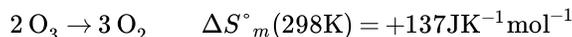


## 16.10: Entropy Changes in Gaseous Reactions

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

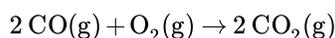


for instance, it is easy to see that  $\Delta S$  should be positive. The two halves of the  $\text{N}_2\text{O}_4$  molecule are forced to move around together before dissociation, but they can move around independently as  $\text{NO}_2$  molecules once dissociation has occurred. A similar argument applies to reactions like



In the form of  $\text{O}_3$ , O atoms are constrained to move around in groups of three, but in the form of  $\text{O}_2$ , only two atoms need move around together, a lesser restriction. Accordingly we expect  $\Delta S$  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,  $\Delta S$  will be positive, while if it decreases, so will  $\Delta S$ . For example, in the reaction



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

### Table of Standard Molar Entropies

| Compound      | $S_m^\circ / \text{J K}^{-1}\text{mol}^{-1}$ | Compound               | $S_m^\circ / \text{J K}^{-1}\text{mol}^{-1}$ |
|---------------|--|------------------------|--|
| <b>Solids</b> |  | <b>Diatomic Gases</b>  |  |
| C (diamond)   | 2.377  |                        |  |
| C (graphite)  | 5.74   | $\text{H}_2$           | 130.7  |
| Si            | 18.8   | $\text{D}_2$           | 145.0  |
| Ge            | 31.1   | HCl                    | 186.9  |
| Sn (gray)     | 44.1   | HBr                    | 198.7  |
| Pb            | 64.8   | HI                     | 206.6  |
| Li            | 29.1   | $\text{N}_2$           | 191.6  |
| Na            | 51.2   | $\text{O}_2$           | 205.1  |
| K             | 64.2   | $\text{F}_2$           | 202.8  |
| Rb            | 69.5   | $\text{Cl}_2$          | 223.1  |
| Cs            | 85.2   | $\text{Br}_2$          | 245.5  |
| NaF           | 51.5   | $\text{I}_2$           | 260.7  |
| MgO           | 26.9   | CO                     | 197.7  |
| AlN           | 20.2   | <b>Triatomic Gases</b> |  |
| NaCl          | 72.1   | $\text{H}_2\text{O}$   | 188.8  |
| KCl           | 82.6   | $\text{NO}_2$          | 240.1  |
| Mg            | 32.7   | $\text{H}_2\text{S}$   | 205.8  |

|                                  |       |                                  |       |
|----------------------------------|-------|----------------------------------|-------|
| Ag                               | 42.6  | CO <sub>2</sub>                  | 213.7 |
| I <sub>2</sub>                   | 116.1 | SO <sub>2</sub>                  | 248.2 |
| MgH <sub>2</sub>                 | 31.1  | N <sub>2</sub> O                 | 219.9 |
| AgN <sub>3</sub>                 | 99.2  | O <sub>3</sub>                   | 238.9 |
| <b>Liquids</b>                   |       | <b>Polyatomic Gases( &gt; 3)</b> |       |
| Hg                               | 76.0  | CH <sub>4</sub>                  | 186.3 |
| Br <sub>2</sub>                  | 152.2 | C <sub>2</sub> H <sub>6</sub>    | 229.6 |
| H <sub>2</sub> O                 | 69.9  | C <sub>3</sub> H <sub>8</sub>    | 269.9 |
| H <sub>2</sub> O <sub>2</sub>    | 109.6 | C <sub>4</sub> H <sub>10</sub>   | 310.2 |
| CH <sub>3</sub> OH               | 126.8 | C <sub>5</sub> H <sub>12</sub>   | 348.9 |
| C <sub>2</sub> H <sub>5</sub> OH | 160.7 | C <sub>2</sub> H <sub>4</sub>    | 219.6 |
| C <sub>6</sub> H <sub>6</sub>    | 172.8 | N <sub>2</sub> O <sub>4</sub>    | 304.3 |
| BCl <sub>3</sub>                 | 206.3 | B <sub>2</sub> H <sub>6</sub>    | 232.0 |
| <b>Monatomic Gases</b>           |       | BF <sub>3</sub>                  | 254.0 |
| He                               | 126.0 | NH <sub>3</sub>                  | 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 specified, since entropy is proportional 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.

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