

# Prediction of Entropy of Vaporization Based on Correlation with the Normal Boiling Point

Reidar Stølevik

The University of Trondheim, Department of University, AVH, N-7055 Dragvoll, Norway

Stølevik, R., 1989. Prediction of Entropy of Vaporization Based on Correlation with the Normal Boiling Point. – Acta Chem. Scand. 43: 860–867.

It has been demonstrated that the entropy of vaporization of a liquid may be estimated from the simple formula  $\Delta S_v^\circ = A \exp(-\Theta/T)$ , where  $T$  is the normal boiling point of the liquid. The empirical parameters  $A$  and  $\Theta$  have been established for the elements and a larger number of inorganic  $XY$ ,  $XY_2$ ,  $XY_3$  and  $XY_4$  halides, and some hydrides. These parameters have characteristic values for each family of structurally related compounds. Missing  $\Delta S_v^\circ$  values may be estimated from our formula if only the normal boiling point is known. Average deviations between observed and calculated values were typically 5–10%. Large deviations from the normal values have been discussed.

It is well known that the entropy of vaporization ( $\Delta S_v^\circ$ ) of many liquids at the normal boiling point ( $T$ ) is approximately equal to  $10.6R$  (Trouton's rule), where  $R$  is the gas constant. According to this rule the heat of vaporization ( $\Delta H_v^\circ$ ) may be obtained from the simple formula  $\Delta H_v^\circ \approx 10.6RT$ .

We want to demonstrate that a superior rule is the simple function  $\Delta S_v^\circ = A \exp(-\Theta/T)$ . Here  $A$  and  $\Theta$  are empirical parameters, and their values have to be established from the available observations. The values  $A/R = 10.6$  and  $\Theta/K = 0$  correspond to Trouton's rule. The function increases from zero at  $T/K = 0$  and approaches the value of  $A$  asymptotically when  $T \gg \Theta$ .  $\Delta S_v^\circ$  is always less than  $A$ .

The same function has already been used in a previous paper<sup>1</sup> in order to correlate the standard entropy and standard heat capacity of a gas at 25°C with the normal boiling point of that compound. Observed heats of vaporization and boiling points were taken from Ref. 2.

## Monoatomic compounds

Values of heats of vaporization  $\Delta H_v^\circ$  for monoatomic elements have been plotted against the values of the normal boiling points in Fig. 1. A straight line corresponding to Trouton's rule is also shown. Clearly the rule is approximately followed for elements with  $T$  less than about 2000 K. However, for elements with higher boiling points the deviations are significant. At 5000 K the deviations are as large as 50%.

$\Delta H_v^\circ$  values for the monoatomic elements in periods 4, 5 and 6 are shown in Figs. 2–4. In each diagram a smooth curve is also shown. This curve has the simple formula  $\Delta H_v^\circ = AT \exp(-\Theta/T)$ , corresponding to  $\Delta S_v^\circ = A \exp(-\Theta/T)$ . The best values of the parameters  $A$  and  $\Theta$  must be determined from the data. Thus, the parameter values are as follows:  $A = 20.9R$  and  $\Theta = 1313$  K for

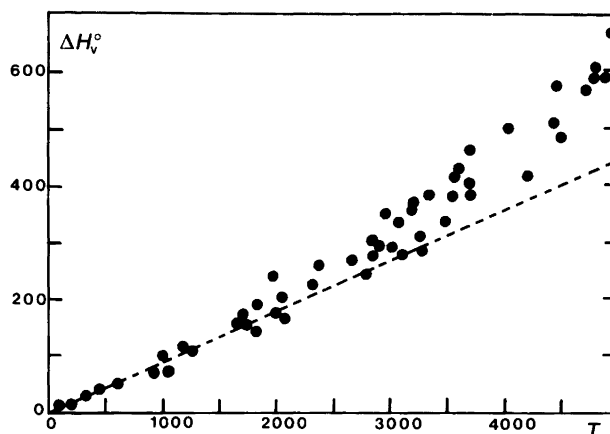


Fig. 1. Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for monoatomic elements at the normal boiling point  $T$  (K). The broken line corresponds to Trouton's rule.

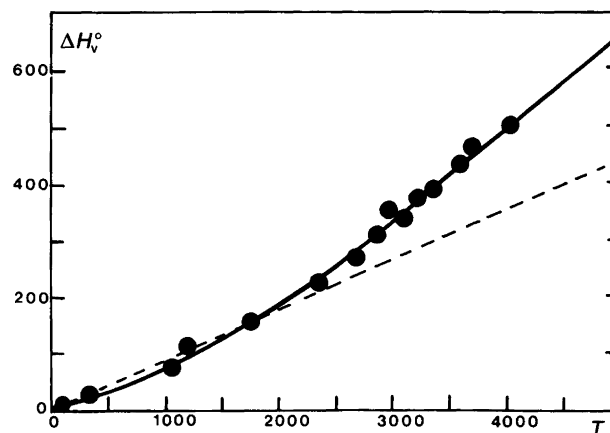


Fig. 2. Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for period-4 elements at the normal boiling point  $T$  (K). The broken line corresponds to Trouton's rule, while the unbroken curve has the formula  $\Delta H_v^\circ = 174T \exp(-1313/T)$ .

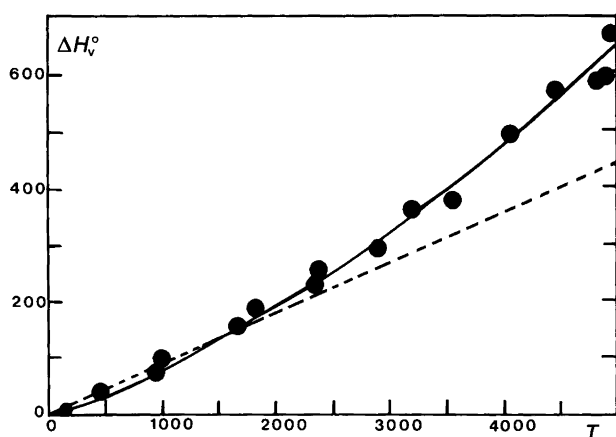


Fig. 3. Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for period-5 elements at the normal boiling point  $T$  (K). The broken line corresponds to Trouton's rule, while the unbroken curve has the formula  $\Delta H_v^\circ = 138T\exp(-550/T)$ .

period 4,  $A = 16.6R$  and  $\Theta = 550$  K for period 5, and  $A = 18.2R$  and  $\Theta = 1150$  K for period 6.

Boiling points and  $\Delta S_v^\circ$  values are shown in Table 1 for the elements of periods 4, 5 and 6, including those elements that are not monoatomic. Using the parameter values above, the average deviation between calculated  $\Delta S_v^\circ$  values and the experimental values in Table 1 are 5% for periods 4 and 5, while for period 6 the average deviation is 10%. If Trouton's rule is used, the average deviations become 15% (period 4), 30% (period 5) and 25% (period 6). Thus the simple formula  $\Delta S_v^\circ = A\exp(-\Theta/T)$  is superior to the rule that  $\Delta S_v^\circ \approx 88$   $\text{J mol}^{-1} \text{K}^{-1}$ .

For the elements  $\text{As}_4$ ,  $\text{Se}_6$ ,  $\text{Br}_2$ ,  $\text{Sb}_4$ ,  $\text{Te}_2$ ,  $\text{I}_2$  and  $\text{At}_2$  the parameter established above should not be used. If these

elements were monoatomic the following  $\Delta S_v^\circ$  values would be expected according to our formula: 46 (Se), 3 (Br), 103 (Sb), 89 (Te) and 41 (I)  $\text{J mol}^{-1} \text{K}^{-1}$ .

Even among the monoatomic elements substantial deviations from the general trends exist. Thus the following  $\Delta S_v^\circ$  values (in  $\text{J mol}^{-1} \text{K}^{-1}$ ) were calculated: 49 (K), 78 (Rb), 47 (Cs), 57 (Zn), 81 (Cd) and 24 (Hg). For the noble gases the deviations are dramatic. However, the formula  $\Delta S_v^\circ = 10.5R\exp(-11/T)$  reproduces the experimental values for the noble gases within  $\pm 5\%$ , except that He has the very low value  $\Delta S_v^\circ = 2.3R$  at  $T = 4.2$  K.

Data for the lanthanides and the actinides are shown in Fig. 5 and Table 2. For boiling points less than about 3500 K the simple rule that  $\Delta S_v^\circ \approx 88$   $\text{J mol}^{-1} \text{K}^{-1}$  is quite

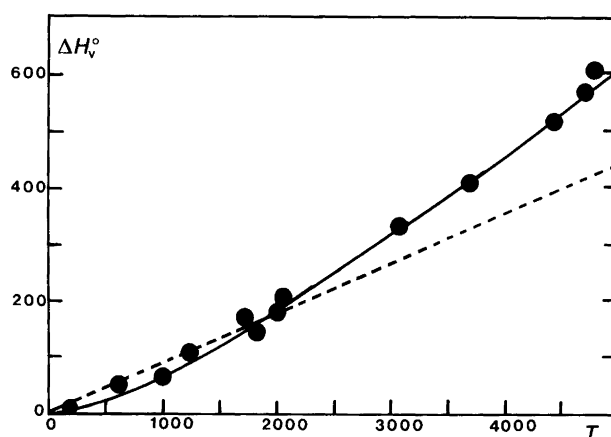


Fig. 4. Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for period-6 elements at the normal boiling point  $T$  (K). The broken line corresponds to Trouton's rule, while the unbroken curve has the formula  $\Delta H_v^\circ = 151T\exp(-1150/T)$ .

Table 1. The entropy of vaporization  $\Delta S_v^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) at the normal boiling point  $T$  for monoatomic elements (atomic Nos. 19–86).

Period 4		Period 5		Period 6				
	$T/\text{K}$	$\Delta S_v^\circ$	$T/\text{K}$	$\Delta S_v^\circ$	$T/\text{K}$	$\Delta S_v^\circ$		
K	1039	76	Rb	961	79	Cs	978	69
Ca	1767	88	Sr	1654	96	Ba	2123	64
Sc	3021	110	Y	3537	104	La	3693	109
Ti	3558	119	Zr	4473	127	Hf	4723	121
V	3623	127	Nb	5031	135	Ta	5807	131
Cr	2963	115	Mo	4923	120	W	5773	143
Mn	2333	95	Tc	4840	121	Re	5950	118
Fe	3023	113	Ru	4323	120	Os	5298	139
Co	3373	113	Rh	4033	123	Ir	4823	127
Ni	3193	117	Pd	3213	113	Pt	4443	110
Cu	2843	108	Ag	2428	106	Au	3081	111
Zn	1180	97	Cd	1038	96	Hg	630	94
Ga	2676	101	In	2353	99	Tl	1730	96
Ge	3123	105	Sn	2896	102	Pb	2024	88
$\text{As}_4$	—	—	$\text{Sb}_4$	1860	104	Bi	1837	83
$\text{Se}_6$	985	109	$\text{Te}_2$	1263	40	Po	1235	84
$\text{Br}_2$	333	89	$\text{I}_2$	458	92	$\text{At}_2$	—	—
Kr	120	76	Xe	165	77	Rn	211	86

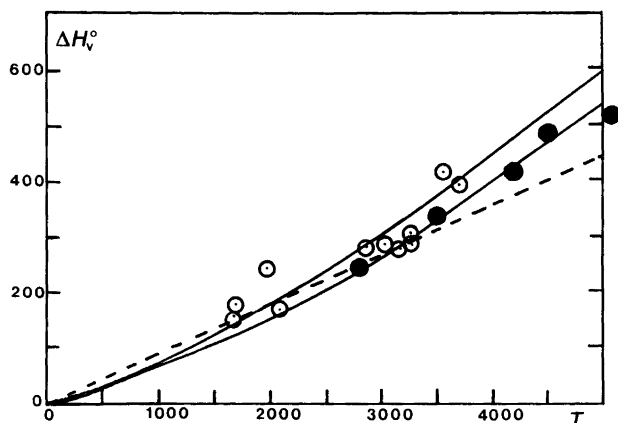


Fig. 5. Heats of vaporization  $\Delta H_v^0$  ( $\text{kJ mol}^{-1}$ ) for lanthanides and actinides at the normal boiling point  $T$  (K). The broken line corresponds to Trouton's rule, while the upper unbroken curve for the lanthanides ( $\circ$ ) has the formula  $\Delta H_v^0 = 138T \exp(-909/T)$  and the lower curve for the actinides ( $\bullet$ ) has the formula  $\Delta H_v^0 = 128T \exp(-955/T)$ .

Table 2. Entropy of vaporization  $\Delta S_v^0$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) at the normal boiling point  $T$  for monoatomic elements (lanthanides and actinides).

Lanthanides		Actinides			
$T/\text{K}$	$\Delta S_v^0$	$T/\text{K}$	$\Delta S_v^0$		
Ce	3743	106	Th	5123	100
Pr	3293	101	Pa	4500	107
Nd	3300	90	U	4203	99
Pm	—	—	Np	5508	61
Sm	2073	80	Pu	3503	96
Eu	1712	103	Am	2873	83
Gd	3273	92	Cm <sup>a</sup>		
Tb	3073	95	Bk		
Dy	2873	98	Cf		
Ho	2873	98	Es		
Er	3173	88	Fm		
Tm	2000	124	Md		
Yb	1700	94	No		
Lu	3600	115	Lr		

<sup>a</sup>For Cm–Lr see discussion in the text.

satisfactory. The best parameters corresponding to the smooth curves in Fig. 5 are  $A = 16.6R$  and  $\Theta = 909 \text{ K}$  for the lanthanides, and  $A = 15.4R$  and  $\Theta = 955 \text{ K}$  for the actinides. These parameter values reproduce the experimental data with an average deviation of about 10%. However, for the element Nb ( $T = 5508 \text{ K}$ ) the expected value of  $\Delta S_v^0$  is  $13R$  according to our formula. The experimental value is only  $7.3R$ . For Tm the expected value is  $10.5R$ , while the observed value is  $14.9R$ .

Boiling points for actinides after Am are not recorded in the literature. However, the following correlations of boiling points and  $\Delta H_v^0$  values ( $\text{kJ mol}^{-1}$ ) are predicted: 160 ( $T = 2000 \text{ K}$ ), 280 ( $T = 3000 \text{ K}$ ), 400 ( $T = 4000 \text{ K}$ ), 530 ( $T = 5000 \text{ K}$ ), 655 ( $T = 6000 \text{ K}$ ), using the parameter

Table 3. Entropy of vaporization  $\Delta S_v^0$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) for diatomic compounds at the normal boiling point  $T$ .

	$T/\text{K}$	$\Delta S_v^0$
Br <sub>2</sub>	332	89
BrF	293	88
Cl <sub>2</sub>	239	86
HBr	206	86
HCl	188	86
HI	238	83
I <sub>2</sub>	457	92
H <sub>2</sub>	20.4	44
F <sub>2</sub>	85	77
ClF	183	85 <sup>a</sup>
DBr	207	86 <sup>a</sup>
DCI	188	85 <sup>a</sup>
DI	238	88 <sup>a</sup>
ICI	371	91 <sup>a</sup>
CsBr	1573	96
CsCl	1593	72
CsI	1553	96
LiBr	1562	94
Lil	1451	67
RbBr	1625	96
RbCl	1654	93
RbI	1577	96
AgBr	1833	105
AgCl	1837	96
AgI	1778	82
NaBr	1720	93
TlBr	1098	94
TlCl	1089	95
TlI	1118	93

<sup>a</sup>Estimated value  $\pm 3\%$ .

values above. The expected uncertainty of these values is about  $\pm 10\%$ .

### Diatomic compounds

Data for diatomic single-bonded compounds are shown in Table 3 and Fig. 6. The data for  $T < 500 \text{ K}$  are best repro-

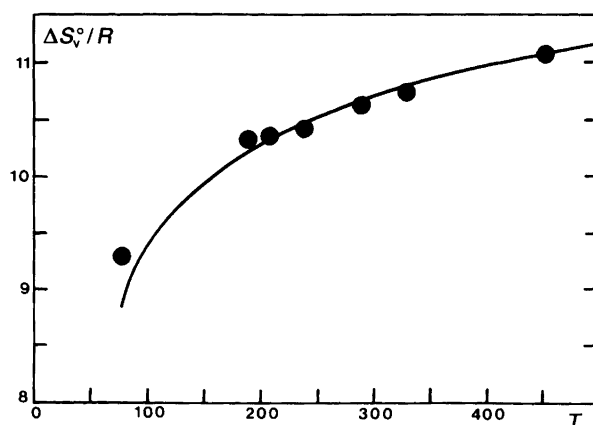


Fig. 6. Entropies of vaporization  $\Delta S_v^0$  for single-bonded diatomic compounds at the normal boiling point  $T$  (K). The curve has the formula  $\Delta S_v^0/R = 11.7 \exp(-25/T)$ .

**Table 4.** Entropy of vaporization  $\Delta S_v^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) for triatomic compounds (bromides and iodides) at the normal boiling point  $T$ .

Bromides			Iodides		
	$T/\text{K}$	$\Delta S_v^\circ$		$T/\text{K}$	$\Delta S_v^\circ$
BeBr <sub>2</sub>	794	126	BaI <sub>2</sub>	2340	79
CdBr <sub>2</sub>	1136	100	BeI <sub>2</sub>	755	128
CaBr <sub>2</sub>	2083	96	CdI <sub>2</sub>	1069	100
PbBr <sub>2</sub>	1185	100	CaI <sub>2</sub>	2028	88
MgBr <sub>2</sub>	1431	104	FeI <sub>2</sub>	1366	77
MnBr <sub>2</sub>	1300	87	PbI <sub>2</sub>	1105	107
HgBr <sub>2</sub>	595	96	HgI <sub>2</sub>	623	95
SrBr <sub>2</sub>	2419	80	SnI <sub>2</sub>	990	101
SnBr <sub>2</sub>	895	152	SrI <sub>2</sub>	2181	87
ZnBr <sub>2</sub>	923	107	ZnI <sub>2</sub>	1003	96
ZrBr <sub>2</sub>	1555	85	ZrI <sub>2</sub>	1300	87
CuBr <sub>2</sub>	1173	100 <sup>a</sup>	EuI <sub>2</sub>	1850	88 <sup>a</sup>
EuBr <sub>2</sub>	2153	100 <sup>a</sup>	MnI <sub>2</sub>	1290	88 <sup>a</sup>
FeBr <sub>2</sub>	1207	100 <sup>a</sup>	SmI <sub>2</sub>	1856	88 <sup>a</sup>
SmBr <sub>2</sub>	2153	100 <sup>a</sup>	YbI <sub>2</sub>	1603	88 <sup>a</sup>
YbBr <sub>2</sub>	2103	100 <sup>a</sup>	MgI <sub>2</sub>	1255	88 <sup>a</sup>

<sup>a</sup>Estimated value  $\pm 10\%$ .

**Table 5.** Entropy of vaporization  $\Delta S_v^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) for triatomic compounds (fluorides and chlorides) at the normal boiling point  $T$ .

Fluorides			Chlorides		
	$T/\text{K}$	$\Delta S_v^\circ$		$T/\text{K}$	$\Delta S_v^\circ$
BaF <sub>2</sub>	2410	118	BaCl <sub>2</sub>	2302	107
BeF <sub>2</sub>	1448	138	BeCl <sub>2</sub>	805	130
CdF <sub>2</sub>	2033	107	CdCl <sub>2</sub>	1234	101
CaF <sub>2</sub>	2783	111	CaCl <sub>2</sub>	1873	126
CoF <sub>2</sub>	2012	110	CrCl <sub>2</sub>	1573	126
CuF <sub>2</sub>	1722	107	FeCl <sub>2</sub>	1297	85
PbF <sub>2</sub>	1573	100	PbCl <sub>2</sub>	1226	103
MgF <sub>2</sub>	2499	106	MgCl <sub>2</sub>	1710	91
HgF <sub>2</sub>	920	100	MnCl <sub>2</sub>	1504	99
SrF <sub>2</sub>	2759	116	HgCl <sub>2</sub>	577	102
ZnF <sub>2</sub>	1773	104	SrCl <sub>2</sub>	2331	106
ZrF <sub>2</sub>	2529	114	SnCl <sub>2</sub>	925	88
EuF <sub>2</sub>	2700	111 <sup>a</sup>	ZnCl <sub>2</sub>	1005	119
MnF <sub>2</sub>	2093	111 <sup>a</sup>	ZrCl <sub>2</sub>	1565	121
NiF <sub>2</sub>	2013	111 <sup>a</sup>	EuCl <sub>2</sub>	2300	103 <sup>a</sup>
SmF <sub>2</sub>	2700	111 <sup>a</sup>	InCl <sub>2</sub>	833	103 <sup>a</sup>
YbF <sub>2</sub>	2653	111 <sup>a</sup>	SmCl <sub>2</sub>	2303	103 <sup>a</sup>
			TeCl <sub>2</sub>	601	103 <sup>a</sup>
			YbCl <sub>2</sub>	2203	103 <sup>a</sup>

<sup>a</sup>Estimated value  $\pm 10\%$ .

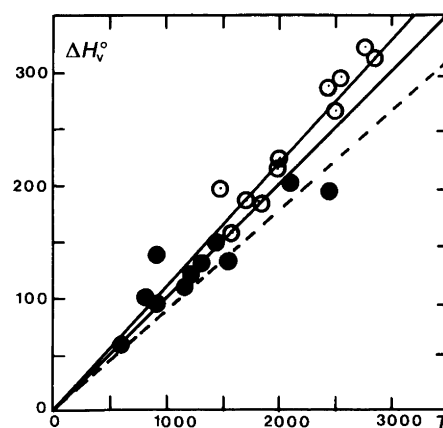
duced by the smooth curve corresponding to  $\Delta S_v^\circ = 11.7R \exp(-25/T)$ . The average deviation between calculated and observed values is 3%. For most compounds having boiling points between 1000 and 2000 K the  $\Delta S_v^\circ$  values are in the range from 10R to 11.6R, while our formula predicts values close to 11.4R and less than 11.7R. The compounds CsCl, LiI, AgBr and AgI show significant deviations from the general trend. The following  $\Delta H_v^\circ$

values were predicted: 15.6 (ClF), 17.8 (DBr), 16.0 (DCI), 20.9 (DI) and 33.8 (ICI) in  $\text{kJ mol}^{-1}$ , with an expected uncertainty of about  $\pm 3\%$ .

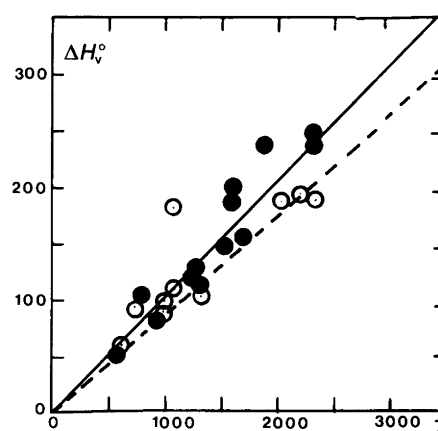
### Triatomic compounds

Data for the  $\text{XY}_2$  compounds are shown in Tables 4 and 5. The general trends are shown in Figs. 7 and 8. It seems a reasonable approximation, for these compounds, to assume that  $\Delta S_v^\circ$  is a constant. Average values are 13.4R (fluorides), 12.4R (chlorides), 12.0R (bromides) and 10.6R (iodides).

The complete set of  $\Delta S_v^\circ$  values for the Group IIB  $\text{XY}_2$  halides is shown in Table 6. These values show a variation of about 25%. The following trends are observed among the  $\Delta S_v^\circ$  values: fluorides  $\approx$  chlorides  $>$  bromides  $>$  iodides, and  $\text{ZnY}_2 \approx \text{CdY}_2 > \text{HgY}_2$ .



**Fig. 7.** Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for  $\text{XF}_2$  compounds ( $\circ$ ) and  $\text{XBr}_2$  compounds ( $\bullet$ ) at the normal boiling point  $T$  (K). The straight lines have the formulas  $\Delta H_v^\circ = 111T$  (fluorides) and  $\Delta H_v^\circ = 103T$  (bromides), while the broken line corresponds to Trouton's rule.



**Fig. 8.** Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for  $\text{XCl}_2$  compounds ( $\circ$ ) and  $\text{XI}_2$  compounds ( $\bullet$ ) at the normal boiling point  $T$  (K). The straight lines have the formulas  $\Delta H_v^\circ = 100T$  (chlorides) and  $\Delta H_v^\circ = 88T$  (iodides).

Table 6.  $\Delta S_v^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) values of the Group IIB halides  $\text{XY}_2$  at the normal boiling point.

	F	Cl	Br	I	Average <sup>a</sup>
Zn	104	119	107	96	107
Cd	107	101	100	100	102
Hg	100	102	96	95	98
Average <sup>b</sup>	104	107	101	97	$\langle 102 \rangle^c$

<sup>a</sup>Horizontally. <sup>b</sup>Vertically. <sup>c</sup>Average of all values.

Table 7.  $\Delta S_v^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) values of the Group IIA halides  $\text{XY}_2$  at the normal boiling point.

	F	Cl	Br	I	Average <sup>a</sup>
Be	138	130	126	128	131
Mg	106	91	104	$(96 \pm 8)^d$	100
Ca	111	126	96	88	105
Sr	116	106	80	79	95
Ba	118	107	<sup>c</sup>	79	101
Average <sup>b</sup>	113	108	93	82	$\langle 100 \rangle^e$

<sup>a</sup>Including all values horizontally. <sup>b</sup>Not including  $\text{BeY}_2$  values.  
<sup>c</sup>Decomposes. <sup>d</sup>Estimated from  $\text{MgBr}_2$ ,  $\text{CaBr}_2$  and  $\text{CaI}$  values.  
<sup>e</sup>Average of all values.

Except for the two compounds  $\text{MgI}_2$  and  $\text{BaBr}_2$ , a complete set of  $\Delta S_v^\circ$  values is also available for the Group IIA halides, as shown in Table 7. Clearly, all  $\text{BeY}_2$  compounds have exceptionally large  $\Delta S_v^\circ$  values. The following trends are observed: fluorides > chlorides > bromides > iodides. However, there are exceptions to these rules. Thus, the values of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  are unusual compared with the remaining values.

For  $\text{MgI}_2$  only the boiling point was available. However, the  $\Delta S_v^\circ$  values  $10.6R$  (Table 4) and  $11.6R$  (Table 7) were

estimated here. The predicted  $\Delta H_v^\circ$  value is therefore equal to  $116 \pm 10 \text{ kJ mol}^{-1}$  for  $\text{MgI}_2$  at the normal boiling point (1255 K).

Finally, one may consider the question whether linear or bent triatomic molecules have significantly different  $\Delta S_v^\circ$  values? The average values are  $(11.8 \pm 2.4)R$  and  $(11.7 \pm 1.8)R$  for linear and bent compounds, respectively (not including the  $\text{BeY}_2$  values). Thus, the difference is insignificant.

### Tetra-atomic compounds

Data for  $\text{XY}_3$  compounds are shown in Table 8 and Figs. 9 and 10. It is seen from Fig. 9 that Trouton's rule is a reasonable approximation for most compounds. However, the  $\Delta S_v^\circ$  values show (Fig. 10) that  $\text{XY}_3$  molecules should be treated as three different families. The best parameter values are  $A = 14.8R$  and  $\Theta = 59 \text{ K}$  for fluorides,  $A = 11.8R$  and  $\Theta = 43 \text{ K}$  for planar molecules and

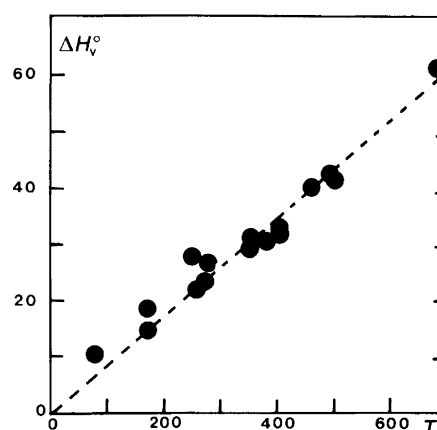


Fig. 9. Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for  $\text{XY}_3$  compounds at the normal boiling point  $T$  (K). The broken line corresponds to Trouton's rule.

Table 8. Entropy of vaporization  $\Delta S_v^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) for tetra-atomic compounds at the normal boiling point  $T$ .

Non-planar molecules		Planar molecules		Fluorides				
$T/\text{K}$	$\Delta S_v^\circ$	$T/\text{K}$	$\Delta S_v^\circ$	$T/\text{K}$	$\Delta S_v^\circ$			
$\text{SbBr}_3$	562	125	$\text{BBr}_3$	365	84	$\text{BF}_3$	172	112
$\text{SbCl}_3$	493	88	$\text{BCl}_3$	285	84	$\text{BrF}_3$	399	107
$\text{SbI}_3$	673	91	$\text{BI}_3$	488	87	$\text{ClF}_3$	285	96
$\text{AsBr}_3$	494	85	$\text{AlI}_3$	658	$92^a$	$\text{NF}_3$	144	81
$\text{AsCl}_3$	403	79	$\text{GaBr}_3$	553	$91^a$	$\text{PF}_3$	172	89
$\text{BiBr}_3$	733	103	$\text{GaCl}_3$	474	$90^a$	$\text{SbF}_3$	649	$112^a$
$\text{BiCl}_3$	720	101	$\text{GaI}_3$	619	$92^a$	$\text{AsF}_3$	324	$102^a$
$\text{PBr}_3$	446	89				$\text{PBrF}_2$	257	89
$\text{PCl}_3$	348	88				$\text{PBr}_2\text{F}$	325	87
$\text{AsI}_3$	676	$99^a$				$\text{PClF}_2$	256	110
$\text{AuCl}_3$	502	$90^a$						
$\text{NCl}_3$	344	$76^a$						

<sup>a</sup>Estimated value  $\pm 5\%$ .

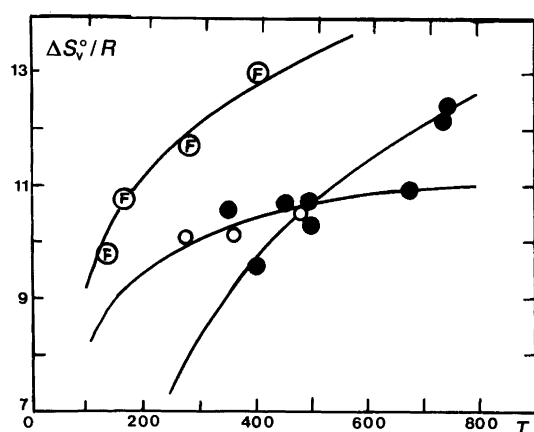


Fig. 10. Entropies of vaporization  $\Delta S_v^\circ$  at the normal boiling point  $T$  (K). The upper curve for fluorides (F) has the formula  $\Delta S_v^\circ/R = 14.8\exp(-59/T)$ . The two lower curves have the formulas  $\Delta S_v^\circ/R = 11.8\exp(-43/T)$  for planar molecules (○), and  $\Delta S_v^\circ/R = 15.7\exp(-189/T)$  for non-planar (●) molecules.

$A = 15.7R$  and  $\Theta = 189$  K for nonplanar molecules. For nine compounds, only the boiling points were recorded. The parameter values above were used when estimating  $\Delta S_v^\circ$  values for these compounds, with an uncertainty of about  $\pm 5\%$ .

Clearly the fluorides have  $\Delta S_v^\circ$  values that are about 20% higher than those of the remaining compounds. However, both  $\text{BF}_3$  and  $\text{SbBr}_3$  are exceptions from the general trends.

Boiling points as well as  $\Delta S_v^\circ$  values are known for three unsymmetrical fluorides. Thus  $\text{PBrF}_2$  has a  $\Delta S_v^\circ$  value close to the expected value for an  $\text{XF}_3$  compound with  $T = 257$  K. Although  $\text{PBr}_2\text{F}$  has a much higher boiling point than  $\text{PBrF}_2$ , the  $\Delta S_v^\circ$  value is lower, and approximately equal to the  $\Delta S_v^\circ$  value of  $\text{PCl}_3$ . The  $\Delta S_v^\circ$  value for  $\text{PClF}_2$  is exceptionally high, even for a fluoride.

We predict the following  $\Delta H_v^\circ$  values ( $\text{kJ mol}^{-1}$ ): 67 ( $\text{AsI}_3$ ), 45 ( $\text{AuCl}_3$ ), 26 ( $\text{NCl}_3$ ), 61 ( $\text{AlI}_3$ ), 50 ( $\text{GaBr}_3$ ), 43 ( $\text{GaCl}_3$ ), 57 ( $\text{GaI}_3$ ), 73 ( $\text{SbF}_3$ ) and 33 ( $\text{AsF}_3$ ), with an expected uncertainty of about  $\pm 5\%$ .

### Penta-atomic compounds

Data for halides as well as hydrides are shown in Table 9 and Figs. 11 and 12. The best parameter values are  $A = 12.7R$  and  $\Theta = 72$  K for symmetrical halides and  $A = 11.4R$  and  $\Theta = 27$  K for hydrides.

As seen from Fig. 12, the two curves tend to overlap in the region between 300 and 400 K. However, the hydrides with boiling points between 100 and 300 K are significantly better represented by the first set of parameters. Unfortunately,  $\text{HCF}_3$  is the only penta-atomic fluoride with an observed  $\Delta S_v^\circ$  value. It is our experience that fluorides have relatively high  $\Delta S_v^\circ$  values compared with other halides in the same family. Thus, the fluorides in Fig. 10 have values about 20% higher than the remaining compounds at the same temperature. It was also found that for triatomic compounds the fluorides had  $\Delta S_v^\circ$  values about 10–25% higher than the other halides at comparable temperatures. From Fig. 12 it is seen that  $\text{HCF}_3$  at  $T = 191$  K has a value above the curves for both hydrides and halides. Thus, the  $\Delta H_v^\circ$  values for the fluorides in Table 10 were predicted using the formula  $\Delta H_v^\circ = 104T\exp(-27/T)$ .

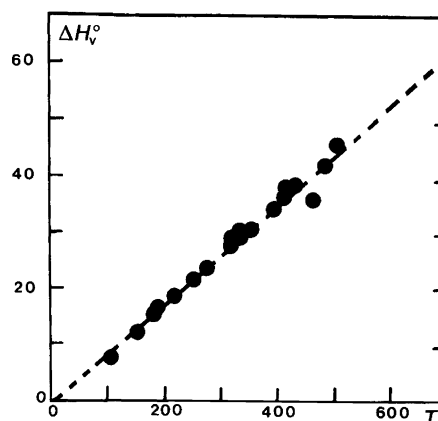


Fig. 11. Heats of vaporization  $\Delta H_v^\circ$  ( $\text{kJ mol}^{-1}$ ) for penta-atomic compounds at the normal boiling point  $T$  (K). The broken curve corresponds to Trouton's rule.

Table 9. Entropy of vaporization  $\Delta S_v^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) for penta-atomic compounds at the normal boiling point  $T$ .

$T/K$	$\Delta S_v^\circ$	Asymmetric molecules		Hydrides				
		$T/K$	$\Delta S_v^\circ$	$T/K$	$\Delta S_v^\circ$			
$\text{CCl}_4$	350	86	$\text{H}_3\text{CBr}$	277	86	$\text{CH}_4$	112	73
$\text{SiCl}_4$	331	87	$\text{H}_3\text{CCl}$	249	87	$\text{SiH}_4$	161	77
$\text{SiBr}_4$	427	89	$\text{H}_3\text{Cl}$	316	86	$\text{GeH}_4$	185	82
$\text{GeCl}_4$	356	83	$\text{H}_2\text{CCl}_2$	314	90	$\text{SnH}_4$	221	84
$\text{GeBr}_4$	460	78	$\text{HCCl}_3$	334	89			
$\text{SnCl}_4$	388	88	$\text{HCF}_3$	191	87			
$\text{SnBr}_4$	480	85	$\text{HSiCl}_3$	307	87			
$\text{VCl}_4$	425	90						
$\text{TiBr}_4$	504	90						
$\text{TiCl}_4$	410	88						
$\text{TeCl}_4$	661	106						

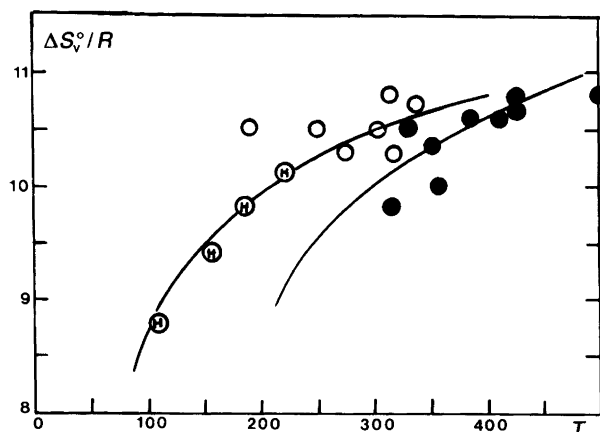


Fig. 12. Entropies of vaporization  $\Delta S_v^0$  for penta-atomic compounds at the normal boiling point  $T$  (K). The upper curve has the formula  $\Delta S_v^0/R = 11.4 \exp(-27/T)$ , while the lower curve has the formula  $\Delta S_v^0/R = 12.7 \exp(-72/T)$ . The points correspond to  $XH_4$  compounds (H),  $XY_4$  compounds (○), and asymmetrical molecules (●) containing both hydrogen and halogen.

For the compounds in Table 10 only boiling points were recorded. The predicted values were estimated using the parameters established for halides and hydrides, as explained above.

### Conclusions

It has been demonstrated that the entropy of vaporization, at the normal boiling point, may be estimated from a simple formula involving two empirical constants and the value of the boiling point itself. The parameters ( $A$  and  $\Theta$ ) have characteristic values for a family of structurally related compounds. It has also been shown that the entropies of vaporization of the monoatomic elements follow the same empirical formula, with different parameter values. Boiling points of the actinides beyond the element Am have not

been recorded. However, a correlation between boiling points and heats of vaporization has been suggested here.

Using available data for 99 inorganic compounds, the missing entropies and heats of vaporization for an additional 56 compounds have been predicted at the normal boiling point. Expected uncertainties in the estimated values are typically 5–10%, but there exist large deviations from the expected normal value within a family of compounds. For the compounds considered here hydrogen bonds do not exist between the molecules. However, consider the three vaporization processes (1)–(3) consuming one mole of liquid.



For the vaporization/dissociation process it is expected that  $\Delta S_2^0 \approx \Delta S_1^0 + \Delta S^0$  (diss.), while for the vaporization/association process it is likely that  $\Delta S_3^0 \approx \Delta S_1^0 - \frac{1}{x} \Delta S^0$  (diss.). Thus, the entropy of vaporization may become greater than the normal value  $\Delta S_1^0$  if the liquid-phase molecules show a greater tendency for association than the gas-phase molecules. On the other hand, if the gas-phase molecules have a greater tendency for association the entropy of vaporization may become smaller than the normal value. Possibly such effects lead to the exceptionally large  $\Delta S_v^0$  values observed for  $BeY_2$  compounds. For  $BeCl_2$  the experimental value is  $15.6R$ , which is about 30% greater than the expected value for an  $XY_2$  chloride (Table 5).  $BeCl_2$  has an unusual chain structure that is also likely to exist partly in the liquid.<sup>3</sup> In the gas phase  $BeCl_2$  tends to form a bridged  $sp^2$  dimer, and dissociation to the linear monomer is not complete below about 900 K. Thus, a greater tendency to associate exists in the liquid phase for  $BeCl_2$ . Also  $BeF_2$ ,  $BeBr_2$  and  $BeI_2$  have very large  $\Delta S_v^0$  values, and probably

Table 10. Heats of vaporization  $\Delta H_v^0$  ( $\text{kJ mol}^{-1}$ ) for penta-atomic compounds at the normal boiling point  $T$ .

	$T/K$	$\Delta H_v^0$	Hydrides		Fluorides			
			$T/K$	$\Delta H_v^0$	$T/K$	$\Delta H_v^0$		
$CBr_4$	463	42	$H_2CBrCl$	342	30	$H_2CF_2$	222	20
$SiI_4$	561	52	$H_2CBrI$	413	38	$HCF_2I$	295	28
$GeI_4$	621	59	$H_2CClI$	382	34	$HCFI_2$	374	36
$SnI_4$	638	60	$H_2CBr_2$	338	30	$H_2CFI$	327	31
$TiI_4$	653	62	$H_3SiCl$	243	21	$HCFBr_2$	338	33
$SiBrCl_3$	354	31	$H_2SiCl_2$	282	24	$H_2CBrF$	292	28
$SiBr_2Cl_2$	377	33	$H_3SiBr$	275	24	$H_2CClF$	264	25
$SiBr_3Cl$	400	35	$H_2SiBr_2$	339	30			
$SiCl_3I$	387	34	$HSiBr_3$	382	34			
$CBrCl_3$	377	33	$H_3SiI$	319	28			
$CBr_3Cl$	432	39	$HSiI_3$	493	44			
$CBr_2Cl_2$	408	36	$HCCl_2I$	405	36			
$CCl_3I$	415	37	$HCBBr_3$	423	39			

these compounds have a greater tendency to associate in the liquid phase than in the vapour. It is known<sup>3</sup> that BeF<sub>2</sub> is monomeric in the vapour.

The largest deviation from the expected  $\Delta S_v^\circ$  value was detected for SnBr<sub>2</sub>. Here the experimental value is 18.3R, while only 12R is expected for a typical XBr<sub>2</sub> compound. It is known that the crystal structure of SnF<sub>2</sub> is composed of Sn<sub>2</sub>F<sub>4</sub> tetramers.<sup>4</sup> Unfortunately, the  $\Delta S_v^\circ$  value of SnF<sub>2</sub> is not known. The observed  $\Delta S_v^\circ$  value of SnCl<sub>2</sub> is 17% greater than the expected value, while for SnI<sub>2</sub> the observed  $\Delta S_v^\circ$  value is 15% lower than expected for XY<sub>2</sub> compounds (Tables 4 and 5).

Considering large positive deviations from the normal  $\Delta S_v^\circ$  values, the following compounds are probably more associated (dimers?) in the liquid phase than in the vapour: AgBr, SnBr<sub>2</sub>, BeY<sub>2</sub> (Y = F, Cl, Br, I), CdI<sub>2</sub>, PbI<sub>2</sub>, SnI<sub>2</sub>, CaCl<sub>2</sub>, CrCl<sub>2</sub>, ZnCl<sub>2</sub>, ZrCl<sub>2</sub>, PClF<sub>2</sub>, BF<sub>3</sub> and SbBr<sub>3</sub>.

Considering large negative deviations from the normal  $\Delta S_v^\circ$  values, the following compounds are probably more associated (dimers?) in the vapour than in the liquid phase: CsCl, LiI, AgI, ZrBr<sub>2</sub>, MnBr<sub>2</sub>, SrBr<sub>2</sub>, BaI<sub>2</sub>, FeI<sub>2</sub>, FeCl<sub>2</sub>, PbF<sub>2</sub>, MgCl<sub>2</sub> and SnCl<sub>2</sub>. It is known that CsCl, MnBr<sub>2</sub> and FeCl<sub>2</sub> exist partly as dimers in the vapour.

Several other methods have been suggested for estimating the entropy of vaporization<sup>5-7</sup> at the normal boiling point. However, in addition to the value of the boiling point, both the critical pressure and the critical temperature must be known for each compound.

If the critical parameters are not known, the entropy-of-vaporization rule of Kistiakowsky,<sup>8</sup>  $\Delta S_v^\circ/R = 4.40 + \ln(T/K)$ , may be used. Fistine<sup>9</sup> improved the accuracy of this equation by employing a multiplicative correction factor that is a function of the compound's class. The various methods have been presented by Reid *et al.*<sup>10</sup>

Our method offers an independent estimate of the entropy of vaporization not suggested earlier.

## References

1. Stølevik, R. *Acta Chem. Scand.* 43 (1989) 758.
2. J. A. Dean, Ed., *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York 1985, pp. 9-107.
3. Greenwood, N. N. and Earnshaw, A. *Chemistry of the Elements*, Pergamon Press, Oxford 1984, p. 128.
4. McDonald, R. C., Ho-Kuen Hau, H. and Eriks, K. *Inorg. Chem.* 15 (1976) 762.
5. Giacalone, A. *Gazz. Chim. Ital.* 81 (1951) 180.
6. Riedel, L. *Chem. Ing. Tech.* 26 (1954) 679.
7. Chen, N. H. *J. Chem. Eng. Data* 10 (1965) 207.
8. Kistiakowsky, W. Z. *Phys. Chem.* 107 (1923) 65.
9. Bondi, A. *J. Chem. Eng. Data* 8 (1963) 371.
10. Reid, R. C., Prausnitz, J. M. and Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd. ed., McGraw-Hill, New York 1977, pp. 181-222.

Received March 13, 1989.