vol. cm³	$-\frac{\Delta V}{V_o}$	$\beta \times 10^{-5}$ cm²/kg	$-\frac{\Delta V}{V_o}$	$\beta^a \times 10^{-5}$ cm²/kg	Molar Vol. cm³	$-\frac{\Delta V}{V_o}$	$\beta \times 10^{-5}$ cm²/kg
0	25.3	0	3.60	31.7	0	3.65	0	3.1	57.3	0	2.93
1,500	-	-	-	-	-	-	.080		-	-	-
1,500	-	-	-	-	-	-	.104		-	-	-
2,000	23.9	.057	2.34	29.7	.063	2.37	.116		54.5	.050	2.15
4,000	22.9	.096	1.80	28.6	.099	1.86	160	2.0	52.4	.086	1.72
6,000	22.2	.125	1.47	27.7	.128	1.53	.194		50.8	.114	1.45
7,300	-	-	-	-	-	-	-		49.9	.129	
7,300	-	-	-	-	-	-	-		48.4	.155	
8,000	21.6	.148	1.26	26.9	.151	1.33	.220		-	-	
10,000	21.1	.168	1.10	26.3	.171	1.18	.241	1.3	47.0	.180	
12,000	20.7	.184	.99	25.8	.187	1.05	.257		46.1	.196	
14,000	20.3	.199	.90	25.3	.202	.96	.271		45.4	.208	
16,000	20.0	.212	.82	24.9	.216	.87	.283		44.8	.219	
18,000	19.6	.225	.76	24.5	.229	.80	.293		44.3	.228	
20,000	19.3	.238	.70	24.1	.241	.74	.303		43.8	.236	(0.55)^b
	No transition (at 130°K)			No transition			I-II transition at 1,500 kg/cm²		I-II transition at 7,300 kg/cm²		
	$\xi = -2.8 + 0.2$			$\xi = -2.4 + 0.2$			$\xi^a = -0.5 \pm 0.2$		$\xi = -1.8 \pm 0.2$		

a. ξ and β are evaluated at 54°K where solid SiH$_4$ is somewhat brittle. These values are not as reliable as those for the other substances. At 80°K the transition occurs at P = 1,500 Kg/cm², giving too short a range of pressure for a satisfactory Murnaghan fit of Phase I data.

b Estimated from slope of volume vs pressure plot.

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Figure Captions

Figure 1   -   Phase Diagram for Solid HCl.

Figure 2   -   Phase Diagram for Solid SiH_4.

Figure 3   -   Phase Diagram for Solid SF_6.

PHASE TRANSITION IN 'SOLID HYDROGEN CHLORIDE