Prediction of Standard Heat Capacity and Entropy of Inorganic XY_3, XY_4 and XY_5 Gases at 25 °C Based on Correlation with the Normal Boiling Point

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It has been demonstrated that the standard heat capacity C_p^0 and the standard entropy S^0 at 25 °C may be estimated from the simple expressions $S^0 = A \exp(-\theta/T)$ and $C_p^0 = B \exp(-\theta/T)$, where T is the normal boiling point (1 atm). The empirical parameters A, B and θ have characteristic values for each family of structurally related compounds. Values of these parameters have been established for inorganic compounds XY_3, XY_4 and XY_5 using available standard thermodynamic data. For many of these compounds data were not available. Missing values may be estimated from our expressions if only the normal boiling point of the compound is known. Average deviations between observed and calculated values were typically 3–10 %.

Values for the boiling points (1 atm) of 98 inorganic halides have previously been recorded.[1] However, standard values of heat capacity and entropy could be found for only 34 of these compounds.

From the curves in Figs. 1–7 it is seen that the values of C_p^0 and S^0 for a compound at 298K and 1 atm are correlated with the value of the normal boiling point. A simple method is hereby suggested for estimating values of C_p^0 and S^0 if only the normal boiling point (T) is known. The empirical relationships in question are:

$$S^0 = A \exp(-\theta/T$$

and $$C_p^0 = B \exp(-\theta/T)$$

The parameters A, B and θ are determined from the available data. Thus, the parameter θ, which is a characteristic temperature, has the same value in both expressions. The ratio S^0/C_p^0 is then a constant equal to A/B for all compounds in a family.

Parameter values were easily found by trial and error. If a least-squares procedure is used, one has to consider the choice of proper weights.

XY_3 Compounds

Data for the XY_3 compounds are shown in Table 1 and Fig. 1. The curves showing best fit to the observations have the parameter values (R is the gas constant):

$A = 56.9R \quad B = 12.6R \quad \theta = 128\text{K}$

However, some points deviate substantially from these curves. Data for the six planar molecules are shown separately in Fig. 2. The best fit was obtained with the parameter values:

$A = 52.8R \quad B = 11.1R \quad \theta = 111\text{K}$

Clearly the fit between calculated and observed points has been improved. Thus the values for planar GaY_3 compounds in Table 1 have been estimated using these parameter values, while for the non-planar halides $SbBr_3$, SbI_3, $AsCl_3$, $BiBr_3$, $AuCl_3$, $FeCl_3$ and NCl_3 the first set of parameters were used.

The points corresponding to fluorides as well as hydrides also deviate from the curves in Fig. 1. Therefore, separate curves for these compounds are shown in Fig. 3. The parameter values for the fluorides are:

$A = 39.8R \quad B = 9.06R \quad \theta = 45\text{K}$

Thus, the values for SbF_3 and AsF_3 in Table 1 were calculated using these parameter values.

For the hydrides the parameter values are:

$A = 40.0R \quad B = 6.69R \quad \theta = 90\text{K}$

The values for BiH_3 were calculated using these values.

The boiling points of the asymmetrical non-planar halides $PBrF_2$, PBr_2F and $PClF_2$ are known. Using the parameters corresponding to fluorides, the following values for S^0/C_p^0 were obtained: $PBrF_2$ (66.3/15.1), PBr_2F (69.5/15.8) and $PClF_2$ (64.7/14.8) in cal mol^{-1} K^{-1}. However, using the

Table 1. XY_3 gases. Standard values of entropy S^0 and heat capacity C_p^0 at 298K. Boiling point T at 1 atm. R is the gas constant.

	T/K	S^0/R	C_p^0/R	Comments
$AlBr_3$	527	42.0	9.06	Planar molecules
AlI_3	658	43.7	9.21	
Bbr_3	365	39.0	8.15	$A = 52.8R$
BCl_3	285	34.9	7.55	$B = 11.1R$
BF_3	172	30.6	6.09	$\theta = 111$K
BI_3	483	42.2	8.51	
$GaBr_3$	553	43	9.1	Estimated
$GaCl_3$	474	42	8.8	values ±3 %
GaI_3	619	44	9.3	
$AsBr_3$	494	43.7	9.51	Non-planar
AsI_3	676	46.7	9.71	molecules
$BiCl_3$	720	43.1	9.56	$A = 56.9R$
ClF_3	285	33.9	7.70	$B = 12.6R$
PBr_3	446	41.6	9.16	$\theta = 138$K
PCl_3	348	37.5	8.66	
$SbBr_3$	562	45	9.8	Estimated
SbI_3	673	46	10.3	values ±3 %
$AsCl_3$	403	40	8.9	
$BiBr_3$	733	47	10.4	
$AuCl_3$	502	43	9.5	
$FeCl_3$	937	49	10.9	
NCl_3	344	38	8.4	
BrF_3	399	35.2	8.00	Fluorides
PF_3	172	32.9	7.05	$A = 39.8R$ $\theta = 45$K
BF_3	172	30.6	6.09	$B = 9.06R$
SbF_3	649	37	8.5	Estimated
AsF_3	324	35	7.9	values ±5 %
NH_3	239	23.2	4.29	Hydrides
SbH_3	255	28.0	4.93	
AsH_3	211	26.8	4.58	$A = 40.0R$ $\theta = 90$K
PH_3	185	25.3	4.08	$B = 6.69R$
BiH_3	290	29	4.9	Estimated ±10 %
$PBrF_2$	257	33	7.5	Asymmetrical
PBr_2F	352	37	8.3	Molecules ±5 %
$PClF_2$	226	32	7.2	See text

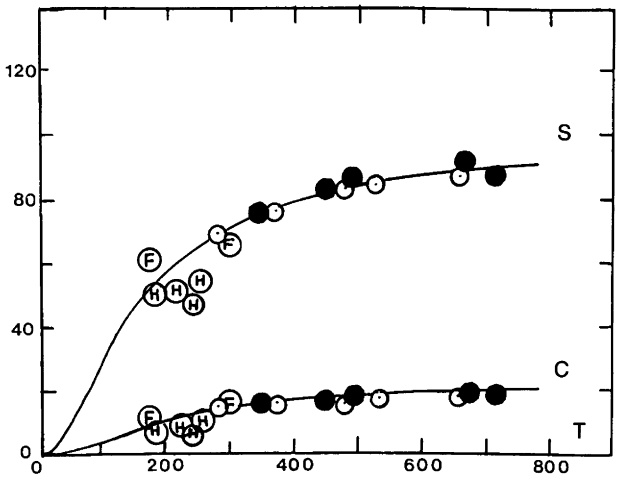

Fig. 1. XY_3 compounds: Standard entropy (S) and heat capacity (C) in cal mol^{-1} K^{-1}. T(K) is the normal boiling point. Data for planar molecules are indicated by open circles, while non-planar molecules are indicated by dark points. Fluorides and hydrides are indicated by the letters F and H, respectively.

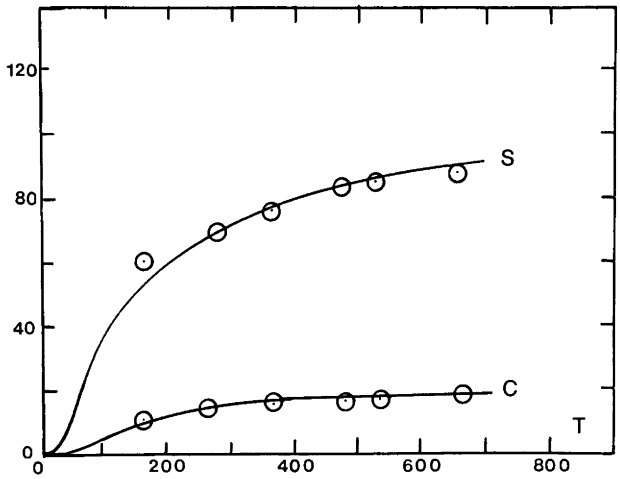

Fig. 2. XY_3 compounds: Standard entropy (S) and heat capacity (C) in cal mol^{-1} K^{-1}. T(K) is the normal boiling point.

first set of parameters corresponding to non-planar compounds the following values were obtained: $PBrF_2$ (66.1/14.6), PBr_2F (76.4/16.9) and $PClF_2$ (61.4/13.6) in cal mol^{-1} K^{-1}. Table 1 gives the averages of these two estimates.

From the data in Table 1 the ratio S^0/C_p^0 is calculated as approximately 4.6 for the halides and 6.0 for the hydrides. Our parameters A and B have ratios between 4.4 and 4.8 for the halides and 6.1 for the hydrides.

The fact that the ratios S^0/C_p^0 are approximately constant within a family of related molecules is our reason for introducing the same θ value in the expressions for S^0 and C_p^0.

In Fig. 3 it can be seen that the S^0 value for NH_3(T = 239K) deviates significantly from the best curve determined for the remaining hydrides. The C_p^0 value for NH_3 is also somewhat lower than expected. No explanation was found.

XY_4 Compounds

Data for XY_4 molecules, and some unsymmetrical molecules containing hydrogen and halogen, are given in Table 2. Curves are shown in Figs. 4–6. Clearly the data for chloro, bromo and iodo compounds fit the curves for S^0 and C_p^0 in Fig. 4. However, data for fluorides and hydrides show substantial deviations from these curves. Parameter values corresponding to the curves in Fig. 4 are:

$A = 71.5R$ $B = 18.4R$ $\theta = 194$K

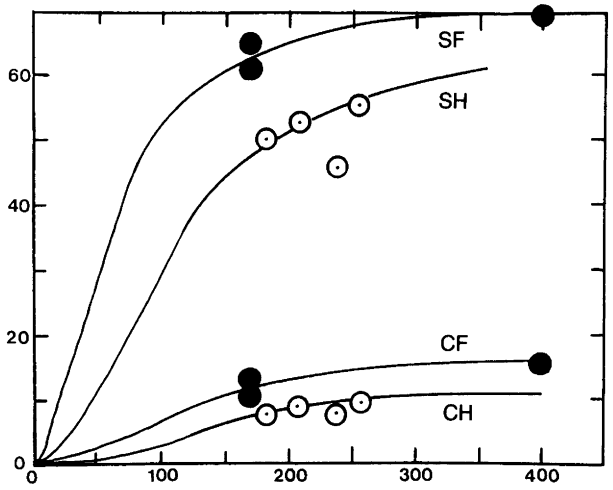

Fig. 3. XY_3 compounds: Standard entropy for fluorides (SF) and hydrides (SH), and heat capacity for fluorides (CF) and hydrides (CH), in cal mol^{-1} K^{-1}. T(K) is the normal boiling point.

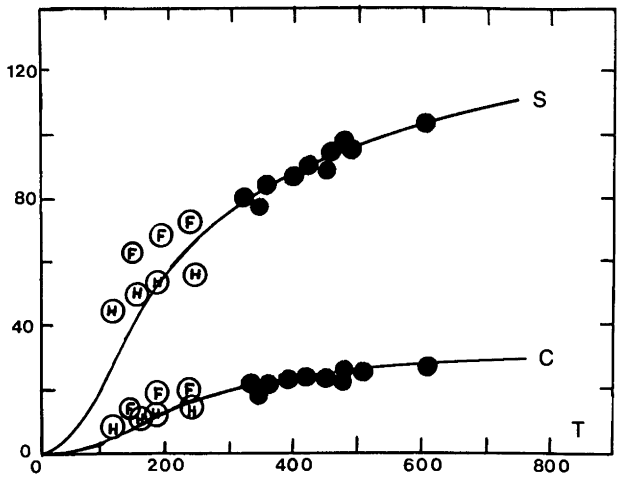

Fig. 4. XY_4 compounds: Standard entropy (S) and heat capacity (C) in cal mol^{-1} K^{-1}. T(K) is the normal boiling point. The dark points indicate data for chlorides, bromides and iodides. Fluorides and hydrides are indicated by the letters F and H, respectively.

Table 2. XY_4 gases. Standard values of entropy S^0 and heat capacity C_p^0 at 298K. Boiling point T at 1 atm. R is the gas constant.

	T/K	S^0/R	C_p^0/R	Comments
GeH_4	185	26.1	5.44	Hydrides
SiH_4	161	24.6	5.13	$A = 36.0R$
SnH_4	221	27.4	5.89	$B = 7.40R$
CH_4	112	22.4	4.30	$\theta = 55$K
SiF_4	187	34.0	8.86	Fluorides:
SF_4	235	36.0	9.36	$A = 48.1R$ $B = 12.7R$
SiH_4	178	32.7	7.30	$\theta = 64$K
CF_4	143	31	7.34	
SeF_4	381	41	10.7	Estimated
TeF_4	370	41	10.7	values ±10 %
$GeBr_4$	460	47.7	12.2	Bromides,
$SiBr_4$	427	45.5	11.7	chlorides,
$SuBr_4$	480	49.5	12.4	iodes:
$TiBr_4$	504	48.0	12.1	$A = 71.5R$
$GeCl_4$	356	41.8	11.6	$B = 18.4R$
$SiCl_4$	331	39.8	10.9	$\theta = 194$K
$TiCl_4$	410	42.7	11.5	
VCl_4	425	43.6	11.6	
GeI_4	612	51.6	12.5	
CBr_4	463	43.0	11.0	
CCl_4	350	37.3	10.0	
$TeCl_4$	661	53	13.7	Estimated
$SnCl_4$	388	43	11.2	values ±3 %
SiI_4	576	51	13.1	
SnI_4	638	53	13.6	
TiI_4	653	53	13.7	
$SiBrCl_3$	354	41	10.6	Asymmetric
$SiBr_2Cl_2$	377	43	10.0	molecules:
$SiBr_3Cl$	400	44	11.3	
$SiCl_3I$	387	43	11.2	±3 %
SiH_3Cl	243	30.2	6.04	Asymmetric
SiH_2Cl_2	282	34.2	7.29	molecules with
SiH_3Br	275	33	8.0	hydrogen and
SiH_2Br_2	339	41	10.0	halogen:
$SiHBr_3$	382	46	11.1	$A = 105.7R$
SiH_3I	319	39	9.4	$B = 25.7R$
$SiHCl_3$	307	37	9.0	$\theta = 321$K
$SiHI_3$	493	55	13.4	±10 %

These parameter values reproduce the observations for chlorides, bromides and iodides. For these compounds, the ratios S^0/C_p^0 have values between 3.7 and 4.1, while A/B is equal to 3.89. Again, the ratio S^0/C_p^0 is approximately a constant.

Curves for fluorides and hydrides are shown in Fig. 5. The compound $SiHF_3$ has been included among the fluorides. Thus, the parameter values are as follows:

for hydrides: $A = 36.0R$ $B = 7.40R$ $\theta = 55$K

for fluorides: $A = 48.1R$ $B = 12.7R$ $\theta = 64$K

Data for the hydrides were reproduced with an average deviation of about ±3 %, while for the fluorides the average deviation was about ±10 %.

Boiling points for several silicon compounds containing both halogen and hydrogen were recorded. The data for SiH_3Cl, SiH_2Cl_2, $SiCl_4$ and $SiBr_4$ were used to establish the curves in Fig. 6. The parameter values are

$A = 105.7R$ $B = 25.7R$ $\theta = 321$K

These values were used for the last six compounds in Table 2.

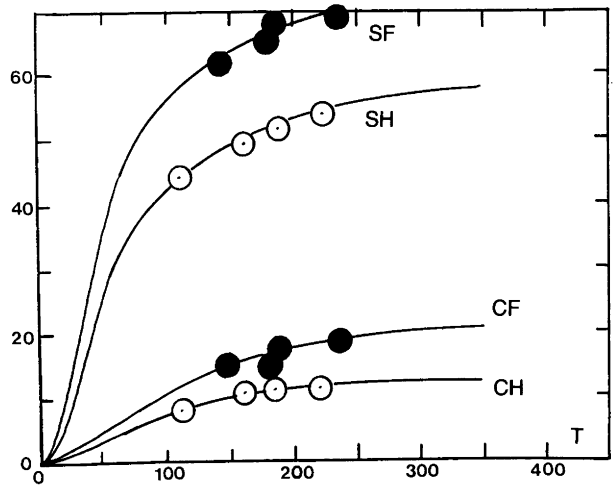

Fig. 5. XY_4 compounds: Standard entropy for fluorides (SF) and hydrides (SH), and heat capacity for fluorides (CF) and hydrides (CH), in cal mol^{-1} K^{-1}. T(K) is the normal boiling point.

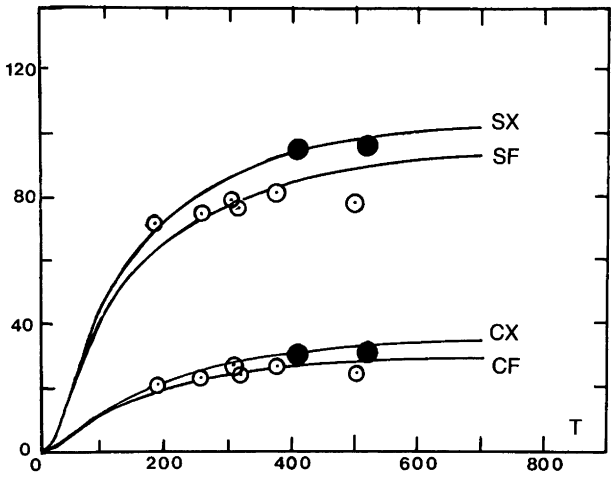

Fig. 7. XY_5 compounds: Standard entropy (SX and SF) and heat capacity (CX and CF) in cal mol^{-1} K^{-1}. T(K) is the normal boiling point. The fluorides correspond to open points, while chlorides are indicated by dark points.

XY_5 Compounds

Results and data for XY_5 molecules are given in Fig. 7 and Table 3. The following parameter values were obtained:

for fluorides: $A = 54.4R$ $B = 16.1R$ $\theta = 95$K
for chlorides: $A = 59.4R$ $B = 19.1R$ $\theta = 94$K

It is our experience with XY_3 and XY_4 compounds that bromides, chlorides and iodides have the same set of parameter values. Thus, the parameters for chlorides were used when estimating values for bromides and iodides in Table 3.

For the fluorides, the ratios S^0/C_p^0 have values between 3.2 and 3.6, while the ratio A/B is equal to 3.4. Again, the ratio S^0/C_p^0 is found to have an approximately constant value for compounds in a related family. From Fig. 7 it can be seen that the points corresponding to NbF_5 at $T = 498$K

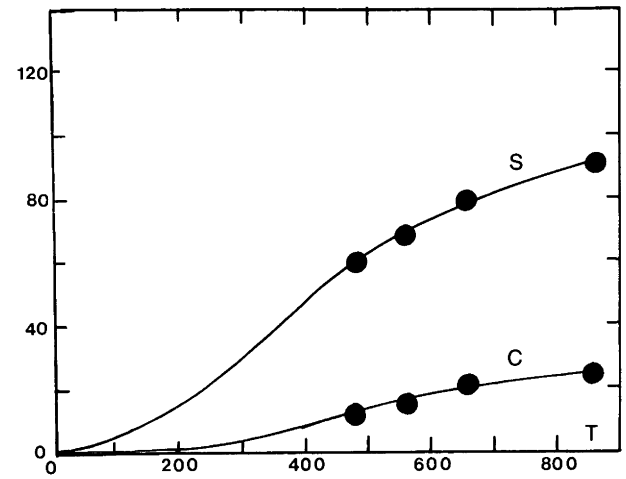

Fig. 6. XY_4 compounds: Standard entropy (S) and heat capacity (C) for SiH_3Cl, SiH_2Cl_2, $SiCl_4$ and $SiBr_4$ in cal mol^{-1} K^{-1}. T(K) is the normal boiling point.

Table 3. XY_5 gases. Standard values of entropy S^0 and heat capacity C_p^0 at 298K. Boiling point T at 1 atm. R is the gas constant.

	T/K	S^0/R	C_p^0/R	Comments
ClF_5	259	37.3	11.7	Fluorides:
IF_5	375	40.3	12.4	$A = 54.4R$
NbF_5	498	38.7	11.7	$B = 16.1R$
PF_5	189	36.2	10.2	$\theta = 95$K
VF_5	321	38.6	11.9	
SbF_5	423	44	12.9	Estimated
BrF_5	315	40	11.9	values ±10 %
CrF_5	390	43	12.6	
MoF_5	487	45	13.2	
OsF_5	499	45	13.1	
RuF_5	500	45	13.3	
TaF_5	502	45	13.3	
$SbCl_5$	413	48.3	14.6	Chlorides:
$NbCl_5$	523	48.2	14.5	$A = 59.4R$ $R = 19.1R$ $\theta = 94$K
$MoCl_5$	537	50	16.0	Estimated
$PaCl_5$	693	52	16.7	values ±5 %
$TaCl_5$	513	50	15.9	
WCl_5	562	50	16.2	
UCl_5	800	53	17.0	
SbI_5	352	46	14.6	Bromides and
$NbBr_5$	545	50	16.1	Iodides:
NbI_5	620	51	16.4	Estimated
$TaBr_5$	595	51	16.3	values ±5 %
TaI_5	670	51	16.1	
WBr_5	634	51	16.5	

deviate significantly from the curves (SF and CF) determined by the remaining fluorides. Both NbF_5 and VF_5 are fluorides of Group VA elements. However, as seen from Table 3 and Fig. 7 the data for VF_5 follow the trend found for other fluorides. It is known that VF_5 is an infinite chain polymer, whereas NbF_5 and TaF_5 are tetramers. In the gas phase these pentafluorides are monomers. Thus, the boiling points of NbF_5 and TaF_5 are higher than expected for monomeric forms. The boiling point of TaF_5 is 502K, and for this compound the values $S^0/R \simeq 38{,}7$ and $C_p^0/R \simeq 11.7$ are expected. For a monomeric compound with boiling point at 502K our parameters for fluorides suggest the values $S^0/R \simeq 45$ and $C_p^0/R \simeq 13.3$, respectively.

Conclusions and discussion

Using standard thermodynamic data for 34 inorganic XY_3, XY_4 and XY_5 gases, it has been demonstrated that entropy and heat capacity at 25 °C and 1 atm may be estimated if only the normal boiling point of a compound is know. The expected uncertainties in the estimated values are typically 3–10 %, depending on the kind of compound considered. Thus, for fluorides the expected uncertainty is 5–10 %, and for other halides 3–5 %. The expected uncertainty for hydrides is about 10 %.

It is our experience that bromides, chlorides and iodides have the same set of parameters, while fluorides and hydrides demand separate parameters.

If a compound is not a simple monomer, deviations from the normal values within the family of compounds to which it belongs are expected. Such a deviation was probably observed for NbF_5.

Based on the data for 34 compounds, and boiling points of additional 64 compounds, the standard entropy and heat capacity of these 64 compounds have been estimated.

Finally, a warning is perhaps needed. Our parameter values have been established for compounds having normal boiling points lower than 600 °C. These parameter values cannot be used with the same degree of confidence for temperatures above 600 °C.

Reference

1. Dean, J. A. *Lange's Handbook of Chemistry,* 13th ed., Mc Graw-Hill, New York 1985.

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