16.9: Some Trends In Entropy Values

A close inspection of the entropy values in the Table of Molar Entropies reveals several trends which can be explained in terms of the factors of molecular mass and restriction of movement.

Table 16.9.1 Molar *Entropy Values*

Compound	S_m^o **/J K^{-1}mol^{-1}**	**Compound**	S_m^o **/J K^{-1}mol^{-1}**
Solids		**Diatomic Gases**	
C (diamond)	2.377		
C (graphite)	5.74	H_2	130.7
Si	18.8	D_2	145.0
Ge	31.1	HCl	186.9
Sn (gray)	44.1	HBr	198.7
Pb	64.8	HI	206.6
Li	29.1	N_2	191.6
Na	51.2	O_2	205.1
K	64.2	F_2	202.8
Rb	69.5	Cl_2	223.1
Cs	85.2	Br_2	245.5
NaF	51.5	I_2	260.7
MgO	26.9	CO	197.7
AlN	20.2	**Triatomic Gases**	
NaCl	72.1	H_2O	188.8
KCl	82.6	NO_2	240.1
Mg	32.7	H_2S	205.8
Ag	42.6	CO_2	213.7
I_2	116.1	SO_2	248.2
MgH_2	31.1	N_2O	219.9
AgN_3	99.2	O_3	238.9
Liquids		**Polyatomic Gases(> 3)**	
Hg	76.0	CH_4	186.3
Br_2	152.2	C_2H_6	229.6
H_2O	69.9	C_3H_8	269.9
H_2O_2	109.6	C_4H_{10}	310.2
CH_3OH	126.8	C_5H_{12}	348.9
C_2H_5OH	160.7	C_2H_4	219.6
C_6H_6	172.8	N_2O_4	304.3
BCl_3	206.3	B_2H_6	232.0

Monatomic Gases		BF_3	254.0
He	126.0	NH_3	192.5
Ne	146.2		
Ar	154.8		
Kr	164.0		
Xe	169.6		

Solids, Liquids, and Gases Perhaps the most obvious feature of the table of molecular entropies is a general increase in the molar entropy as we move from solids to liquids to gases. In a solid, the molecules are only capable of restricted vibrations around a fixed point, but when a solid melts, the molecules, though still hampered by their mutual attraction, are much freer to move around. Thus when a solid melts, the molar entropy of the substance increases. When a liquid vaporizes, the restrictions on the molecules' ability to move around are relaxed almost completely and a further and larger increase in the entropy occurs. When 1 mol of ice melts, for example, its entropy increases by 22 J K^{-1}, while on boiling the entropy increase is 110 J K^{-1}.

Molecular Complexity A second clear trend in the table is the higher molar entropy of substances with more complex molecules. To some extent this is due to the mass since on the whole more complex molecules are heavier than simpler ones. However, we still find an increase of entropy with complexity when we compare molecules of very similar masses:

Substance	**Ar(*g*)**	**$F_2(g)$**	**$CO_2(g)$**	**$C_3H_8(g)$**
$S_m°$/J K^{-1} mol^{-1}	155	202.7	213.6	269.9
Molar mass/g mol^{-1}	40	38	44	44
Number of atoms	1	2	3	11

The more atoms there are in a molecule, the more ways the molecule can change its shape by vibrating. In consequence there are more ways in which the energy can be distributed among the molecules.

Strength of Bonding Another trend in entropy, most noticeable in the case of solids, is the decrease in the entropy as the forces between the atoms, molecules, or ions increases. A good example is the three solid compounds

Substance	**NaF(*s*)**	**MgO(*s*)**	**AlN(*s*)**
$S_m°$(298 K)/J K^{-1} mol^{-1}	51.5	26.8	20.2
Molar mass/g mol^{-1}	42.0	40.3	41.0

which are isoelectronic with sodium fluoride. Since there is very little difference in the molar masses, the entropy decrease can only be attributed to the increase in the coulombic attraction between the ions as we move from the singly charged ions Na^+ and $F^–$ through the doubly charged ions Mg^{2+} and $O^{2–}$, to the triply charged ions $A1^{3+}$ and $N^{3–}$. (While it is true that there is a fair degree of covalent character to the bonding in AIN, the effect of this will be to increase the strength of the bonding.)

Example 16.9.1: Molar Entropy

From each of the following pairs of compounds choose the one with the higher standard molar entropy at 25°C. Give brief reasons for your choice.

a) HBr(*g*), HCl(*g*) **c)** $ND_3(g)$, Ne(*g*) **e)** $C_2H_6(g)$, $C_2H_4(g)$ **b)** Cs(*s*), Cs(*l*) **d)** KCl(*s*), CaS(*s*)

Solution

a) HBr and HCl are very similar except for their mass. HBr will have a higher entropy because of its greater mass. **b)** At the same temperature, the liquid form of a substance always has a higher entropy than the solid. **c)** ND_3 (D = deuterium) and Ne have almost identical molar masses (20 g mol^{-1}) However, since ND_3 is more complex, it can vibrate and rotate while Ne cannot. ND_3 will have the higher entropy. **d)** KCl and CaS are isoelectronic. Because both anion and cation are doubly charged in CaS, the ions are more tightly held to each other and can vibrate less readily. Thus KCl must have the higher entropy. **e)** On all counts C_2H_6 must have a higher entropy than C_2H_4. C_2H_6 is heavier and more complex than C_2H_4. In addition there is free rotation about the C—C bond in C_2H_6 but hindered rotation about the C=C bond in C_2H_4.