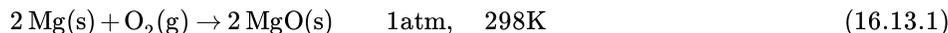


16.13: Including the Surroundings

In order to determine whether a reaction is spontaneous or not, it is not sufficient just to determine ΔS_m , the entropy difference between products and reactants. As an example, let us take the reaction



Since this reaction occurs at the standard pressure and at 298 K, we can find ΔS from the [standard molar entropies](#):

$$\Delta S = \Delta S_m^\circ(298\text{K}) = 2S_m^\circ(\text{MgO}) - S_m^\circ(\text{O}_2) \quad (16.13.2)$$

$$= (2 \times 26.8 - 2 \times 32.6 - 205.0) \frac{\text{J}}{\text{mol K}} \quad (16.13.3)$$

$$= -216.6 \frac{\text{J}}{\text{mol K}} \quad (16.13.4)$$

This result would suggest that the reaction is not spontaneous, but in fact it is. Once ignited, a ribbon of magnesium metal burns freely in air to form solid magnesium oxide in the form of a white powder. The reaction is plainly spontaneous even though ΔS is negative. Why is this not a contradiction of the second law?

The answer is that we have failed to realize that the entropy change which the magnesium and oxygen atoms undergo as a result of the reaction is not the only entropy change which occurs. The oxidation of magnesium is a highly exothermic reaction, and the heat which is evolved flows into the surroundings, *increasing their entropy as well*. There are thus *two* entropy changes which we must take into account in deciding whether a reaction will be spontaneous or not: (1) the change in entropy of the *system* actually undergoing the chemical change, which we will indicate with the symbol ΔS_{sys} ; and (2) the change in entropy of the *surroundings*, ΔS_{surr} , which occurs as the surroundings absorb the heat energy liberated by an exothermic reaction or supply the heat energy absorbed by an endothermic reaction.

Of these two changes, the first is readily obtained from tables of entropy values. Thus, for the oxidation of magnesium, according to Eq. 16.13.1, ΔS_{sys} has the value already found, namely, $-216.6 \text{ J K}^{-1} \text{ mol}^{-1}$.

The second entropy change, ΔS_{surr} , can also be derived from tables, as we shall now show.

When a chemical reaction occurs at atmospheric pressure and its surroundings are maintained at a constant temperature T , then the surroundings will absorb a quantity of heat, q_{surr} equal to the heat energy given off by the reaction.

$$q_{\text{surr}} = -\Delta H \quad (16.13.5)$$

(The negative sign before ΔH is needed because q_{surr} is positive if the surroundings absorb heat energy, but ΔH is negative if the system gives off heat energy for them to absorb.) If we now feed Eq. 16.13.5 into Eq. (1) in the [section on measuring entropy](#), we obtain an expression for the entropy change of the surroundings in terms of ΔH :

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-\Delta H}{T} \quad (16.13.6)$$

Using this equation it is now possible to find the value of ΔS_{surr} from [table of standard enthalpies of formation](#). In the case of the oxidation of magnesium, for example, we easily find that the enthalpy change for



is given by

$$\Delta H = \Delta H_m^\circ(\text{MgO}) = 2 \times -601.8 \frac{\text{J}}{\text{mol K}} = -1204 \frac{\text{J}}{\text{mol K}}$$

Substituting this result into Eq. 16.13.6 we then find

$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{1204 \times 10^3 \text{ J mol}^{-1}}{298 \text{ K}} = 4040 \text{ J K}^{-1} \text{ mol}^{-1}$$

If a reaction is spontaneous, then it is the total entropy change ΔS_{tot} , given by the *sum* of ΔS_{surr} and ΔS_{sys} , which must be positive in order to conform to the second law. In the oxidation of magnesium, for example, we find that the total entropy change is given by

$$\Delta S_{\text{tot}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} = (4040 - 216.6) \frac{\text{J}}{\text{mol K}} = 3823 \frac{\text{J}}{\text{mol K}}$$

This is a positive quantity because the entropy increase in the surroundings is more than enough to offset the decrease in the system itself, and the second law is satisfied. In the general case the total entropy change is given by

$$\Delta S_{tot} = \Delta S_{surr} + \Delta S_{sys} = -\frac{\Delta H}{T} + \Delta S_{sys}$$

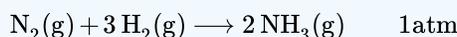
The second law requires that this sum must be positive; i.e.,

$$-\frac{\Delta H}{T} + \Delta S_{sys} > 0 \quad (16.13.7)$$

This simple inequality gives us what we have been looking for: a simple criterion for determining whether a reaction is spontaneous or not. Since both ΔH and ΔS can be obtained from tables, and T is presumably known, we are now able to predict in advance whether a reaction will be uphill or downhill.

✓ Example 16.13.1: Spontaneous Reaction

Using the [Table of Some Standard Enthalpies of Formation at 25°C](#) and the [Table of Standard Molar Entropies](#) find $\Delta H_m^\circ(298\text{ K})$ and $\Delta S_m^\circ(298\text{ K})$ for the reaction



Predict whether the reaction will be spontaneous or not at a temperature of (a) 298 K, and (b) 1000 K.

Solution

We find from the Table of Some Standard Enthalpies of Formation that

$$\Delta H_m^\circ(298\text{K}) = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \quad (16.13.8)$$

$$= 2\Delta H_f^\circ(\text{NH}_3) - \Delta H_f^\circ(\text{N}_2) - 3\Delta H_f^\circ(\text{H}_2) \quad (16.13.9)$$

$$= (-2 \times 46.1 - 0.0 - 0.0)\text{kJ mol}^{-1} = -92.2\text{kJ mol}^{-1} \quad (16.13.10)$$

and from the Table of Standard Molar Entropies:

$$\Delta S_m^\circ(298\text{K}) = \sum \Delta S_m^\circ(\text{products}) - \sum \Delta S_m^\circ(\text{reactants}) \quad (16.13.11)$$

$$= 2\Delta S_m^\circ(\text{NH}_3) - \Delta S_m^\circ(\text{N}_2) - 3\Delta S_m^\circ(\text{H}_2) \quad (16.13.12)$$

$$= (2 \times 192.2 - 191.5 - 3 \times 130.6)\text{ J K}^{-1}\text{ mol}^{-1} = -198.9\text{ J K}^{-1}\text{ mol}^{-1} \quad (16.13.13)$$

a) At 298 K the total entropy change per mol N_2 is given by

$$\Delta S_{tot} = \frac{-\Delta H_m^\circ}{T} + \Delta S_{sys}^\circ = \frac{92.2 \times 10^3\text{ J mol}^{-1}}{298\text{ K}} - 198.9\text{ J K}^{-1}\text{ mol}^{-1} \quad (16.13.14)$$

$$= (309.4 - 198.9)\text{ J K}^{-1}\text{ mol}^{-1} = 110.5\text{ J K}^{-1}\text{ mol}^{-1} \quad (16.13.15)$$

Since the total entropy change is positive, the reaction is spontaneous:

b) Since tables are available only for 298 K, we must make the approximate assumption that neither ΔH nor ΔS varies greatly with temperature. Accordingly we assume

$$\Delta H_m^\circ(1000\text{ K}) = \Delta H_m^\circ(298\text{ K}) = -92.2\text{kJ mol}^{-1} \quad (16.13.16)$$

$$\text{and } \Delta S_m^\circ(1000\text{ K}) = \Delta S_m^\circ(298\text{ K}) = -198.9\text{ J K}^{-1}\text{ mol}^{-1} \quad (16.13.17)$$

$$\Delta H_m^\circ(1000\text{ K}) = \Delta H_m^\circ(298\text{ K}) = -92.2\text{ kJ mol}^{-1}$$

$$\text{and } \Delta S_m^\circ(1000\text{ K}) = \Delta S_m^\circ(298\text{ K}) = -198.9\text{ J K}^{-1}\text{ mol}^{-1}$$

Thus for 1 mol N_2 reacted,

$$\Delta S_{tot} = \frac{-\Delta H_m^\circ}{T} + \Delta S_{sys}^\circ = \frac{92.2 \times 10^3\text{ J mol}^{-1}}{1000\text{ K}} - 198.9\text{ J K}^{-1}\text{ mol}^{-1} \quad (16.13.18)$$

$$= (92.2 - 198.9)\text{ J K}^{-1}\text{ mol}^{-1} = -106.7\text{ J K}^{-1}\text{ mol}^{-1} \quad (16.13.19)$$

Since the total entropy change is negative at this high temperature, we conclude that N_2 and H_2 will not react to form NH_3 , but that rather NH_3 will decompose into its elements.

Apart from enabling us to predict the direction of a chemical reaction from tables of thermodynamic data, the inequality [Eq. 16.13.7] shows that three factors determine whether a reaction is spontaneous or not: the enthalpy change ΔH , the entropy change ΔS , and the temperature T . Let us examine each of these to see what effect they have and why.

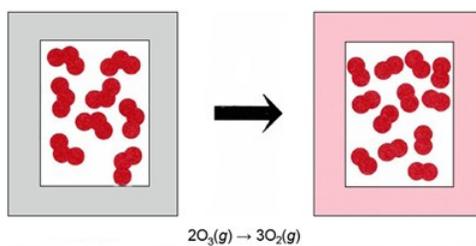
The enthalpy change, ΔH As we well know, if ΔH is negative, heat will be released by the reaction and the entropy of the surroundings will be increased, while if ΔH is positive, the surroundings will decrease in entropy. At room temperature we usually find that this change in the entropy of the surroundings as measured by $-\Delta H/T$ is the major factor in determining the direction of a reaction since ΔS is almost always small by comparison. This explains why *at room temperature most spontaneous reactions are exothermic*. On the molecular level, as we saw in [the sections on enthalpy, heat and energy](#), an exothermic reaction corresponds to a movement from a situation of weaker bonding to a situation of stronger bonding. The formation of more and/or stronger bonds is thus a big factor in tending to make a reaction spontaneous. **The entropy change, ΔS_{sys}** If the system itself increases in entropy as a result of the reaction (i.e., if ΔS_{sys} is positive), this will obviously contribute toward making the total entropy change positive and the reaction spontaneous. As we saw in the previous section of this chapter, reactions for which ΔS is positive correspond to the relaxation of some of the constraints on the motion of the atoms and molecules in the system. In particular, dissociation reactions and reactions in which the amount of substance in the gas phase increases correspond to reactions for which ΔS is positive. **The temperature, T** Because it alters the magnitude of $-\Delta H/T$ relative to ΔS , the temperature regulates the relative importance of the enthalpy change and the entropy change in determining whether a reaction will be spontaneous or not. As we lower the temperature, the effect of a reaction on the entropy of its surroundings becomes more and more pronounced because of the operation of the “boy in the living room” effect. As we approach absolute zero, the value of $-\Delta H/T$ begins to be an infinitely large positive or negative quantity, and ΔS becomes insignificant by comparison.

At a very low temperature, therefore, whether the reaction is spontaneous or not will depend on the sign of ΔH , i.e., on whether the reaction is exothermic or endothermic. By contrast, as we raise the temperature to very high values, the “boy in the bedroom” effect takes over and the reaction affects the entropy of its surroundings to an increasingly smaller extent until finally it is only the value of ΔS_{sys} which determines the behavior of the reaction. In short, *whether a reaction is spontaneous or not is controlled by the sign of ΔH at very low temperatures and by the sign of ΔS at very high temperatures.*

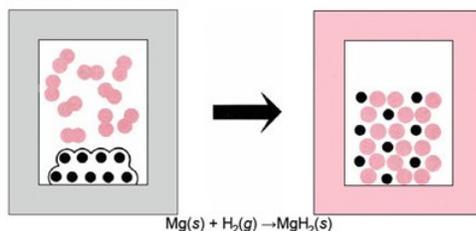
Since ΔH can be positive or negative and so can ΔS , there are four possible combinations of these two factors, each of which exhibits a different behavior at high and low temperatures. All four cases are listed and described in the next table, and they are also illustrated by simple examples in Figure 16.13.1 In this figure the surroundings are indicated by a shaded border around the reaction system. If the reaction is exothermic, the border changes from gray to pink, indicating that the surroundings have absorbed heat energy and thus increased in entropy. When the border changes from pink to gray, this indicates an endothermic reaction and a decrease in the entropy of the surroundings. In each case the change in entropy of the system should be obvious from an increase or decrease in the freedom of movement of the molecules and/or atoms.

Table 16.13.1 Effect of Temperature on the Spontaneity of a Reaction.

Case	Sign of ΔH	Sign of ΔS	Behavior
1	–	+	Spontaneous at all temperatures
2	–	–	Spontaneous only at low temperatures
3	+	+	Spontaneous only at high temperatures
4	+	–	Never spontaneous

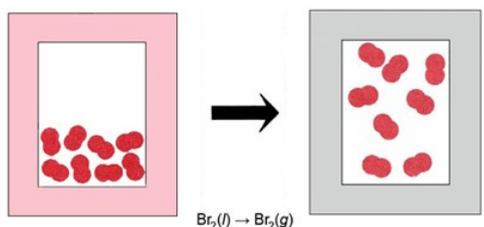


Case I. ΔH negative and ΔS positive. These reactions produce an increase in the entropy both in the system itself and in the surroundings, and are spontaneous at all temperatures.

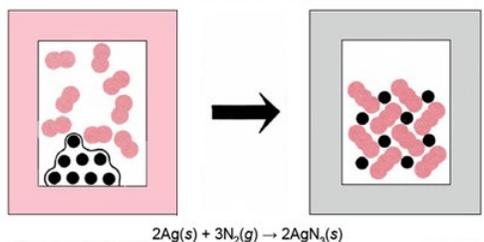


Case II. ΔH negative and ΔS negative. At low temperatures reactions in this class are spontaneous, because of the entropy increase they cause in the surroundings. At high temperatures the decrease in entropy of the system becomes the controlling factor, and the reaction ceases to be spontaneous.

Figure 16.13.1 Shows two of four different thermodynamic types of chemical reactions. In both cases, ΔH is positive.



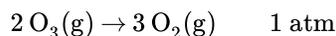
Case III. ΔH positive and ΔS positive. At low temperatures reactions in this class are nonspontaneous, because their occurrence decreases the entropy of the surroundings. As the temperature is raised, the entropy increase of the system becomes more important and the reaction becomes spontaneous.



Case IV. ΔH positive and ΔS negative. The entropy of both surroundings and system is decreased by this type of reaction which is thus nonspontaneous at all times.

Figure 16.13.2 Shows the other two thermodynamic types of chemical reactions. In both cases, ΔH is negative.

Case I: Reaction is exothermic, and ΔS_{sys} is positive The example illustrated in Figure 16.13.1I is the decomposition of ozone to oxygen.



for which $\Delta H_m^\circ(298 \text{ K}) = -285 \text{ kJ mol}^{-1}$ and $\Delta S_m^\circ(298 \text{ K}) = +137 \text{ J K}^{-1} \text{ mol}^{-1}$. A reaction of this type is always spontaneous because the entropy of both the surroundings and the system are increased by its occurrence.

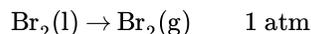
Case 2: Reaction is exothermic, and is ΔS_{sys} negative The example illustrated in Figure 16.13.1(II) is the reaction of magnesium metal with hydrogen gas to form magnesium hydride:



for which $\Delta H_m^\circ(298 \text{ K}) = -76.1 \text{ kJ mol}^{-1}$ and $\Delta S_m^\circ(298 \text{ K}) = -132.1 \text{ J K}^{-1} \text{ mol}^{-1}$. Reactions of this type can be either spontaneous or nonspontaneous depending on the temperature. At low temperatures when the effect on the surroundings is most important, the exothermic nature of the reaction makes it spontaneous. At high temperatures the effect of ΔS_{sys} predominates. Since ΔS_{sys} is

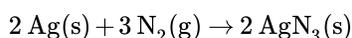
negative (free H_2 molecules becoming fixed H^- ions), the reaction must become nonspontaneous at high temperatures. Experimentally, solid MgH_2 will not form from its elements above 560 K, and any formed at a lower temperature will decompose.

Case 3: Reaction is endothermic, and ΔS_{sys} is positive The example illustrated in Figure 16.13.2 (III) is the vaporization of liquid bromine:



for which $\Delta H_m^\circ(298 \text{ K}) = +31.0 \text{ kJ mol}^{-1}$ and $\Delta S_m^\circ(298 \text{ K}) = 93.1 \text{ J K}^{-1} \text{ mol}^{-1}$. This example is usually classified as a physical rather than as a chemical change, but such distinctions are not important in thermodynamics. As in the previous case this reaction can be spontaneous or nonspontaneous at different temperatures. At low temperatures, bromine will not boil because the entropy increase occurring in the bromine as it turns to vapor is not enough to offset the decrease in entropy, which the surroundings experience in supplying the heat energy which is needed for the change in state. At higher temperatures the entropy effect on the surroundings becomes less pronounced, and the positive value of ΔS_{sys} makes the reaction spontaneous. At 101.3 kPa (1atm) pressure, bromine will not boil below 331 K (58°C), but above this temperature it will.

Case 4: Reaction is endothermic, and ΔS_{sys} is negative The example illustrated in Figure 16.13.2IV is the reaction between silver and nitrogen to form silver azide, AgN_3 :



for which $\Delta H_m^\circ(298 \text{ K}) = +620.6 \text{ kJ mol}^{-1}$ and $\Delta S_m^\circ(298 \text{ K}) = -461.5 \text{ J K}^{-1} \text{ mol}^{-1}$. Reactions of this type can never be spontaneous. If this reaction were to occur, it would reduce the entropy of both the system and the surroundings in contradiction of the second law. Since the forward reaction is nonspontaneous, we expect the reverse reaction to be spontaneous. This prediction is borne out experimentally. When silver azide is struck by a hammer, it decomposes explosively into its elements!

✓ Example 16.13.2: Classifying Reactions

Classify the following reactions as one of the four possible types (cases) just described. Hence suggest whether the reaction will be spontaneous at (i) a very low temperature, and (ii) at a very high temperature.

	$\Delta H_m^\circ(298 \text{ K})/$ kJ mol^{-1}	$\Delta S_m^\circ(298 \text{ K})/$ $\text{J K}^{-1} \text{ mol}^{-1}$
a) $\text{N}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NF}_3(\text{g})$	-249	-277.8
b) $\text{N}_2(\text{g}) + 3\text{Cl}_2(\text{g}) \rightarrow 2\text{NCl}_3(\text{g})$	+460	-275
c) $\text{N}_2\text{F}_4(\text{g}) \rightarrow 2\text{NF}_2(\text{g})$	+93.3	+198.3
d) $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$	-2044.7	+101.3

Solution

a) This reaction is exothermic, and ΔS is negative. It belongs to type 2 and will be spontaneous at low temperatures but nonspontaneous at high temperatures.

b) Since this reaction is endothermic and ΔS is negative, it belongs to type 4. It cannot be spontaneous at any temperature.

c) Since this reaction is endothermic but ΔS is positive, it belongs to type 3. It will be spontaneous at high temperatures and nonspontaneous at low temperatures. (All dissociation reactions belong to this class.)

d) This reaction belongs to type 1 and is spontaneous at all temperatures.

Table of Some Standard Enthalpies of Formation at 25°C

Compound	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ/\text{kcal mol}^{-1}$	Compound	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ/\text{kcal mol}^{-1}$
$\text{AgCl}(\text{s})$	-127.068	-30.35	$\text{H}_2\text{O}(\text{g})$	-241.818	-57.79

Compound	$\Delta H_f/\text{kJ mol}^{-1}$	$\Delta H_f/\text{kcal mol}^{-1}$	Compound	$\Delta H_f/\text{kJ mol}^{-1}$	$\Delta H_f/\text{kcal mol}^{-1}$
AgN ₃ (s)	+620.6	+148.3	H ₂ O(l)	-285.8	-68.3
Ag ₂ O(s)	-31.0	-7.41	H ₂ O ₂ (l)	-187.78	-44.86
Al ₂ O ₃ (s)	-1675.7	-400.40	H ₂ S(g)	-20.63	-4.93
Br ₂ (l)	0.0	0.00	HgO(s)	-90.83	-21.70
Br ₂ (g)	+30.907	+7.385	I ₂ (s)	0.0	0.0
C(s), graphite	0.0	0.00	I ₂ (g)	+62.438	+14.92
C(s), diamond	+1.895	+0.453	KCl(s)	-436.747	-104.36
CH ₄ (g)	-74.81	-17.88	KBr(s)	-393.798	-94.097
CO(g)	-110.525	-26.41	MgO(s)	-601.7	-143.77
CO ₂ (g)	-393.509	-94.05	NH ₃ (g)	-46.11	-11.02
C ₂ H ₂ (g)	+226.73	+54.18	NO(g)	+90.25	+21.57
C ₂ H ₄ (g)	+52.26	+12.49	NO ₂ (g)	+33.18	+7.93
C ₂ H ₆ (g)	-84.68	-20.23	N ₂ O ₄ (g)	+9.16	+2.19
C ₆ H ₆ (l)	+49.03	+11.72	NF ₃ (g)	-124.7	-29.80
CaO(s)	-635.09	-151.75	NaBr(s)	-361.062	-86.28
CaCO ₃ (s)	-1206.92	-288.39	NaCl(s)	-411.153	-98.24
CuO(s)	-157.3	-37.59	O ₃ (g)	+142.7	+34.11
Fe ₂ O ₃ (s)	-824.2	-196.9	SO ₂ (g)	-296.83	-70.93
HBr(g)	-36.4	-8.70	SO ₃ (g)	-395.72	-94.56
HCl(g)	-92.307	-22.06	ZnO(s)	-348.28	-83.22
HI(g)	+26.48	+6.33			

Above is a table of standard enthalpies of formation at 25°C. This is the enthalpy change which occurs when a compound is formed from its constituent elements. For instance, the enthalpy of formation value of $\Delta H_m = -285.8 \text{ kJ mol}^{-1}$ is the enthalpy change for the reaction: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$. It is important to note that the enthalpy of formation for an element in its most stable state is 0. Using these enthalpies of formation and [Hess' Law](#) the enthalpy change of any reaction involving the compounds with a known enthalpy of formation can be determined.

This table is found on [CoreChem:Standard Enthalpies of Formation](#)

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