16.10: Entropy Changes in Gaseous Reactions

Knowing what factors affect the magnitude of the entropy often enables us to predict whether the entropy of the products will be greater or less than that of the reactants in a given chemical reaction. This is particularly true for gaseous reactions. In a dissociation reaction like

$$\mathrm{N_2O_4(g) \rightarrow NO_2 + NO_2} \qquad \Delta S_m^\circ(298\mathrm{K}) = +176\mathrm{JK^{-1}mol^{-1}}$$

for instance, it is easy to see that ΔS should be positive. The two halves of the N_2O_4 molecule are forced to move around together before dissociation, but they can move around independently as NO_2 molecules once dissociation has occurred. A similar argument applies to reactions like

$$\mathrm{2\,O_3 \rightarrow 3\,O_2} \qquad \Delta S^\circ{}_m(298\mathrm{K}) = +137\mathrm{JK^{-1}mol^{-1}}$$

In the form of O_3, O atoms are constrained to move around in groups of three, but in the form of O_2, only two atoms need move around together, a lesser restriction. Accordingly we expect ΔS to be positive for this reaction.

A further extension of this argument leads us to the general conclusion that in any reaction involving gases if the amount of substance in the gaseous phase increases, ΔS will be positive, while if it decreases, so will ΔS. For example, in the reaction

$$\mathrm{2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)}$$

The amount of gas decreases from 3 to 2 mol (i.e., Δn = –1 mol). The entropy change should thus be negative for this reaction. From the Table of Standard Molar Entropies we can readily find that $\Delta S_m°$(298 K) has the value –173 J K^{-1} mol^{-1}.

Table of Standard Molar Entropies

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		

This table shows molar entropies for the standard conditions of 298.15 K (25°C) and 101.3 kPa. Such conditions need to be specificed, since entropy is propotional to substance amount, and dependent on temperature, pressure. Entropy is also dependent upon volume, but since the amount, *n*, temperature, and pressure are given, volume is implicitly defined. This table is taken from CoreChem:Standard Molar Entropies, and is also used on CoreChem:Dependence of S on Molecular Structure as well as CoreChem:Some Trends In Entropy Values.
