16.8: Dependence of S on Molecular Structure

Since they all refer to the same temperature and pressure, and also to 1 mol of substance, any differences in the entropy values listed in the table of standard entropies must be due to *differences in the molecular structure* of the various substances listed. There are two aspects of the molecular structure of a substance which affect the value of its entropy: (1) The degree to which the movement of the atoms and molecules in the structure is restricted—the less restricted this movement, the greater the entropy. (2) The mass of the atoms and molecules which are moving—the greater the mass, the larger the entropy. We will consider each of these factors in turn.

Table 16.8.1 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

BCl₃	206.3	B₂H₆	232.0
Monatomic Gases		BF₃	254.0
He	126.0	NH₃	192.5
Ne	146.2		
Ar	154.8		
Kr	164.0		
Xe	169.6		

Restrictions on the Movement of Atoms and Molecules We have already encountered two examples of how the removal of a restriction on the motion of molecules allows an increase in the number of alternative ways in which the molecules can arrange themselves in space. The first of these is the case of the ring and chain forms of 1,4-butanediol discussed in the section on the molecular view of equilibrium, and displayed in figures 2 and 3 in that section. When the two ends of this molecule hydrogen bond to form a ring, the result is a fairly rigid structure. However, if the restricting influence of the hydrogen bond is removed, the more flexible chain form of the molecule is capable of many more alternative configurations. As a result, we find that W for a mole of molecules in the chain form is very much larger than W for a mole of molecules in the ring form. The chain form turns out to have a molar entropy which is 41 J K⁻¹ mol⁻¹ higher than that for the ring form.

A second example of the effect of relaxing a restriction on molecular motion is the expansion of a gas into a vacuum. When the molecules have more freedom of movement, many more alternative arrangements are possible, and hence W is larger. As we have already calculated, doubling the volume of a gas increases its molar entropy by 5.76 J K⁻¹ mol⁻¹.

Mass of the Atoms and Molecules We showed that when quantum mechanics is applied, the energies of a moving particle are confined to certain specific values and not those in between. The allowed energies, or **energy levels**, for a particle in a box were given by equation 4 in the section on wave mechanics:

$$E_k = n^2 \frac{h^2}{8md^2}$$

From this equation we can see that the larger the mass m of a particle, the smaller the value of its energy E_k for a given value of the quantum number n. Furthermore, the larger the value of m, the smaller the *difference* between E_{k2} (for $n = 2$) and E_{k1} (for $n = 1$). No matter what kind of energy is involved—rotational, vibrational, or translational—this is always found to be true. *The greater the mass of a particle, the closer together its energy levels.*

The effect of closeness of energy levels on the entropy is shown in Figure 16.8.1. The more closely spaced the levels, the more different ways the same quantity of energy can be distributed among them. This applies in general for any number of particles and any quantity of energy. Therefore, *the heavier the molecules of a substance, the larger its molar entropy*. This effect is quite obvious among the noble gases—their molar entropies increase steadily with molar (and hence molecular) mass.
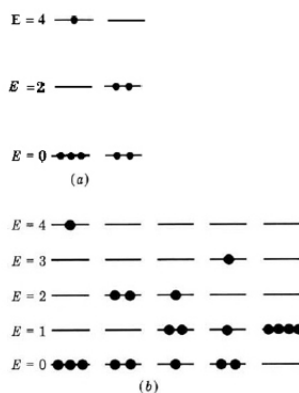

Figure 16.8.1 Effect of molecular mass on entropy. (a) The energy levels available to light molecules are widely spaced. If the spacing is two units, and if four units of energy are supplied to four molecules, only two arrangements are possible: either one molecule has all the energy, or two molecules have two units each. (b) For heavier molecules the energy levels are closer together. If the spacing is one unit, and four units of energy are supplied, three more ways of distributing the energy are possible. Therefore the entropy is greater.

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