

## Ch. 7. Entropy and free energy

It is common sense that some natural phenomena happen spontaneously in nature, without any help, in nature whereas others do not. For example, one would expect a ball on a hill to roll down instead of rolling up. How does common sense apply in chemistry? Why some reactions happen spontaneously whereas others do not. For example, methane ( $\text{CH}_4$ ) spontaneously burns with oxygen ( $\text{O}_2$ ), producing carbon dioxide, and water. Differently, if we mix water and carbon dioxide,  $\text{CH}_4$  is not spontaneously produced. Thermodynamics helps make sense of spontaneity in physics and chemistry. In particular, three thermodynamic properties—enthalpy, entropy, and Gibbs free energy—are commonly used to predict different aspects of spontaneity. At the same time, spontaneity in chemistry is indeed related to equilibrium and these properties can be translated into equilibrium constants.

### 7.1 Spontaneity

Chemical kinetics is a discipline that deals with the pace of chemical reactions by using activation energies, concentrations, and temperatures. It also deals with the different pathways of reaction. However, chemical kinetics does not provide information about the reasons why chemical reactions happen. Thermodynamics informs about the direction in which a chemical reaction occurs spontaneously and the reasons for this reaction to happen, without informing about the speed at which the process occurs. It uses thermodynamic functions—enthalpies, entropies, and Gibbs free energies—to understand the factors that favor the spontaneity of a reaction. Overall, kinetics and thermodynamics are complementary disciplines in chemistry as it is convenient to gain insight into the pace and spontaneity of chemical reactions.

*Spontaneity* A spontaneous process happens naturally, without any help or external input. For example, ice spontaneously melts at room temperature, without any help. Still, spontaneity happens under a certain set of conditions. For example, ice melts at room temperature but does not melt at  $-5^\circ\text{C}$ , as the process in these conditions is not spontaneous. Other spontaneous processes are the rusting of iron at room temperature, or the freezing of water below  $0^\circ\text{C}$ . Spontaneous processes have a natural tendency to occur. Still, this tendency might not be actualized in practice. At the same time, this natural tendency to occur is not linked in any way to the speed or rate of the process. For example, diamonds have a natural tendency to become graphite. Still, the rate of this change is so slow that in human years it does never occur. Remember that thermodynamics addresses spontaneity whereas kinetics address the rate of occurrence of a process.



## 7.2 Entropy

Entropy, represented with an  $S$ , refers to the spreading of energy and composition of a system. Energy and matter have the tendency to spread and this spreading is represented by entropy. Think about a glass full of hot water and how water is going to spontaneously cool down, as the energy spreads between the glass and its environment. Similarly, think about a gas container opened in vacuum, and how gas molecules spontaneously will leave the container and spread out. Overall, entropy has a macroscopic and microscopic description, with these two descriptions converging into a cohesive concept.

*The meaning of Entropy,  $S$*  Entropy is represented with the letter  $S$ . Qualitatively, it is a measure of the spreading in space of the energy of a system, or simply the system. For example, in a glass full of hot water, the energy is concentrated in the glass as the water molecules initially have high thermal energy. With time, the system evolves naturally so that heat spreads between the room and the container. The initial state (glass with hot water) has lower entropy than the final state (glass with thermalized water). Another example, think about a concentrated solution separated from a more diluted system by means of a membrane. Initially, the entropy of the system is low, as one side of the container has a high density of molecules whereas the other side has a lower density. As the molecules diffuse and the concentration equalizes. In this case, the entropy of the initial state (a concentrated and a diluted solution) is lower than the entropy of the final system (two solutions of equal concentration). These two examples represent how energy and matter spread as entropy increases in spontaneous processes. On one hand, entropy, just like enthalpy, is a *state function* in thermodynamics which means that the change of entropy of a system when going from an initial into a final state is independent of the path taken to arrive from the initial into the final state. On the other hand, entropy is an *extensive property* that depends on the size of the system and for example the entropy change when heating 2 moles of gas is larger than when heating 1 mole of gas.

*A macroscopic description of entropy* Overall an entropy change is associated with the flow of heat. The change of entropy associated with the heat flow, at constant temperature, can be computed using the expression below, called generalized Clausius relation:

$$\Delta S = \frac{q}{T} \quad (7.1)$$

where:

$\Delta S$  is the entropy change

$q$  is the reversible heat transferred

$T$  is the absolute temperature (in K)

This expression refers to  $q$  that is the heat enhanced reversibly, exchanging heat in very tinny bits so that the temperature does not change significantly. The larger the heat exchanges the larger the entropy change. At the same time, a larger entropy change will be associated with the heat exchange at low temperatures than at high temperatures. The entropy change resulting from a heat flow can be referred to as *thermal entropy*. Formula 7.1 is one of the ways to mathematically describe the *second law of thermodynamics* that says that a system and its surroundings—an isolated system—evolve spontaneously increasing its overall entropy.



## Sample Problem 1

We warm up a cup of vegetable oil in the microwave, at low power and for a long time, giving 40KJ of heat to the oil. Calculate the entropy change experienced by the oil at 30°C.

**SOLUTION**

We will calculate the thermal entropy by means of Clausius' relation given that the heat is 40000J and the fixed temperature is  $30 + 273 = 303\text{K}$ . Remember as the oil (this is the system under study) receives heat the numerical value of heat of positive and also we need absolute temperature in Clausius' relation. We finally have that:

$$\Delta S = \frac{q}{T} = \frac{40000}{303} = 132\text{J/K}$$

As a final comment, mind that the heat exchange has happened reversibly as they point the microwave functions at a low power and for a low time.

**STUDY CHECK**

We cool down a cup of vegetable oil with a water bath, so that the oil releases 20KJ of heat to the bath. Calculate the entropy change experienced by the oil at 40°C.

►Answer: 63.9J/K

*A microscopic description of entropy* A mathematical or molecular level description of entropy was suggested by Ludwig Boltzmann. Entropy depends on the number of energetically equivalent microstates, that is, the number of different ways in which a system existing in a given state can be arranged. The Boltzmann formula for entropy is:

$$S = k_B \ln(W) \quad (7.2)$$

where:

$S$  is the entropy of a system

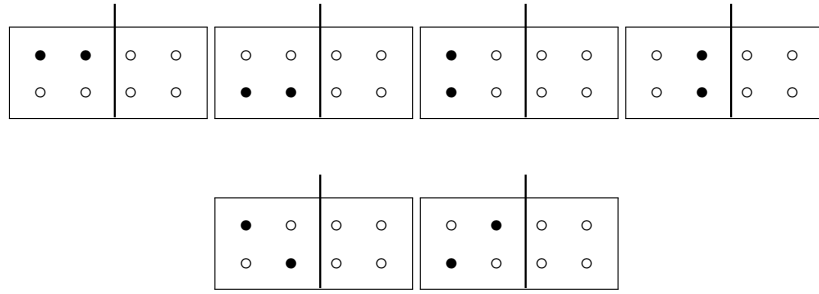
$k_B$  is the Boltzmann constant ( $1.381 \times 10^{-23} \text{ J/K}$ )

$W$  is the number of microstates

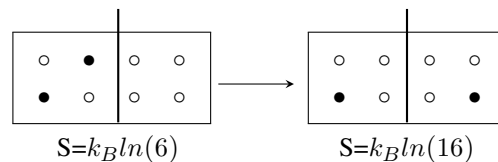
The Boltzmann's constant results from statistical thermodynamics—probabilistic thermodynamics—being related to the ideal gas constant through  $R = N_A \cdot k_B$ , with  $N_A$  Avogadro's number. At the same time,  $W$  is the number of microstates of the system that is the number of different ways in which the particles of a system can be differently arranged for a given energy. Hence the molecular-level description of entropy is closely related to probability and we may imagine that the system exists in numerous microstates of short existence. When measuring the system we are indeed measuring a time average of the properties of the different microstates. The larger the number of microstates—the more ways a particular state can be achieved—the most probable the configuration—the greater is the likelihood of finding that state.

Let us analyze an example to describe the meaning of microstate and the use of Boltzmann entropy. Imagine a box with two identical ideal-gas particles and two compartments. In each compartment, the particles can occupy four different locations, with two locations on the top part of the compartment and two locations on the bottom part. Each of the particle arrangements would be a microstate. Let us now analyze the

number of equivalent microstates when the box is closed so that the particles cannot jump into the other compartment. Below are all possible microstates for this scenario:



The number of different arrangements represented above is  $X=6$ , and the entropy associated with this system would be  $k_B \ln(6)$  that is  $2.5 \times 10^{23}$  J/K. Now, if we open the separation between the two compartments so that the molecules can freely move from one compartment to the other, the number of microstates increases considerably. We would have three different scenarios: (1) the scenario in which the particles stay in the left compartment, (2) the scenario in which the particles stay in the right compartment, (3) the scenario in which the particles are spread between both compartments. What situation do you think is more feasible? In particular, we have a set of six configurations in which both particles populate the left compartment and a set of six configurations in which both particles populate the right compartment. The entropy for these two scenarios is  $k_B \ln(6)$ . We would also have a set of 16 configurations in which each particle populates a different compartment. The entropy for these two scenarios is  $k_B \ln(16)$ . The Boltzmann formula suggests that the most feasible scenario, the scenario with higher entropy, corresponds to the spreading of particles between both compartments. As we will see along the chapter, the situation in which each particle populates a different compartment has larger entropy and hence it would be the most probable scenario.



The calculation of different microstates come from the close study of the situation in hand. In the scenario described above, we had two compartments and four possible locations. Each molecule had a single state or orientation. One can also find the case that the molecules have several states. For example, CO molecules can be found in two different orientations when an external field is applied. In the case of multiple molecular arrangements it is convenient to use the formula below:

$$W = A^N \quad (7.3)$$

where:

$A$  is the number of molecular states

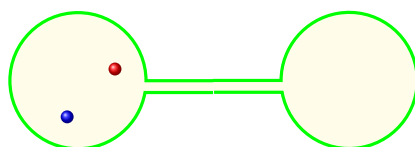
$W$  is the number of microstates

For example for the scenario of two molecules with two different orientations we will have  $2^2$  microstates.

The type of probability related to the number of configurations in space is called *positional probability* and the entropy resulting from positional probability is called *positional entropy*. Positional probability can be used to understand phenomena such as the change of state of the dissolution of solids in liquids. When a solid becomes liquid the number of possible microstates increases and hence entropy increases as well. Similarly, when dissolving a solute into a liquid, the number of microstates and entropy increases. However, computing the number of microstates to estimate positional entropy is not practical for large systems with numerous configurations. The number of microstates increases exponentially with the number of particles to the point that, for large systems, is not practical to compute entropy using Equation 7.2.

### Sample Problem 2

The image below represents two different ideal gas-molecules in a two-bulb container. The molecules are able to travel from one side to the other.



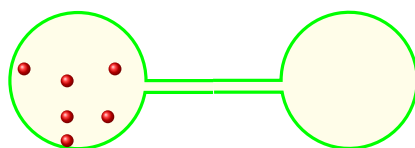
Answer the following questions: (a) What is the total number of microstates in this system (b) What is the most likely arrangement of the molecules (c) What is the least likely arrangement of the molecules (d) What is the probability of finding the system in the most likely arrangement of the molecules

### SOLUTION

Overall we have three different scenarios. We can find all the molecules in the left container, all the molecules in the right container, or one molecule in the left and the other in the right. As the molecules are different, we only have one microstate in which both are in a single container. Differently, we have two different microstates in which the particles are distributed. Overall we have 4 microstates, the probability of finding the particles on both sides would be  $2/4 \times 100 = 50\%$ .

### STUDY CHECK

The image below represents six ideal gas-molecules in a two-bulb container. The molecules are able to travel from one side to the other.



Answer the following questions: (a) What is the total number of microstates in this system (b) What is the most likely arrangement of the molecules (c) What is the least likely arrangement of the molecules (d) What is the probability of finding the system in the most likely arrangement of the molecules

►Answer: (a) 3 microstates: left population, right population, mixed (b) mixed distribution (c) left or right population (d)  $5/7 \times 100$

*Equivalence between microscopic and macroscopic entropy* We have addressed two different definitions of entropy, a macroscopic definition based



on heat and a microscopic definition based on configurations. Each description is based in a different formula. The macroscopic description of entropy is based on the Clausius' formula whereas the microscopic description is based on Boltzmann's formula. Here we will explain why both descriptions are indeed equivalent. First, both types of entropies are state functions, macroscopic entropy depends on the initial and final temperature, volume or pressure and not the path taken to reach the final state. Similarly, the microscopic entropy depends on the initial and final microstates, not the transition between both states. Macroscopic entropy is extensive and depends on the size of the system, and microscopic entropy is extensive as well as the larger the system the more configurations would be. Finally, when the size of a system increases the energy levels that its particle occupies become more packed and the particles are able to distribute among these states. At low temperatures all particles occupy only the lowest level energy level and hence there is only one configuration or micro state for the system, being its entropy zero.

## 7.3 Standard molar entropies

Enthalpies are relative properties and when we compute the formation energy of water we need the formation energy of oxygen and oxygen gas. These two values are zero and are assumed the reference. Entropies are absolute values. The term absolute refers to the absolute scale of temperatures where the lowest value is well defined and equal to zero. Similarly, there is the lowest value for entropy two and we will discuss this value when dealing with the third law of thermodynamics.

*Standard molar entropies,  $S^\circ$*  The standard molar entropy of a substance is the absolute entropy of one more substance at 1 atm. Entropies are absolute properties in contrast to other relative thermodynamic functions like the enthalpy in which a set of molecular states act as a reference. A few standard entropy values are tabulated in Table 7.1 at one bar and 25 °C, the conventional temperature of reporting thermodynamic data. More values are tabulated in Table 7.5, at the end of the chapter. The units of molar entropy are J/molK. Molar entropies tend to be small values—as the unit joule is a small unit of energy. Finally, entropies can be positive or negative values.

### Sample Problem 3

Using the thermodynamic tables at the end of the chapter, locate the values of molar entropies for the following molecules:  $\text{O}_{2(g)}$ ,  $\text{NH}_{3(g)}$ ,  $\text{K}_{(s)}$ ,  $\text{SiBr}_{4(l)}$ .

#### **SOLUTION**

The molar entropy of oxygen as is 205.0 J/molK, whereas the molar entropy for gas ammonia is 192.3 J/molK. The molar entropy for solid potassium is 64.2 J/molK, whereas the molar entropy for liquid silicon tetrabromide is 277.8 J/molK.

#### **STUDY CHECK**

Using the thermodynamic tables at the end of the chapter, locate the values of molar entropies for the following molecules: (a)  $\text{Ag}_{(s)}$  (b)  $\text{SO}_{2(g)}$  (c)  $\text{Zn}_{(s)}$  (d)  $\text{Br}_{2(l)}$

►Answer: (a) 42.6 J/molK (b) 248.1 J/molK (c) 41.6 J/molK (d) 152.2 J/molK



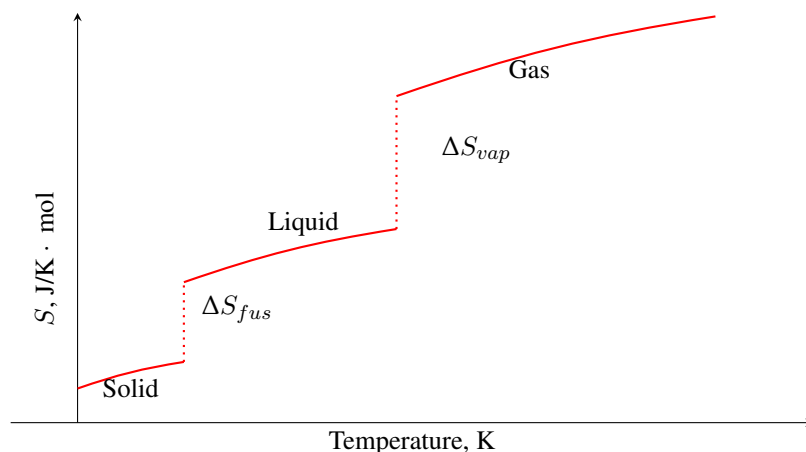
*Factors affecting  $S$*  We can qualitatively rationalize the trends between the standard molar entropy values for different substances and for different conditions (temperature, volume, pressure) by using some simple rules described below:

‡ **The state of matter:** The standard entropy of gases is larger than the standard entropy of liquids as gases present large degree of freedom (possible configurations) than liquids. The standard entropy of liquids is larger than the standard entropy of solids as liquids present large degree of freedom than solids. The molecules of a liquid molecules can jiggle more in comparison with the molecules of a solid. Overall, we can assume that liquids and solid has almost null entropy whereas gases have very large entropy. For example, the entropies of ice, water and steam are respectively 41, 69.95, and 69.95 J/molK.

‡ **Molar mass:** For monoatomic substances (e.g. Ne, Ar, etc.) the larger the atomic weight the larger entropy. This is because the energy levels of larger molecules are more packed, and hence are easier to access at a given temperature.

‡ **Molecular complexity:** For substances with comparable molar mass ( $O_3$  and  $F_2$ ), the more complex the molecule the larger entropy, as the number of degrees of freedom are directly correlated with the number of microstates.

‡ **Temperature:** Temperature increases entropy as the system have more accessible microstates. The plot below represents the entropy change with temperature for a substance.



**Figure 7.1** Entropy as function of temperature indicating the entropy changes for the fusion and vaporization processes.

‡ **Number of particles:** The larger the number of particles of a system, the larger entropy, as the more particles the more microstates or possible configurations.

‡ **Volume:** The larger the volume of a system, the larger entropy, as the larger volume the more microstates or possible configurations.

#### Sample Problem 4

Compare entropy for the following systems: (a) Liquid ammonia at 25°C and 1 bar and gas ammonia at 25°C and 1 bar (b) Liquid ammonia at 25°C and 1 bar and liquid ammonia at 45°C and 1 bar (c) 3 moles of an ideal gas and 5 moles of the same gas at fixed temperature and pressure

#### SOLUTION

Gas ammonia has a larger entropy than liquid ammonia as gases in general tend





to have larger entropy. When dealing with temperature, the higher temperature the higher entropy. Hence liquid ammonia at 45°C and 1 bar will have a larger entropy than liquid ammonia at 25°C and 1 bar. Finally, entropy is an extensive property and 5 moles of a gas will have larger entropy than 3 moles of the same gas.

### STUDY CHECK

Compare entropy for the following systems: (a) CO<sub>2</sub> at 25°C and 1 bar and SO<sub>2</sub> at 25°C and 1 bar (b) 3L of a gas at 25°C and 1 bar and 4L of the same gas at 25°C and 1 bar (c) H<sub>2</sub> at 25°C and 1 bar and He at 25°C and 1 bar

►Answer: (a) SO<sub>2</sub> (b) 4L (c) H<sub>2</sub>

**Table 7.1 Standard entropy S° at 25 °C in J/(mol·K)**

Substance	S°	Substance	S°	Substance	S°	Substance	S°
Br <sub>2</sub> (l)	152	Br <sub>2</sub> (g)	245	CH <sub>3</sub> OH(l)	127	CH <sub>3</sub> OH(g)	240
CS <sub>2</sub> (l)	151	CS <sub>2</sub> (g)	238	H <sub>2</sub> O(l)	70	H <sub>2</sub> O(g)	189
H <sub>2</sub> O <sub>2</sub> (l)	233	H <sub>2</sub> O <sub>2</sub> (g)	189	Rb(s)	70	Rb(g)	170
Cs(s)	83	Cs(g)	176	He(g)	126	Ne(g)	146
Ar(g)	155	Kr(g)	164	O <sub>3</sub> (g)	238	F <sub>2</sub> (g)	203

## 7.4 Calculating entropy changes

We have that when a system receives heat its entropy increases. At the same time, when a system receives heat its temperature increases. Therefore, there should be a relation between the temperature increase and the entropy increase. At the same time if we compress or decompress a gas at constant temperature, its entropy also changes based on the change of volume or the change of pressure. In particular, if we apply some mechanical work to a system so its volume decreases its entropy will increase as the system has received work—mechanical energy. Mind the opposite trend here. Similarly, if the pressure of a system increases as a result of applying an external force its entropy will also increase.

*Entropy change and temperature* The following formula can be used to calculate the entropy change of a system when its temperature increases (or decreases). Temperature changes can be measured at constant volume or constant pressure and as such, the formula will have to be adjusted for these two different conditions.

$$\Delta S = C \ln \left( \frac{T_2}{T_1} \right) \quad (7.4)$$

where:

$\Delta S$  is the entropy change in J/K

$C$  is heat capacity in J/K

$T_1$  is the absolute initial temperature (in K)

$T_2$  is the absolute final temperature (in K)





$C$  represents the heat capacity. Mind molar heat capacity  $C_m$  and heat capacity  $C$  are related by the number of moles:  $C = n \cdot C_m$ . If the change in temperature is measured at constant pressure, the molar heat capacity is called constant-pressure molar heat capacity  $C_{p,m}$ , whereas if the change in temperature is measured at constant volume, the molar heat capacity is called constant-volume molar heat capacity  $C_{v,m}$ . For ideal gases the  $C_{v,m}$  values are (mind  $R$  is the constant of the gases 8.314J/molK):  $\frac{3}{2}R$  (for atoms),  $\frac{5}{2}R$  (for linear molecules), and  $\frac{6}{2}R$  (for nonlinear molecules). For ideal gases the  $C_{p,m}$  values are:  $\frac{5}{2}R$  (for atoms),  $\frac{7}{2}R$  (for linear molecules), and  $\frac{8}{2}R$  (for nonlinear molecules).  $C_{p,m}$  and  $C_{v,m}$  are related by  $C_{p,m} = C_{v,m} + R$ .

*Entropy change and volume* The following formula can be used to calculate the entropy change of an ideal gas when its volume changes at constant temperature. A volume decrease will cause an entropy decrease:

$$\Delta S = nR \ln \left( \frac{V_2}{V_1} \right) \quad (7.5)$$

where:

$\Delta S$  is the entropy change in J/K

$n$  is the number of moles

$R$  is the constant of the gases in energy units (8.314J/molK)

$V_1$  is the initial volume

$V_2$  is the final volume

*Entropy change and pressure* The following formula can be used to calculate the entropy change of an ideal gas when its pressure changes at constant temperature. A pressure decrease will cause an entropy increase:

$$\Delta S = nR \ln \left( \frac{P_1}{P_2} \right) \quad (7.6)$$

where:

$\Delta S$  is the entropy change in J/K

$n$  is the number of moles

$R$  is the constant of the gases in energy units (8.314J/molK)

$P_1$  is the initial pressure

$P_2$  is the final pressure

*Entropy change, pressure and volume* The following formula can be used to calculate the entropy change of an ideal gas when its pressure and volume change at constant temperature.

$$\Delta S = nR \ln \left( \frac{P_1}{P_2} \right) + nR \ln \left( \frac{V_2}{V_1} \right) \quad (7.7)$$

where:

$\Delta S$  is the entropy change

$n$  is the number of moles

$R$  is the constant of the gases in energy units (8.314J/molK)

$P_1$  and  $V_1$  is the initial pressure and volume

$P_2$  and  $V_2$  is the final pressure and volume



## Sample Problem 5

A 5L sample of Helium, an ideal gas, at 1atm is heated from 300K to 400K. (a) Calculate the entropy change if the gas is heated at constant volume. (b) Calculate the entropy change if the gas is heated at constant pressure.

**SOLUTION**

We have that the formula that related the entropy change with a temperature change is:

$$\Delta S = C \ln \left( \frac{T_2}{T_1} \right)$$

Still the heat capacity can be computed at constant volume or constant pressure. For an ideal monoatomic gas, the molar heat capacity at constant volume is  $\frac{3}{2}R$ , whereas the molar heat capacity at constant pressure is  $\frac{5}{2}R$ . Therefore, as we need heat capacities and not molar heat capacity, we have that the heat capacity at constant volume is  $n \cdot \frac{3}{2}R$ , whereas the heat capacity at constant pressure is  $n \cdot \frac{5}{2}R$ , with  $n$  being the number of moles. At this point we have that the entropy change at constant volume would be  $n \cdot \frac{3}{2}R \ln \left( \frac{T_2}{T_1} \right)$ , whereas the entropy change at constant pressure would be  $n \cdot \frac{5}{2}R \ln \left( \frac{T_2}{T_1} \right)$ . The number of moles of gas is:

$$n = \frac{PV}{RT} = \frac{1 \cdot 5}{0.082 \cdot 300} = 0.20 \text{ moles}$$

the initial temperature is  $T_1 = 300\text{K}$  and the final temperature is  $T_2 = 400\text{K}$ . Therefore the entropy change at constant volume would be:

$$\Delta S_V = 0.20 \cdot \frac{3}{2} \cdot 8.314 \ln \left( \frac{400}{300} \right) = 0.71 \text{ J/K}$$

and the entropy change at constant pressure would be:

$$\Delta S_p = 0.20 \cdot \frac{5}{2} \cdot 8.314 \ln \left( \frac{400}{300} \right) = 1.19 \text{ J/K}$$

We have that for a monoatomic ideal gas, the entropy change at constant pressure is larger than the entropy change at constant volume.

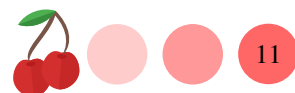
**STUDY CHECK**

A  $4.9 \times 10^{-3} \text{ mol}$  sample of methane is heated from 100K to 300K. Assuming ideal gas behavior: (a) Calculate the entropy change if the gas is heated at constant volume. (b) Calculate the entropy change if the gas is heated at constant pressure.

►Answer: (a) 0.13 J/K (b) 0.18 J/K

## 7.5 Calculating entropy changes in chemical reactions

This section covers the calculation and estimation of the entropy change of a reaction. Entropies as well as enthalpies are tabulated and one can compute the entropy change of a reaction by using the tabulated molar entropies. On the other hand it is very convenient to be able to estimate the just the sign of the entropy change of a reaction. Here we will provide a set of general rules to do this.



*Standard entropy of reaction,  $\Delta S_R^\circ$*  We can calculate the standard entropy of a reaction in a similar way as we calculate the standard enthalpy of a reaction:

$$\Delta S_R^\circ = \Delta S_{products}^\circ - \Delta S_{reactants}^\circ \quad \text{Entropy change} \quad (7.8)$$

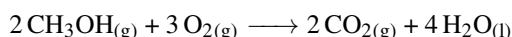
where:

$\Delta S_R^\circ$  is the standard entropy change of the reaction

$\Delta S_{products}^\circ$  is the standard entropy of all products

$\Delta S_{reactants}^\circ$  is the standard entropy of all reactants

It is important to take into account the stoichiometric coefficients. For example, for the reaction:



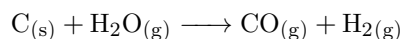
We have the entropy values of:  $S^\circ(\text{CH}_3\text{OH}_{(g)})=239.7 \text{ J/K} \cdot \text{mol}$ ,  $S^\circ(\text{O}_{2(g)})=161.1 \text{ J/K} \cdot \text{mol}$ ,  $S^\circ(\text{CO}_{2(g)})=213.79 \text{ J/K} \cdot \text{mol}$ , and  $S^\circ(\text{H}_2\text{O}_{(l)})=69.95 \text{ J/K} \cdot \text{mol}$ . We can calculate  $\Delta S_R^\circ$ :

$$\begin{aligned} \Delta S_R^\circ &= \Delta S_{products}^\circ - \Delta S_{reactants}^\circ = \\ &= \left( 2 \cdot S^\circ(\text{CO}_{2(g)}) + 4 \cdot S^\circ(\text{H}_2\text{O}_{(l)}) \right) - \left( 2 \cdot S^\circ(\text{CH}_3\text{OH}_{(g)}) + 3 \cdot S^\circ(\text{O}_{2(g)}) \right) \\ &= \left( 2 \cdot 213.79 + 4 \cdot 69.95 \right) - \left( 2 \cdot 239.7 + 3 \cdot 161.1 \right) = -255.32 \text{ J/K} \end{aligned}$$

*Interpreting  $\Delta S_R^\circ$*  If the entropy change of a reaction is positive we will say that the reaction produces entropy. Similarly, if the entropy change of a reaction is negative we will say that the reaction consumes entropy. An analog trend can be found for the change of enthalpy—remember the enthalpy of the heat measured at constant pressure conditions—so if the enthalpy change of a reaction is positive we say the reaction is endothermic and consumes heat, whereas a negative enthalpy change for a reaction means the reaction produces heat.

#### Sample Problem 6

Calculate the entropy change of the following reaction and give an interpretation based on the sign of the change:



Given:  $S^\circ(\text{C}_{(s)})=5.69 \text{ J/K} \cdot \text{mol}$ ,  $S^\circ(\text{H}_2\text{O}_{(g)})=188.7 \text{ J/K} \cdot \text{mol}$ ,  $S^\circ(\text{CO}_{(g)})=197.9 \text{ J/K} \cdot \text{mol}$ ,  $S^\circ(\text{H}_{2(g)})=131 \text{ J/K} \cdot \text{mol}$ .

#### SOLUTION

Using the formula for  $\Delta S_R^\circ$  we have:

$$\begin{aligned} \Delta S_R^\circ &= \Delta S_{products}^\circ - \Delta S_{reactants}^\circ = \\ &= \left( S^\circ(\text{CO}_{(g)}) + S^\circ(\text{H}_{2(g)}) \right) - \left( S^\circ(\text{C}_{(s)}) + S^\circ(\text{H}_2\text{O}_{(g)}) \right) \\ &= \left( 197.9 + 131 \right) - \left( 5.69 + 188.7 \right) = 134.51 \text{ J/K} \end{aligned}$$

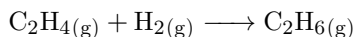
This produces entropy.

#### STUDY CHECK

Calculate the entropy change of the following reaction and give an interpretation



based on the sign of the change:



Given:  $S^\circ(\text{C}_2\text{H}_4(\text{g})) = 219.5 \text{ J/K} \cdot \text{mol}$ ,  $S^\circ(\text{C}_2\text{H}_6(\text{g})) = 229.5 \text{ J/K} \cdot \text{mol}$ ,  
 $S^\circ(\text{H}_2(\text{g})) = 131 \text{ J/K} \cdot \text{mol}$ .

► Answer:  $-121 \text{ J/K}$ , consumes entropy

*Stimate the sign for  $\Delta S_R^\circ$*  Often times we are more interested in predicting the sign of the entropy change of a reaction than to compute the exact value. This is because the sign can be used in order to estimate whether a reaction proceeds spontaneously. Two basic rules are used in order to estimate the entropy change sign:

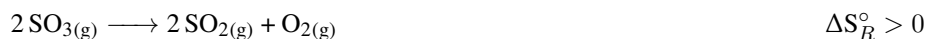
✎ **The state of matter:** solids and liquids have very low entropy in comparison to gases. For example, in the case below, we have the production of liquid water from ice produces entropy as liquids have more entropy than solids:



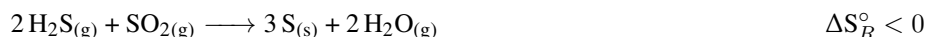
On the other hand, the condensation of water vapor to produce a liquid consumes entropy, as liquids have less entropy than gases:



✎ **The number of molecules:** the larger the number of molecules of gas the larger entropy. For example, in the reaction below we have that we produce three molecules from two molecules. Hence, the entropy increases.

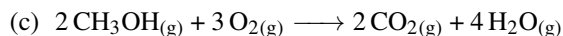
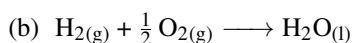
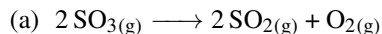


However, this rule only works if we only take into account the number of gas molecules. For example, in the reaction below we produce two gas molecules from three gas molecules and hence we lose entropy:



#### Sample Problem 7

Estimate the sign of the entropy change for the following reactions:



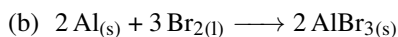
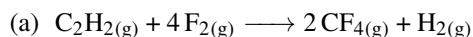
#### SOLUTION

We will calculate the change on the number of moles of gases in the reaction  $\Delta n$  in order to estimate the sign of the entropy change. This is just the total number of product molecules with respect to the total number of reactant molecules. We have that  $\Delta n$  for the first reaction is 1 and hence  $\Delta S_R^\circ > 0$ . For the second reaction we have that  $\Delta n$  is  $-1.5$  and hence  $\Delta S_R^\circ < 0$ . Remember that liquids and solids are not counted towards  $\Delta n$  as their entropy is very small. Finally for

the last reaction, we have that  $\Delta n$  is 1 and hence  $\Delta S_R^\circ > 0$ .

### ◆ STUDY CHECK

Estimate the sign of the entropy change for the following reactions:



► Answer:  $\Delta S_R^\circ > 0$ ,  $\Delta S_R^\circ \simeq 0$

## 7.6 The second and third law of thermodynamics

The second law of thermodynamics claims that any spontaneous evolution is accompanied by an increase in entropy. However, the entropy of certain common systems spontaneously decreases. For example, ice freezes below  $0^\circ\text{C}$  going from less-ordered liquid water to more-ordered ice. At the same time, cold packs spontaneously get colder going from a high-temperature and entropy state into a low-temperature low-entropy state. In order to understand how some systems decrease their entropy spontaneously, we need to further our analysis of the system taking into account not only the system under study but also its surroundings.

*System, its surroundings and the universe* Thermodynamics studies systems involving heat transfer such as a hot cup of coffee cooling down in a room or a chemical reaction happening at a beaker on a lab bench. The system just means the problems we are dealing with, for example, the cup of coffee or the beaker. However, every system has its surroundings. For example, the cup of coffee is surrounded by air and the beaker is in contact with the lab bench. The surroundings of a system represent everything else but the system and in general tend to be as important as the system, in particular when understanding the changes of entropy during a spontaneous change. Both the system and its surroundings are called the universe, which is an isolated system. If we study how a system loses heat or a reaction consumes entropy it is convenient to think about where the heat goes or where the entropy lost is coming from.

*Calculating  $\Delta S_{surr}^{T,P}$*  Now, let us focus on the surroundings of the system under study considering only fixed temperature and pressure conditions. If a system loses heat, the heat is received by its surroundings. To calculate the entropy of the surroundings we just need to use the formula working under fixed pressure and temperature conditions (think about a reaction happening on an open beaker in which pressure is always atmospheric and temperature will always be room temperature):

$$\Delta S_{surr}^{T,P} = -\frac{\Delta H}{T} \quad (7.9)$$

where:

$\Delta S_{surr}^{T,P}$  is the entropy change on the surroundings

$\Delta H$  is the enthalpy change on the system

$T$  is the absolute temperature

This formula derives from Clausius expression that related the entropy change with heat, given that the surroundings receive or give away the heat exchanged by the



system—hence the negative sign—and under fixed-pressure conditions, heat is equivalent to enthalpy. Moreover, as the surroundings are in general larger than the system its temperature will not change and any heat transfer will be reversible. Also, this expression predicts that the same heat exchanged at higher temperatures is less effective in changing the surroundings' entropy. At the same time, an exothermic process will increase the entropy of the surroundings whereas an endothermic process will decrease the entropy of the surroundings.

*Calculating  $\Delta S_{univ}$ : the second law of thermodynamics* Now that we have included the surroundings in our analysis we can combine both the system and its surroundings in order to track the overall change in entropy in the universe:

$$\Delta S_{univ} = \Delta S + \Delta S_{surr} = \Delta S - \frac{\Delta H}{T} \quad (7.10)$$

where:

$\Delta S_{univ}$  is the entropy change on the universe

$\Delta S$  is the entropy change on the system

$\Delta H$  is the enthalpy change on the system

$T$  is the absolute temperature

Overall, the *second law of thermodynamics* states that spontaneous process increase the entropy of the universe. If a reaction is exothermic and heat is being released the entropy of the surroundings increase whereas the entropy of the system can increase or decrease. If this change is negative, it has to be smaller than the entropy increase of the surroundings if the process is spontaneous. If a reaction is endothermic and heat is being absorbed the entropy change of the system has to be positive enough to compensate the decrease of entropy of the surroundings if the process is spontaneous.

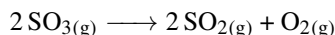
ℙ  $\Delta S_{univ} > 0$ : The forward process or reaction is spontaneous

ℙ  $\Delta S_{univ} = 0$ : The process or reaction is in equilibrium

ℙ  $\Delta S_{univ} < 0$ : The forward process or reaction is not spontaneous hence the backwards is spontaneous

#### Sample Problem 8

For the reaction:



we have that  $\Delta H_R^\circ$  is -93kJ/mol and  $\Delta S_R^\circ$  is -199J/mol. Calculate the entropy change on the system, its surroundings and the overall universe at 25 °C.

#### SOLUTION

We have that the system is just the reaction we observe, hence  $\Delta S_{sys}^\circ = -199$  J/mol. The entropy change of the surroundings—the environment where the reaction takes place—is:

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T} = -\frac{-93}{298} = 0.312 \text{ kJ/mol} = 312 \text{ J/mol}$$

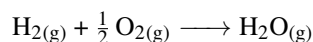
If we combine both contributions we have that the entropy change of the universe is:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = -199 + 312 = 113 \text{ J/mol}$$

As this value is positive, the reaction will happen spontaneously at that temperature.

### ◆ STUDY CHECK

For the reaction:



we have that  $\Delta H_R^\circ$  is  $-250\text{kJ/mol}$  and  $\Delta S_R^\circ$  is  $-45\text{J/K} \cdot \text{mol}$ . Calculate the entropy change on the system, its surroundings and the overall universe at  $298\text{K}$ .

►Answer:  $\Delta S_{\text{surr}} = 839\text{J/K} \cdot \text{mol}$ ,  $\Delta S_{\text{univ}} = 884\text{J/K} \cdot \text{mol}$

**Entropy and equilibrium** A system without tendency to change is a system in static equilibrium. A system in dynamic equilibrium has the same tendency to change through forward or backwards evolution. For example, a reaction reaches chemical equilibrium when the mixtures of reactants and products reached a point in which the forward reaction and the backwards reaction have the same speed. A system reaches thermal equilibrium when it releases and gains heat with its surroundings at the same speed. A system reaches mechanical equilibrium—a gas in a piston—when it contracts and expands at the same speed. When an isolated system has reached equilibrium the entropy of the universe does not change:

$$\Delta S_{\text{univ}} = 0 \quad (7.11)$$

**The third law of thermodynamics** Entropy is an absolute—not relative—property. The third law of thermodynamics established the lower possible entropy value that a system can reach under certain conditions. We have that from a microscopic or molecular point of view entropy is associated with the number of molecular configurations,  $W$ . For a perfect crystal—a crystalline material without any defects—at the lowest possible temperature, that is the absolute zero in the Kelvin scale,  $0\text{K}$ , there is no molecular motion and hence the system would have only one possible configuration ( $W=1$ ) that would lead to a null entropy ( $k_B \ln 1$ ).

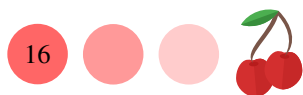
$$\Delta S_s(0\text{K}) = 0 \quad \text{3rd law of thermodynamics} \quad (7.12)$$

where:

$\Delta S_s$  is the entropy of a perfect crystal at  $0\text{K}$

The entropy of a solid depends on the number of the number of molecules and the number of possible configurations of each molecule of the solid. For a solid with for example two molecules and with each molecule having three possible configuration we'll have  $2^3$  possible microstates and the entropy will be  $k_B \ln 2^3$ . Given that  $\ln a^b = b \ln a$  we have  $3 \cdot k_B \ln 2$ . The entropy of a solid depends on the number of the number of molecules and the number of possible configurations of each molecule of the solid. For a solid with for example two molecules and with each molecule having three possible configurations we'll have  $2^3$  possible microstates and the entropy will be  $k_B \ln 2^3$ . Given that  $\ln a^b = b \ln a$  we have  $3 \cdot k_B \ln 2$ . For a larger sample, containing one mole of atoms, the number of microstates is very larger, in particular  $2^{6.02 \times 10^{23}}$ . Hence the value of the entropy is  $6.02 \times 10^{23} \cdot k_B \ln 2 = 5.75\text{J/K}$ . This value is called the residual entropy of a sample, the entropy at  $0\text{K}$  that results from positional disorder.





## Sample Problem 9

Calculate the residual entropy for one mole of methane  $\text{CH}_4$  at 0K.

**SOLUTION**

Methane has four possible arrangements due to its symmetry as the molecules of methane are tetrahedral. Hence for a mole of molecules we have that the residual entropy would be

$$6.02 \times 10^{23} \cdot k_B \ln 4 = 11.5 \text{ J/K}$$

given that  $k_B = 1.38 \times 10^{-23} \text{ J/K}$ .

**STUDY CHECK**

Calculate the residual entropy for one mole of water at 0K and compare your value with the experimental result of  $3.4 \text{ J/K}$ . Assume water has two equivalent configurations.

►Answer: 5.76

*The laws of thermodynamics: a review* There are four laws of thermodynamics. The zeroth law deals with heat transfer and says that two systems in thermal equilibrium are also in thermal equilibrium with a third system equilibrated with one of them. On the other hand, the first law of thermodynamics deals with internal energy, claiming that the internal energy of a system is conserved. The second law deals with entropy claiming that the entropy of the universe can only increase. Finally, the last and third law of thermodynamics deals with the scale of entropies defining the minimum entropy value.

## 7.7 Gibbs free-energy

We have addressed two thermodynamic functions at this point: enthalpy and entropy. The first is associated with the energy exchange whereas the second is associated with the spreading of energy. At the same time, the second law of thermodynamics helps predicts the spontaneity of a process. Still, this second law is written in terms of two different entities, the system, and its surroundings. If we combine both the entropy and the enthalpy we obtain a new thermodynamic function associated with spontaneity, the Gibbs free-energy.

*Definition of Gibbs free-energy* The Gibbs free-energy is just a combination of enthalpy and entropy for a given temperature:

$$G = H - T \cdot S \quad (7.13)$$

Working at constant temperature, we can compute the change in Gibbs free energy as:

$$\Delta G^T = \Delta H - T \Delta S \quad \text{Gibbs free-energy} \quad (7.14)$$

where:

$\Delta G^T$  is the Gibbs free-energy change at constant temperature

$\Delta H$  is the enthalpy change

$\Delta S$  is the entropy change

$T$  is the temperature

Gibbs free-energy is a state function that only depends on the final and initial state and not the path followed. At the same time, Gibbs free-energy depends on temperature and pressure—we will discuss more about this at the end of the section. More importantly, the change in Gibbs free-energy is associated with the spontaneity of the process. Gibbs free-energy decreases with temperature and the decrease is sharper for gases in comparison to liquids, and at the same time, the decrease is also sharper for liquids in comparison to solids.

*Gibbs free-energy and spontaneity* The Gibbs free-energy change of a reaction is associated with the spontaneity of the process or with its state of equilibrium. In particular, reactions that produce Gibbs free-energy are nonspontaneous. Differently, reaction consuming free-energy are indeed spontaneous. Finally, reaction without a change in free-energy are in equilibrium.

☞  $\Delta G < 0$ : The reaction is spontaneous

☞  $\Delta G = 0$ : The reaction is in equilibrium

☞  $\Delta G > 0$ : The reaction is nonspontaneous

This is because the expression of Gibbs free energy is related to the total entropy change of the universe given by the second law of thermodynamics:

$$\Delta G^T = \Delta H - T\Delta S \quad \text{and} \quad T\Delta S_{univ}^{T,P} = -(\Delta H - T\Delta S) \quad (7.15)$$

Hence, we have that

$$\Delta G^T = T\Delta S_{univ}^{T,P} \quad (7.16)$$

This last expression means that an increase in total entropy is accompanied by a decrease in Gibbs free energy at constant pressure and temperature. At the same time the expression indicates that the direction of spontaneous change corresponds to a decrease of Gibbs free energy, at constant temperature and pressure.

*Estimating spontaneity based on the sign of  $H$  and  $S$*  As Gibbs free-energy depends on the enthalpy and entropy. We can estimate the sign of  $\Delta G$  from the signs of  $\Delta H$  and  $\Delta S$ . Table 7.2 below show the different sign combinations.

**Table 7.2 Sign combination of entropy and enthalpy in connection with  $G$**

$\Delta H$ Sign	$\Delta S$ Sign	$\Delta G$ Sign	Spontaneity
–	+	–	Always spontaneous
+	–	+	Always nonspontaneous
–	–	– for $T < T_c$ and + for $T > T_c$	Conditionally Spontaneous: below $T_c$
+	+	+ for $T < T_c$ and – for $T > T_c$	Conditionally Spontaneous: above $T_c$

The reasoning behind the different sign combinations is that as Gibbs free-energy is related to minus the entropy, to achieve a final negative value of  $G$  we need negative enthalpy and positive entropy that would lead to a spontaneous process that consumes free-energy. In other words, exothermic processes that produce heat and processes that produce entropy are spontaneous. Differently, endothermic processes that consume



heat and processes that consume entropy are nonspontaneous. For entropy and enthalpy changes with the same sign, then the spontaneity will depend on temperature. For example, to carry endothermic processes and processes that produce entropy, we would need high temperatures that help enthalpy. In the case of an exothermic process that consumes entropy, we would need low temperatures that help alleviate the entropy. For both cases, the critical temperature for spontaneity is given by:

$$T_c = \frac{\Delta H}{\Delta S} \quad (7.17)$$

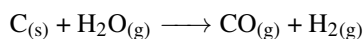
where:

$T_c$  is the critical temperature for spontaneity in Kelvins

Mind that the units of  $\Delta H$  tend to be kJ/mol, whereas the units of  $\Delta S$  tend to be J/mol. Therefore, we need to remove the kilo prefix to calculate  $T_c$ . For example, to combine an enthalpy value of 100KJ/mol with an entropy value of 5J/mol, we would have to convert the enthalpy value into 100000J/mol.

#### Sample Problem 10

For the reaction:



we have that  $\Delta H_R^\circ$  is 113kJ/mol and  $\Delta S_R^\circ$  is 133J/K·mol. Indicate whether the reaction will proceed spontaneously. Will it proceed at 200K? Will it proceed at 900K?

#### SOLUTION

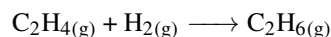
When the entropy change and the enthalpy change have the same sign, the reaction will be conditionally spontaneous. In this case, we would need to overcome the positive enthalpy change and we can do this at very high temperatures. In particular, temperatures higher than a critical value give by:

$$T_c = \frac{\Delta H}{\Delta S} = \frac{113 \times 10^3}{133} = 850\text{K}$$

The reaction will not proceed at temperatures below 850K as such it will not proceed at 100, but it will work at 900K.

#### STUDY CHECK

For the reaction:



we have that  $\Delta H_R^\circ$  is -135kJ/mol and  $\Delta S_R^\circ$  is -120J/K·mol. Indicate under which temperature conditions will the reaction proceed spontaneously.

►Answer: spontaneous below 1125K

*Standard Gibbs free-energy of formation* The Gibbs free-energy  $G$  of a compound depends on temperature, pressure as well as composition, which means that for every pressure, temperature, and molarity we have a different free-energy value. Similar to the case of enthalpy, a standard state is defined in order to tabulate the free-energy values  $\Delta G^\circ$  (see Table 7.5). The standard states of an element represent its most stable form at 1atm and 298K. In the case of solutions, the standard state corresponds to

a 1 molar concentration and in the case of gases to a 1 atm pressure. Table 7.3 list the reference state for a few elements. For example, you can find Bromine as a solid, liquid or gas. However, its natural state is liquid. That is the reason why  $\Delta G^\circ(\text{Br}_{2(g)}) = 3\text{KJ/mol}$ , whereas  $\Delta G^\circ(\text{Br}_{2(l)}) = 0\text{KJ/mol}$ . In general, for metals, its natural state is solid. For non-metallic elements, such as hydrogen, oxygen, nitrogen, fluorine, chlorine, its natural state is in the form of a diatomic gas molecule. For example,  $\Delta G^\circ(\text{H}_{2(g)}) = 0\text{KJ/mol}$ ,  $\Delta G^\circ(\text{N}_{2(g)}) = 0\text{KJ/mol}$  or  $\Delta G^\circ(\text{O}_{2(g)}) = 0\text{KJ/mol}$ . For the case of carbon, its natural state is graphite,  $\Delta G^\circ(\text{C}_{\text{graphite}(s)}) = 0\text{KJ/mol}$ . Molecules such as  $\text{H}_2\text{O}$  or  $\text{NO}$  have standard free-energy different than zero. Mind that molecules are made of elements. The establishment of a Gibbs free energy scale based on a set of reference states allows the calculation of standard Gibbs free energies of formation  $\Delta G_f^\circ$ : the Gibbs free energy of formation per mole of the formation of a compound from its elements on its most stable states. The values for Gibbs free energy of formation  $\Delta G_f^\circ$  are tabulated at  $25^\circ\text{C}$ . These values inform about the stability of the compound with respect to its elements. For example,  $\Delta G_f^\circ$  for ammonia is  $-16\text{KJ/mol}$ , which means that ammonia is thermodynamically stable and will not decompose to produce hydrogen and nitrogen spontaneously. Different,  $\Delta G_f^\circ$  for  $\text{NO}_2$  is  $51\text{KJ/mol}$ . This positive value indicates that nitrogen dioxide will spontaneously decompose into nitrogen and oxygen. Still, even when the decomposition of a chemical is favored by the laws of thermodynamics, its rate might be slow, and only kinetics can inform about the timing of the decomposition. Chemicals are called labile (nonlabile) when they decompose or react quickly (slowly).

**Table 7.3 Standard states for different elements. For all  $\Delta G^\circ = 0 \text{ KJ/mol}$**

Element	Standard state	Element	Standard state
Hydrogen	$\text{H}_{2(g)}$	Oxygen	$\text{O}_{2(g)}$
Nitrogen	$\text{N}_{2(g)}$	Chlorine	$\text{Cl}_{2(g)}$
Iron	$\text{Fe}_{(s)}$	Aluminium	$\text{Al}_{(s)}$
Carbon	$\text{C}_{\text{graphite}(s)}$	Phosphorus	$\text{P}_{4(s)}$
Fluorine	$\text{F}_{2(g)}$	Bromine	$\text{Br}_{(l)}$
Mercury	$\text{Hg}_{(l)}$	Sulfur	$\text{S}_{8(s)}$
Iodine	$\text{I}_{2(s)}$	Silicon	$\text{Si}_{(s)}$

*Standard free-energy of a reaction,  $\Delta G_R^\circ$*  We can calculate the standard free-energy of a reaction in a similar way as we calculate the standard enthalpy or entropy of a reaction:

$$\Delta G_R^\circ = \Delta G_{\text{products}}^\circ - \Delta G_{\text{reactants}}^\circ \quad \text{Free-energy change} \quad (7.18)$$

where:

$\Delta G_R^\circ$  is the standard Gibbs free-energy change of the reaction

$\Delta G_{\text{products}}^\circ$  is the standard Gibbs free-energy of all products

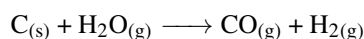
$\Delta G_{\text{reactants}}^\circ$  is the standard Gibbs free-energy of all reactants

There are two possible ways to calculate  $\Delta G_R^\circ$ . We can compute  $\Delta G_R^\circ$  from the enthalpy and entropy change at fixed 298K. Remember the standard thermodynamic parameters are computer at this temperature. Or we can compute  $\Delta G_R^\circ$  from the tabulated  $G_R^\circ$  values. The next two examples walk you through these two possible scenarios.



## Sample Problem 11

Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



Compound	$\Delta H_f^\circ$	$S^\circ$
$\text{C}_{(\text{s})}$	0	5.7
$\text{H}_2\text{O}_{(\text{g})}$	-241.8	188.7
$\text{CO}_{(\text{g})}$	-110.5	197.6
$\text{H}_{2(\text{g})}$	0	130.6

**SOLUTION**

As we have the standard formation enthalpy values and the standard entropy values, we can compute the entropy and enthalpy of reaction. We have that:

$$\begin{aligned}\Delta H_R^\circ &= \Delta H_{\text{products}}^\circ - \Delta H_{\text{reactants}}^\circ = \\ & \left( \Delta H_f^\circ(\text{CO}_{(\text{g})}) + \Delta H_f^\circ(\text{H}_{2(\text{g})}) \right) - \left( \Delta H_f^\circ(\text{C}_{(\text{s})}) + \Delta H_f^\circ(\text{H}_2\text{O}_{(\text{g})}) \right) \\ &= (-110.5 + 0) - (0 + -241.8) = 131.3 \text{ kJ}\end{aligned}$$

We also have:

$$\begin{aligned}\Delta S_R^\circ &= \Delta S_{\text{products}}^\circ - \Delta S_{\text{reactants}}^\circ = \\ & \left( \Delta S^\circ(\text{CO}_{(\text{g})}) + \Delta S^\circ(\text{H}_{2(\text{g})}) \right) - \left( \Delta S^\circ(\text{C}_{(\text{s})}) + \Delta S^\circ(\text{H}_2\text{O}_{(\text{g})}) \right) \\ &= (197.6 + 130.6) - (5.7 + 188.7) = 133.8 \text{ J/K}\end{aligned}$$

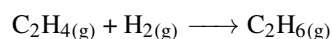
We have that the Gibbs free-energy will be:

$$\Delta G = \Delta H - T\Delta S = 131.3 \times 10^3 - 298 \cdot 133.8 = 91427.6 \text{ J} = 91.4 \text{ kJ}$$

As the free-energy is positive the reaction is not spontaneous. The reason for this non-spontaneity is the endothermicity. As such working at high temperatures we can overcome the enthalpy, in particular working at temperatures higher than 981K.

**STUDY CHECK**

Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



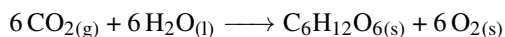
Compound	$\Delta H_f^\circ$	$S^\circ$
$\text{C}_2\text{H}_{4(\text{g})}$	-52.5	219.5
$\text{H}_{2(\text{g})}$	0	130.6
$\text{C}_2\text{H}_{6(\text{g})}$	-84.7	229.5

$$\blacktriangleright \Delta H_R^\circ = -32 \text{ kJ}; \Delta S_R^\circ = -120.6 \text{ J/K}; \Delta G_R^\circ = 4 \text{ kJ}; \text{spontaneous for } T < 265 \text{ K}$$

In the following example we will show how to compute Gibbs free-energy of a reaction by means of standard Gibbs free-energies of the molecules involved in the reaction.

## Sample Problem 12

Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



Compound	$\Delta G_f^\circ$
$\text{CO}_{2(g)}$	-394.4
$\text{H}_2\text{O}_{(l)}$	-237.2
$\text{C}_6\text{H}_{12}\text{O}_{6(s)}$	-910.56

**SOLUTION**

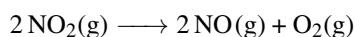
We can compute the Gibbs free-energy of a reaction by means of the free-energies of the molecules involved in the reaction:

$$\begin{aligned} \Delta G_R^\circ &= \Delta G_{products}^\circ - \Delta G_{reactants}^\circ = \left[ \Delta G_f^\circ(\text{C}_6\text{H}_{12}\text{O}_{6(s)}) + \right. \\ &\quad \left. 6\Delta G_f^\circ(\text{O}_{2(g)}) \right] - \left[ 6 \cdot \Delta G_f^\circ(\text{CO}_{2(g)}) + 6 \cdot \Delta G_f^\circ(\text{H}_2\text{O}_{(l)}) \right] \\ &= \left[ -910.56 - 6 \cdot 0 \right] - \left[ 6 \cdot -394.4 + 6 \cdot -237.2 \right] = 2879 \text{ KJ} \end{aligned}$$

As the free-energy is positive the reaction is not spontaneous.

**STUDY CHECK**

Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



Compound	$\Delta G_f^\circ$
$\text{NO}_{2(g)}$	51.3
$\text{NO}_{(g)}$	86.6

$$\blacktriangleright \Delta G_R^\circ = 71 \text{ kJ}; \text{ nonspontaneous}$$

## 7.8 Gibbs free-energy and equilibrium

We can use the principles of thermodynamics to study different phase transitions such as the transition between solid and liquid (melting or fusion) or liquid and gas (vaporization or boiling). These phase transitions are examples of equilibrium. During these transitions the temperature remains constant and all energy supplied is used to convert molecules between the two equilibrated phases and not to warm up the system. For example, the boiling point of water at 1 atm is 100°C and during boiling—also called vaporization—even when we continue the heating the temperature of water remains constant at 100°C until all water molecules become vapor. At the same time during a phase transition the Gibbs free energy of the two phase in equilibrium are the same.

*Gibbs free-energy in equilibrium* In equilibrium a system does not evolve in any direction, or it evolved back and forth in the same direction. For example in equilibrium a reaction proceed forward and backwards at the same pace. In these



conditions, the total entropy of the system and universe do not change ( $\Delta S_{univ}^{T,P} = 0$ ). In these conditions the Gibbs free energy do not change either. Overall we have:

$$\Delta G^{T,P} = 0 \quad (7.19)$$

*Gibbs free-energy and phase transitions* Gibbs free energy are useful to calculate phase transition temperatures, that is the temperature to melt a solid or vaporize a liquid. As a phase transition is an equilibrium process and as in equilibrium we have that  $\Delta G_{T,P}^{\circ} = 0$  we can estimate the fusion and vaporization temperatures using the formulas below involving the entropy and enthalpy values for a phase transition (see Table 7.4 for those values):

$$T_{fus} = \frac{\Delta H_{fus}^{\circ}}{\Delta S_{fus}^{\circ}} \quad \text{and} \quad T_{vap} = \frac{\Delta H_{vap}^{\circ}}{\Delta S_{vap}^{\circ}} \quad (7.20)$$

where:

$T_{melt}$  and  $T_{vap}$  are the fusion and vaporization temperature in Kelvins

$\Delta H_{fus}^{\circ}$  and  $\Delta S_{fus}^{\circ}$  is the enthalpy and entropy of fusion

$\Delta H_{vap}^{\circ}$  and  $\Delta S_{vap}^{\circ}$  is the enthalpy and entropy of vaporization

The following example describes how to compute phase transition temperatures using thermodynamic data.

#### Sample Problem 13

Calculate the fusion and vaporization temperatures of benzene given that  $\Delta H_{fus}^{\circ} = 10.9 \text{ kJ/mol}$ ,  $\Delta H_{vap}^{\circ} = 33.9 \text{ kJ/mol}$ ,  $\Delta S_{fus}^{\circ} = 38.0 \text{ J/mol} \cdot \text{K}$  and  $\Delta S_{vap}^{\circ} = 87.19 \text{ J/mol} \cdot \text{K}$ .

#### SOLUTION

In order to calculate the temperature of fusion for benzene we just need to divide the enthalpy and entropy of fusion making sure the units are consistent (converting enthalpy into J/mol)

$$T_{fus} = \frac{\Delta H_{fus}^{\circ}}{\Delta S_{fus}^{\circ}} = \frac{10.9 \times 10^3}{38.0} = 287 \text{ K}$$

Similarly, in order to calculate the temperature of vaporization for benzene we just need to divide the enthalpy and entropy of vaporization making sure the units are consistent (converting enthalpy into J/mol)

$$T_{vap} = \frac{\Delta H_{vap}^{\circ}}{\Delta S_{vap}^{\circ}} = \frac{33.9 \times 10^3}{87.19} = 389 \text{ K}$$

#### STUDY CHECK

Estimate the fusion and vaporization temperatures in celcius of water given that  $\Delta H_{fus}^{\circ} = 6.007 \text{ kJ/mol}$ ,  $\Delta H_{vap}^{\circ} = 40.66 \text{ kJ/mol}$ ,  $\Delta S_{fus}^{\circ} = 22.00 \text{ J/mol} \cdot \text{K}$  and  $\Delta S_{vap}^{\circ} = 109.00 \text{ J/mol} \cdot \text{K}$ .

► -0.3°C and 100°C



Entropies and enthalpies of phase transition at 1atm

$T_{fus}^{\circ}$ (kJ/mol)	$\Delta H_{vap}^{\circ}$ (kJ/mol)	Compound	$\Delta S_{fus}^{\circ}$ (J/mol·K)	$\Delta S_{vap}^{\circ}$ (J/mol·K)
88	6.447	Ar(g)	14.17	74.53
	29.8	Br <sub>2</sub> (g)	39.76	88.61
9	33.9	C <sub>6</sub> H <sub>6</sub> (g)	38.00	87.19
7	11.72	CH <sub>3</sub> COOH(g)	40.40	61.90
1	40.66	H <sub>2</sub> O(g)	22.00	109.00
5	23.35	NH <sub>3</sub> (g)	28.93	97.41

*Gibbs free-energy and work* The Gibbs free-energy of a reaction gives an estimate of the thermodynamic feasibility of a reaction. In other words, if Gibbs free-energy predicts that a reaction will not likely happen there is no need to invest time in energy trying to make a reaction work. The change in Gibbs free-energy, as its name indicates, also gives insight into the maximum amount of work—in particular nonexpansive work—that can be extracted from a system (chemical reaction, an engine, etc). More precisely,  $\Delta G$  represents the maximum amount of work that can be extracted from a system at a fixed pressure and temperature conditions. It represents the amount of useful energy to do work that a system has. When this value is positive, it represents the amount of work that needs to be put into the system in order to make the process work:

$$w \leq \Delta G_R \quad (7.21)$$

Gibbs free energy also tells about how efficient the energy conversion is. Let us analyze the energy contained in the battery of a cell phone. We could use this energy to produce work and power the cell phone. However, every electricity flow implies a loss of heat due to friction, and hence all energy contained in the battery could only be used if the electricity flow is very very small and under these conditions, the battery will not be able to do real work. Hence, energy can only fully used to do work in a hypothetical scenario in which the process works reversibly. However, all real processes are irreversibly and energy will always be lost. For such reason, it will take more energy to charge a battery than the energy given by the battery, as an irreversible electric flow implies energy loss. In other words, energy irreversibly used degrades on its use.

## 7.9 Gibbs free-energy and pressure conditions

Thermodynamics studies states of equilibrium, whereas chemical kinetics studies the rate at which chemical reactions reach equilibrium. Gibbs free energy  $\Delta G$  is a thermodynamic function used to describe how a system spontaneously approaches equilibrium. During a spontaneous chemical reaction,  $\Delta G$  decreases until reaching a minimum value when the reaction reaches equilibrium. Differently,  $\Delta G^{\circ}$ —defined in standard pressure conditions—has a fixed value that does not change during a reaction. Still, this function depends on temperature and pressure and until now we did not address how the pressure conditions affect the equilibrium.

*Impact of pressure on Gibbs free-energy* The standard Gibbs free-energy of reaction is calculated at standard pressure conditions (1 atm) and tabulated at 298K. What if we are not in standard conditions? When a reaction involving gas-phase reactants advances towards equilibrium forming products, the pressure in the container



increases. As gas molecules are being produced the pressure will depart from 1 atm. We can use the following expression to include the effect of pressure on  $\Delta G_R^\circ$ :

$$\Delta G_R = \Delta G_R^\circ + RT \ln Q_p \quad (7.22)$$

where:

$\Delta G_R$  is the Gibbs free-energy of a reaction not at standard conditions

$\Delta G_R^\circ$  is the Gibbs free-energy of a reaction at standard conditions (1 atm and 298 K)

$Q_p$  is the reaction ratio in terms of pressure

$R$  is the constant of the gases in energy units (8.314 J/mol · K)

$T$  is the absolute temperature

Pressure is another variable—similar to temperature—that can be used to favor chemical reactions. For example, the reaction between hydrogen and iodine exhibits a positive standard Gibbs free-energy ( $\Delta H_R^\circ = +53 \text{ kJ}$ ;  $\Delta S_R^\circ = +166.3 \text{ J/K}$ ). Under standard conditions, at 1 atm and 298 K, the reaction will not likely happen



Including the effects of pressure on the calculation of Gibbs free energy we have that at very low products pressures and relatively large reactant pressures ( $P_{\text{HI}} = 1 \times 10^{-5}$  atm and  $P_{\text{H}_2} = 1 \times 10^5$  atm) Gibbs free energy is negative:

$$\begin{aligned} \Delta G_R &= \Delta G_R^\circ + RT \ln Q_p = \Delta G_R^\circ + RT \ln \left[ \frac{P_{\text{HI}}^2}{P_{\text{H}_2}} \right] \\ &= 3.44 \times 10^3 + 8.314 \cdot 298 \ln \left[ \frac{(1 \times 10^{-5})^2}{1 \times 10^5} \right] = -8.2 \times 10^4 \text{ J/mol} \end{aligned}$$

These calculations demonstrate that one can tune the pressure conditions to favor a reaction. In general large reactant pressures and low products pressures can alleviate positive Gibbs free-energy values.

#### Sample Problem 14

Predict whether the reaction will proceed spontaneously at 298 K under the following pressure conditions:  $P_{\text{NO}_2} = 1 \times 10^5$  atm and  $P_{\text{N}_2\text{O}_4} = 1 \times 10^{-5}$  atm



#### SOLUTION

The working pressure-conditions consist of large product pressures and small reactant pressures, and these conditions do not tend to favor spontaneity. Before proving this, we need to remember to remove the kilo prefix in the standard Gibbs free energy value, as  $R$  is expressed in J:

$$\begin{aligned} \Delta G_R &= \Delta G_R^\circ + RT \ln Q_p = \Delta G_R^\circ + RT \ln \left[ \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \right] \\ &= 5.4 \times 10^3 + 8.314 \cdot 298 \ln \left[ \frac{(1 \times 10^5)^2}{1 \times 10^{-5}} \right] = 9 \times 10^4 \text{ J/mol} \end{aligned}$$

As Gibbs free-energy is a positive number, the reaction will not proceed spontaneously.

### STUDY CHECK

Predict whether the reaction will proceed spontaneously at 298K under the following pressure conditions:  $P_{\text{NO}_2} = 1 \times 10^{-5}$  atm and  $P_{\text{N}_2\text{O}_4} = 1 \times 10^5$  atm



$$\Delta G_R = -8 \times 10^4 \text{J/mol spontaneous}$$

*Relationship between  $\Delta G_R^\circ$  and  $K_p$*  On one hand, at fixed pressure and temperature, the Gibbs free-energy does not change:  $\Delta G_R = 0$ . On the other hand, at fixed pressure and temperature, the entropy of the universe does not change:  $\Delta S_{\text{univ}} = 0$ .

At the same time, in equilibrium conditions, the value of the equilibrium constant is the same as the value of the reaction ratio:  $Q_p = K_p$ . Hence, we can relate the equilibrium constant and the standard Gibbs free-energy:

$$\Delta G_R^\circ = -RT \ln K_p \quad (7.23)$$

where:

$K_p$  the equilibrium constant in terms of pressure

$\Delta G_R^\circ$  is the Gibbs free-energy of a reaction at standard conditions (1atm and 298K)

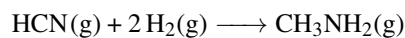
$R$  is the constant of the gases in energy units (8.314J/mol · K)

$T$  is the absolute temperature

In other words, the value of the equilibrium constant and the standard Gibbs free-energy convey the same information. On one hand, when  $\Delta G_R^\circ < 0$  we have that  $K_p > 1$  and in the reactive mixture we will have more products than reactants: the reaction will happen spontaneously. On the other hand, when  $\Delta G_R^\circ > 0$  we have that  $K_p < 1$  and in the reactive mixture will have more reactants than products: the reaction will not happen spontaneously.

### Sample Problem 15

Use the data below to calculate the equilibrium constant of the reaction at 400K:



Compound	$G_f^\circ$ (KJ/mol)
$\text{CH}_3\text{NH}_2\text{(g)}$	23.99
$\text{HCN}_{(s)}$	124.7

### SOLUTION

We can compute the Gibbs free-energy of a reaction by means of the free-energies of the molecules involved in the reaction:

$$\begin{aligned} \Delta G_R^\circ &= \Delta G_{\text{products}}^\circ - \Delta G_{\text{reactants}}^\circ = \\ & \left[ \Delta G_f^\circ(\text{CH}_3\text{NH}_2\text{(g)}) \right] - \left[ 1 \cdot \Delta G_f^\circ(\text{HCN}_{(g)}) + 2 \cdot \Delta G_f^\circ(\text{H}_2\text{(g)}) \right] \\ &= \left[ 23.99 \right] - \left[ 1 \cdot 124.7 + 2 \cdot 0 \right] = -100.71 \text{KJ} \end{aligned}$$



Now we can convert the Gibbs free-energy of the reaction into  $K_c$ . Mind that we need to remove the Kilo prefix in the Gibbs free energy:

$$-100.71 \times 10^3 = -RT \ln K_p = -8.314 \cdot 400 \ln K_p$$

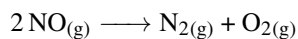
Solving for  $K_p$  we have that:

$$K_p = e^{\frac{100.71 \times 10^3}{8.314 \cdot 400}} = 1.4 \times 10^{13}$$

We have that, as the Gibbs free-energy of reaction is negative, the value of the equilibrium constant is larger than 1. This means that the reaction will proceed spontaneously and that there will have more products than reactants in the reaction mixture.

### ◆ STUDY CHECK

Use the data below to calculate the equilibrium constant of the reaction at 400K given that  $G_f^\circ(\text{NO}_{(g)})=87.60\text{KJ/mol}$ :



$$\blacktriangleright K_p = 7.6 \times 10^{22}$$





Table 7.5 Standard thermodynamic functions at 1 atm and 298 K.\*

Substance	$\Delta H_f^\circ$ (KJ/mol)	$\Delta G_f^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol·K)	Substance	$\Delta H_f^\circ$ (KJ/mol)	$\Delta G_f^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol·K)	Substance	$\Delta H_f^\circ$ (KJ/mol)	$\Delta G_f^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol·K)	Substance	$\Delta H_f^\circ$ (KJ/mol)	$\Delta G_f^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol·K)
Al(s)	0	0	28.3	Ba(BrO <sub>3</sub> ) <sub>2</sub> (s)	-752.7	-577.4	243.0	BN(s)	-254.4	-228.4	14.8	CaCl <sub>2</sub> ·6H <sub>2</sub> O(s)	-2607.9	-2205.0	284.9
Al <sub>2</sub> (g)	5483.9	NA <sup>†</sup>	149.9	Ba(BrO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O(s)	-1054.8	-824.6	292.5	B <sub>2</sub> S <sub>3</sub> (s)	-240.6	-229.0	57.4	Ca(ClO <sub>4</sub> ) <sub>2</sub> (s)	-736.8	NA <sup>†</sup>	233.0
Al(aq)	-524.7	-481.2	—	Ba <sub>2</sub> (s)	-602.1	-609.0	167.0	Br <sub>2</sub> (l)	0	0	152.2	Ca(ClO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(s)	-1948.9	-1476.8	433.5
AlF <sub>3</sub> (s)	-1504.1	-1425.1	66.4	Ba <sub>2</sub> ·2H <sub>2</sub> O(s)	-1216.7	NA <sup>†</sup>	0.63	Br <sub>2</sub> (g)	30.9	3.1	245.4	CaBr <sub>2</sub> (s)	-682.8	-663.6	130.0
AlCl <sub>3</sub> (s)	-704.2	-628.9	110.7	Ba(FO <sub>3</sub> ) <sub>2</sub> (s)	-1027.2	-864.8	249.0	Br <sub>2</sub> (g)	30.9	3.1	245.4	CaBr <sub>2</sub> ·6H <sub>2</sub> O(s)	-2506.2	-2153.1	410.0
AlCl <sub>3</sub> ·6H <sub>2</sub> O(s)	-2691.6	NA <sup>†</sup>	—	Ba(FO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O(s)	-1322.1	-1104.2	297.0	Br <sub>2</sub> (g)	-233.9	-238.7	163.4	Ca(BrO <sub>3</sub> ) <sub>2</sub> (s)	-718.8	NA <sup>†</sup>	227.6
AlBr <sub>3</sub> (s)	-527.2	-488.4	163.2	BaO(s)	-553.5	-525.1	70.4	Cd	0	0	51.8	CaI <sub>2</sub> (s)	-533.5	-528.9	142.0
AlI <sub>3</sub> (s)	-313.8	-300.8	159.0	Ba(OH) <sub>2</sub> (s)	-634.3	-572.0	65.7	Cd <sub>2</sub> <sup>+</sup>	2623.5	NA <sup>†</sup>	167.7	Ca <sub>2</sub> ·8H <sub>2</sub> O(s)	-2929.6	NA <sup>†</sup>	—
Al <sub>2</sub> O <sub>3</sub> (s)	-1675.7	-1582.4	50.9	BaCO <sub>3</sub> (s)	-1216.3	-1137.6	112.1	Cd <sub>2</sub> <sup>+</sup>	2623.5	NA <sup>†</sup>	167.7	Ca(FO <sub>3</sub> ) <sub>2</sub> (s)	-1002.5	-893.3	230.1
Al(OH) <sub>3</sub> (s)	-1287.4	-1149.8	85.4	Ba(HCO <sub>3</sub> ) <sub>2</sub> (s)	-1921.6	-1734.3	192.0	CdF <sub>2</sub> (s)	-700.4	-647.7	77.4	Ca(FO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O(s)	-1293.3	NA <sup>†</sup>	—
Al(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O(s)	-2850.5	-2203.9	467.8	Ba(NO <sub>3</sub> ) <sub>2</sub> (s)	-921.1	-796.7	213.8	CdCl <sub>2</sub> (s)	-391.5	-344.0	115.3	Ca(FO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O(s)	-2780.7	-2267.7	451.9
Al <sub>2</sub> S <sub>3</sub> (s)	-723.8	NA <sup>†</sup>	decomp.	BaS(s)	-460.0	-456.0	78.2	CdCl <sub>2</sub> ·H <sub>2</sub> O(s)	-688.4	-587.1	167.8	CaO(s)	-635.1	-604.0	39.7
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s)	-3440.0	-3100.1	239.3	BaSO <sub>4</sub> (s)	-1473.2	-1362.3	151.9	Cd(ClO <sub>4</sub> ) <sub>2</sub> (aq)	-334.6	-94.8	290.8	Ca(OH) <sub>2</sub> (s)	-986.1	-898.6	83.4
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O(s)	-5311.7	-4622.6	469.0	BaSO <sub>4</sub> (s)	-1473.2	-1362.3	151.9	Cd(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O(s)	-2052.7	NA <sup>†</sup>	—	CaC <sub>2</sub> (s)	-59.1	-64.8	69.9
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O(s)	-8878.9	-7437.5	—	BaCrO <sub>4</sub> (s)	-1428.0	-1338.8	132.2	CdBr <sub>2</sub> (s)	-316.2	-296.3	137.2	CaCO <sub>3</sub> (s), calcite	-1206.9	-1128.8	92.9
Sb	2703.3	NA <sup>†</sup>	168.7	BaC <sub>2</sub> O <sub>4</sub> (s)	-1368.6	NA <sup>†</sup>	5.2 × 10 <sup>-5</sup>	CdI <sub>2</sub> (s)	-203.3	-201.4	161.1	CaCO <sub>3</sub> (s), aragonite	-1207.1	-1127.8	88.7
Sb <sub>2</sub> (g)	145.1	147.7	232.7	BaC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O(s)	-1971.1	NA <sup>†</sup>	5.20 × 10 <sup>-5</sup>	Cd(IO <sub>3</sub> ) <sub>2</sub> (s)	NA <sup>†</sup>	377.1	NA <sup>†</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub> (s)	-635.1	-743.2	193.3
SbF <sub>3</sub> (s)	-915.5	-807.0	105.4	Be	0	0	9.5	CdO(s)	-258.2	-228.4	54.8	Ca(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O(s)	-1540.8	-1229.3	269.4
SbCl <sub>3</sub> (s)	-382.2	-323.7	184.0	Be <sub>2</sub> <sup>+</sup>	2993.0	NA <sup>†</sup>	136.2	Cd(OH) <sub>2</sub> (s)	-560.7	-473.6	96.0	Ca(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O(s)	-1838.0	-1471.9	319.2
SbCl <sub>5</sub> (l)	-440.2	-350.2	301.0	BeF <sub>2</sub> (s)	-1026.8	-979.5	53.2	Cd(CN) <sub>2</sub> (s)	162.2	-209.0	104.2	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(s)	-2132.3	-1713.5	375.3
Sb <sub>2</sub> O <sub>6</sub> (s)	-1440.6	-1268.2	220.9	BeCl <sub>2</sub> (s)	-1808.3	-1563.0	243.1	Cd(NO <sub>3</sub> ) <sub>2</sub> (s)	-456.3	-259.0	197.9	CaS(s)	-482.4	-477.4	56.5
Sb <sub>2</sub> S <sub>3</sub> (black)(s)	-174.9	-173.6	182.0	BeCl <sub>2</sub> ·4H <sub>2</sub> O(s)	-353.5	-354.0	112.1	Cd(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O(s)	-1055.6	-748.9	NA <sup>†</sup>	CaSO <sub>4</sub> (s)	-1156.0	NA <sup>†</sup>	—
Sb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s)	-2402.5	NA <sup>†</sup>	—	BeBr <sub>2</sub> (s)	-609.6	-580.3	14.1	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(s)	-1649.0	-1217.1	NA <sup>†</sup>	CaSO <sub>4</sub> ·0.5H <sub>2</sub> O(s)	-1431.1	-1321.9	106.7
As	0	0	35.1	BeO(s)	-609.6	-580.3	14.1	CdSO <sub>4</sub> (s)	-933.3	-822.8	123.0	CaSO <sub>4</sub> ·2H <sub>2</sub> O(s)	-2022.6	-1797.4	194.1
As <sub>2</sub> (s)	0	0	35.1	Be(OH) <sub>2</sub> (s)	-902.4	-815.0	51.9	CdSO <sub>4</sub> ·2.67H <sub>2</sub> O(s)	-1729.4	-1465.3	229.6	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)	-4120.8	-3884.8	236.0
As <sub>2</sub> Br <sub>3</sub> (s)	5950.2	NA <sup>†</sup>	162.3	Be(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O(s)	-787.8	NA <sup>†</sup>	0.804	Cs	0	0	—	CaC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	-1379.0	-1277.4	133.9
AsF <sub>3</sub> (l)	-956.3	-909.1	181.2	BeSO <sub>4</sub> (s)	-234.3	-232.0	35.0	Cs <sub>2</sub> (s)	458.0	NA <sup>†</sup>	169.7	CaC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O(s)	-1674.9	-1514.0	156.5
AsF <sub>5</sub> (g)	-920.6	-905.7	289.0	BeSO <sub>4</sub> ·4H <sub>2</sub> O(s)	-1205.2	-1093.9	77.9	Cs <sub>2</sub> <sup>+</sup>	-553.5	-525.5	92.8	CaSi <sub>2</sub> (s)	-151.0	NA <sup>†</sup>	decomp.
AsCl <sub>3</sub> (l)	-305.0	-259.4	216.3	Bi	0	0	56.9	CsCl <sub>3</sub> (s)	-443.0	-414.5	101.2	CaSiO <sub>3</sub> (s)	-1634.9	-1549.7	81.9
AsBr <sub>3</sub> (s)	-197.5	-169.0	161.1	Bi <sub>2</sub> <sup>+</sup>	5005.7	NA <sup>†</sup>	—	CsClO <sub>3</sub> (s)	-411.7	-307.9	156.1	Ca <sub>2</sub> SiO <sub>4</sub> (s)	-2307.5	-2192.8	127.7
As <sub>2</sub> O <sub>3</sub> (s)	-653.0	-571.0	117.0	BiCl <sub>3</sub> (s)	-379.1	-315.1	177.0	CsClO <sub>4</sub> (s)	-443.1	-314.3	175.1	C(s), graphite	0	0	5.7
As <sub>2</sub> O <sub>5</sub> (s)	-924.9	-782.4	105.4	Bi(ClO <sub>3</sub> ) <sub>3</sub> (s)	-366.9	-322.2	120.5	CsBr(s)	-405.8	-391.4	113.1	C(s), diamond	716.7	671.3	158.0
As <sub>2</sub> O <sub>3</sub> (s)	-169.0	-168.6	163.6	BiI <sub>3</sub> (s)	-105.0	-175.3	233.9	CsI(s)	-380.7	-380.7	184.0	C <sub>2</sub> (g)	836.8	780.4	199.3
As <sub>4</sub> O <sub>6</sub> (s)	-1314.0	-1153.0	223.0	Bi <sub>2</sub> S <sub>3</sub> (s)	-573.9	-493.7	151.5	Cs <sub>2</sub> O(s)	NA <sup>†</sup>	-380.2	146.9	C <sub>3</sub> (g)	793.5	773.1	212.1
Ba	0	0	66.9	Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s)	-2544.3	-2583.6	NA <sup>†</sup>	CsOH(s)	-417.2	-359.0	86.0	CCl <sub>4</sub> (l)	-134.0	-65.3	214.4
Ba(s)	1660.5	NA <sup>†</sup>	170.2	B	0	0	59	CsHCO <sub>3</sub> (s)	-966.1	-831.8	130.0	CO(g)	-110.5	-137.2	197.6
Ba <sub>2</sub> <sup>+</sup>	-537.0	-560.8	9.6	B <sub>2</sub>	7468.0	NA <sup>†</sup>	138.5	CsNO <sub>3</sub> (s)	-506.0	-406.6	155.2	CO <sub>2</sub> (g)	-393.5	-394.4	213.6
Ba <sub>2</sub> (aq)	-178.7	-132.2	NA <sup>†</sup>	B <sub>2</sub> H <sub>6</sub> (g)	35.6	86.6	232.0	Cs <sub>2</sub> SO <sub>4</sub> (s)	-1443.0	-1323.7	211.9	CO <sub>2</sub> (aq)	-413.8	-386.0	117.6
BaF <sub>2</sub> (s)	-1207.1	-1156.9	96.4	B <sub>2</sub> H <sub>6</sub> (g)	-137.0	-1120.3	254.0	Ca	0	0	41.4	CO <sub>3</sub> <sup>2-</sup> (aq)	-677.1	-527.8	-56.9
BaCl <sub>2</sub> (s)	-858.6	-810.4	123.7	BF <sub>3</sub> (g)	—	—	—	Ca <sub>2</sub> <sup>+</sup>	1925.0	NA <sup>†</sup>	154.8	C <sub>2</sub> N <sub>2</sub> (g)	-307.9	296.3	242.1

[illegible]





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