

An Introduction to Chemical Thermodynamics

Part 2—Entropy, Molecular Disorder, and the Second and Third Laws

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ABSTRACT

This is the second in a series of articles, prepared at the request of the publisher of this Journal, presenting an introductory outline of chemical thermodynamics and chemical kinetics, with emphasis on those aspects of particular relevance to pyrotechnics. The First Law of Thermodynamics, which was the subject of the first article, cannot explain the direction of change in the physical world. The Second Law of Thermodynamics states that spontaneous change is always associated with an increase in the entropy of the universe. The universe is simply the system of interest plus its surroundings, assumed to be isolated from external influences, while the entropy is a thermodynamic state function. Much of this article is taken up by a discussion of entropy. The relationship between entropy and spontaneous change is clarified when entropy is interpreted as a measure of molecular disorder. The Gibbs Free Energy is a thermodynamic state function that allows the entropy change in the system and its surroundings to be predicted from the thermodynamic properties of the system alone. It provides the basis for predicting the direction of change in chemical systems. Finally, the Third Law of Thermodynamics states that the molar entropy of a pure substance is zero at the absolute zero of temperature. This is developed from Boltzmann's relationship between entropy and the number of molecular arrangements consistent with the properties of a system. It is shown how the Third Law permits the calculation of absolute values for the molar entropies of pure substances.

Keywords: thermodynamics, entropy, free energy

Introduction

The first article in this series^[1] showed how the *energy changes* involved in a chemical process can be calculated from the standard enthalpies of formation of the reactants and products. The energy change, however, does not tell us whether or not a process will occur. For example, melting ice absorbs energy and freezing water releases energy, yet both processes can occur spontaneously, depending on the temperature.

In this article the thermodynamic properties that allow the direction and extent of change in chemical systems to be predicted will be introduced and explained. Applications of these concepts to chemical systems of interest to pyrotechnists will form the third in this series of articles.

Spontaneous Processes

In chemical thermodynamics a “spontaneous” process means one that will continue to equilibrium *once it has been started*, without further input of external work. This is different from the usage in ordinary speech, where something is said to be “spontaneous” if it happens “of its own accord”. The reaction of aluminium with hydrochloric acid is spontaneous in both the conventional and the thermodynamic senses. That between aluminium and potassium perchlorate is spontaneous in the thermodynamic sense, but not in the conventional. The reasons why many thermodynamically spontaneous pro-

cesses are not spontaneous in the conventional sense are dealt with by *chemical kinetics*, to be discussed in a future article in this series.

A New State Function: The Entropy

The First Law summarizes the experience of many generations of scientists and engineers that energy cannot be created or destroyed, but is merely *transferred* in one form or another. If you watch a movie that is being run in reverse, you will see examples of energy being transferred in ways that are completely consistent with the First Law, but which never happen in the real world. Something that could happen in such a movie, but not in the real world, would be a balloon inflating by itself as air rushes into it from the room. A block of ice might emerge from a bucket of hot water, with the water coming to the boil as the ice freezes. Neither one of these processes conflicts with the First Law, but neither has ever been observed. There is clearly a preferred direction of change in the real world.

In the real world, gas at high pressure will spontaneously flow to a region of low pressure, until the pressure in both regions is the same. A cold object and a hot object in contact will come to an intermediate temperature. In each case, the system has come to equilibrium. It has also lost the ability to perform work. A system with gas at different pressures could do work through a fan or turbine placed between the two regions. A system with two bodies at different temperatures could do work through a heat engine placed between the two bodies. In coming to equilibrium, *the system has lost the ability to do work, but the internal energy of the system has not changed*. No work has been done, and no heat has been exchanged with the surroundings, so the internal energy must be the same. Energy that was once available to do work has somehow become unavailable, as the system has come to equilibrium.

In the examples just given, at the beginning of the process some thermodynamic state function was different in various parts of the system. In one case, the pressure was different. In another, the temperature was different. To reach equilibrium, the system changed in such a way that the state functions became equal in all parts of the system. This leads to an important ques-

tion. Is there a state function that can be used to indicate whether or not a *chemical* system is in thermodynamic equilibrium? Clearly pressure and temperature will not suffice. A mixture of potassium perchlorate and powdered aluminium might well be at uniform temperature and pressure, but it is certainly very far from a state of thermodynamic equilibrium. A new state function is needed. To arrive at it, however, requires a measure of the loss of ability to perform work that accompanied the attainment of equilibrium in the two simple examples just discussed.

In the nineteenth century Clausius^[2a] introduced a thermodynamic state function called the **entropy** (symbol S) that provides just such a measure. The word comes from a Greek word meaning “transformation” or “change”.

Recall that for any process the change in internal energy is

$$\Delta U = q - w$$

where ΔU is the change in the internal energy of the system, q is the heat absorbed by the system and w is the work done by the system.

Recall, too, that the *maximum* work done by a system in coming to equilibrium is w_{rev} , the work that is done when equilibrium is reached in a *reversible* process. A reversible, or *quasi-static*, process is one in which all change takes place infinitely slowly, so that the system is in equilibrium at each step in the process. Such processes occur only in the imaginations of thermodynamicists; no natural process takes place in the manner just described. Nonetheless, the concept of a reversible process is important because it allows powerful mathematical tools (the calculus) to be applied to problems that would otherwise be extremely difficult or impossible to model mathematically. For the present discussion, the important point is that the work done and the heat absorbed, in the reversible process taking a system from one state to another, is the *maximum* possible for that change in internal energy.

For each very small step in a reversible process, the First Law of thermodynamics becomes

$$dU = dq_{rev} - dw_{rev}$$

The symbol “d” can be taken to mean “an extremely small change in”.

The heat absorbed by the system (dq_{rev}) during this very small change was absorbed at a particular temperature T . Because dq_{rev} is extremely small, T can be taken as constant over the time taken for the change. The ratio dq_{rev}/T , taken at every step during a change from a first state 1 to a second state 2 leads to a new state function called the **entropy**. The change in entropy, ΔS , is defined by

$$\Delta S = S_2 - S_1 = \int_1^2 dq_{rev}/T$$

The integral sign \int (the elongated “S”) in this equation is simply an instruction to add up (“sum”) the quantities that follow. Stated in words, the right hand side of the equation means “the sum of the ratio dq_{rev}/T for every step in the process, starting at State 1 and ending at State 2”.

The direction of change in the physical world can be predicted from the entropy change. Change will always occur in such a way that the *entropy of the universe increases*. This is one way of expressing the **Second Law of Thermodynamics**. Recall that in thermodynamics the word “universe” means the system of interest plus its surroundings, and that the system and its surroundings are assumed to be totally isolated from external influences. A thermodynamic “universe” could be, for example, a piece of experimental apparatus enclosed in a perfectly insulated box.

Molecular Interpretation of the Entropy

The entropy, as introduced in classical thermodynamics, is a rather abstract concept. It is not obvious why the ratio of heat absorbed in a reversible process to the temperature at which the absorption occurs should be associated with the direction of change in the physical world. The situation becomes completely different when we think about what entropy means in terms of the behavior of molecules. It is then possible to express the Second Law very crudely, but accurately, as “moving molecules get into a mess”.

The Natural Tendency to get into a Mess

It is a matter of personal experience that there is a natural tendency for things to get into a mess.

Everybody knows how difficult it is to keep a kitchen or workshop tidy. Unless you take care to put everything back where it belongs, the place soon gets messed up. Why? Simply because there are *millions upon millions* of ways of putting things in a room that make it look a mess, but *relatively few* ways of arranging things that make it look tidy. That is consistent with the old adage “a place for everything, and everything in its place”. According to that rule, there is only *one* arrangement of things that is consistent with the room being tidy. At the other extreme, who could say how many ways there are of putting things in a room that would make the room look untidy?

Sometimes an untidy room is described as “disordered”. In thermodynamics “disorder” has a particular technical meaning that is consistent with the common usage of the word, but is more rigorously defined. The amount of disorder (in the thermodynamic sense of the word) associated with a particular state of a room is simply an indication of how many ways of arranging things in the room are consistent with that state. For example, the state described by “a perfectly tidy room” might be consistent with just one possible arrangement; the “degree of disorder” of “a perfectly tidy room” is therefore low; indeed, it could be no lower. At the other extreme, because the description “a very untidy room” would be consistent with countless possible arrangements, the degree of disorder of “a very untidy room” is very high.

Messiness Among the Molecules

Go into a tidy room, pick something up, and then put it down without thinking about where you are putting it, and chances are that it will not land in a place that will make the room tidy. Do that with two or three or more things, and the degree of disorder begins to increase significantly.

Exactly the same sort of thing happens on the molecular scale. With molecules, however, it is necessary to think of different *velocities* as

well as different *positions*. To begin with, it's useful to imagine what would happen if molecules had no tendency whatsoever to stick to each other. At a given temperature (room temperature, for example) such molecules would be continually jostling around, incessantly colliding with each other and rebounding to collide over and over again. Left to themselves, they would spontaneously distribute themselves over a vast number of different arrangements of position and velocity. This is the same as saying that a collection of these imaginary molecules would naturally get into a state of disorder. Having no inherent stickiness, they would have no impediment to getting themselves well and truly mixed up. They would be in that chaotic state that we call a *gas*.

The Effect of Temperature on Molecular Disorder

What would happen if the temperature were to increase? Recall the discussion of the Equation of State of a Perfect Gas in the first article in this series. If the pressure were constant, the gas would expand. More space would be available for the molecules to move around, and they could take up even more different arrangements of their positions. What about their velocities? Obviously, since temperature is a measure of the average molecular kinetic energy, and kinetic energy is proportional to the square of the velocity, the average velocity of the molecules would be greater at the higher temperature. Detailed analysis of the behavior of large collections of randomly colliding molecules^[3a] shows that the molecules can have a huge range of velocities, and the way in which they distribute themselves over that range depends on the temperature. At low temperatures most molecules have velocities that are rather close to the average velocity. At high temperatures the distribution of velocities is much broader, with more molecules having velocities very different from the average. A proper treatment of the relationship between molecular velocity and temperature would require a discussion of statistical mechanics,^[3b,4] which is beyond the scope of this article. The important point is that an *increase in temperature* means an increase in the *spread of molecular velocities* and thus an *increase in disorder*.^[5]

Attractions between Mixing Molecules

So far, the molecules have been imagined to have no tendency to stick to each other. They would spontaneously mix themselves into a state of disorder by their random motion. A world made of such molecules would be completely disordered on the molecular level but completely uniform on the large scale. It would be a rather dull place. Fortunately, real molecules always have a tendency to stick together because of attractive forces arising from electrostatic interactions. If molecules have opposite electrical charges, as for example gaseous sodium and chloride ions (Na^+ and Cl^-) these attractive forces can be very strong indeed. Even the most simple and symmetrical molecules (atoms of helium or argon, for example) have a slight tendency to stick together. The distribution of electrons in each atom is continually changing, and when the atoms are very close, the electrons in each atom come under the influence of the nuclear charge of the other. This results in a small attractive force between the atoms.

These attractive forces make a great difference to the behavior of atoms and molecules at low temperatures. Imagine a collection of atoms, all of the same kind, with each atom having a rather high average kinetic energy. For example, this could be a quantity of argon gas in a container at room temperature. The atoms are continually colliding; as they collide, they have a slight tendency to stick together. The attractive force is very weak, however, and at high temperatures is negligible. Now suppose that the sample of argon is cooled by some sort of refrigerator, to the point where the average kinetic energy of the atoms is so low that colliding atoms can start to stick together and form clumps. If the temperature is low enough, some of the gas will condense into a *liquid*. A more ordered state of matter (liquid) has spontaneously appeared from a more disordered one (gas).

Order Here, Disorder There

It seems that cooling the gas has made the world a more orderly place. This conclusion would seem even more valid if the cooling process were to continue to the point where all the argon condensed to a crystalline solid, with the atoms neatly arranged in a beautifully regular array. That is certainly a more ordered arrangement of atoms than the original chaotic swarm of atoms filling the whole container. There is no doubt that the degree of molecular disorder in the container has been reduced.

In thermodynamics, however, what happens in the container is only part of the story. What about the surroundings? Recall that the sample of gas was originally at room temperature, and a refrigerator was used to cool it. For argument's sake, the refrigerator can be assumed to be perfectly efficient: it simply takes a quantity of energy from the gas, and dumps it into the outside world. On the molecular level, this means that the molecules of the outside world can now move more rapidly and are therefore able to become even more disordered.

As will be shown later, the increase in molecular disorder in the outside world must at the very least equal the decrease in molecular disorder that happened when the gas condensed into a liquid, or when the liquid condensed into a solid. Because of the natural tendency of randomly moving molecules to get mixed up, *the entire physical world tends to become more disordered on the molecular scale*. Parts of the world can be made very orderly, but the ordering process inevitably results in some other part of the world becoming even more disordered.

To return to the example of the untidy room, imagine you are in a small room that is so full of stuff that you are up to your elbows in objects. You try to tidy the room, but as you pick up things and put them where they need to go, your movements stir up all the objects around you, and they get into more of a mess than they were originally. In a room, and in the world at large, there is no way around the fact that objects moved at random are inevitably going to end up in a mess.

It must be admitted, of course, that continuous random rearrangement of a set of objects

does have some chance of putting the objects into one of the rare orderly arrangements. That chance would be greater if there were only a few objects being moved around, but even then the objects would remain ordered for only an instant. As the number of objects increases, the number of possible arrangements increases tremendously, and the fraction of time that the objects spend in orderly arrangements becomes completely insignificant compared to the time that they spend in disordered arrangements.

The statement that the world becomes more disordered on the molecular scale is another way of stating the Second Law of Thermodynamics.

The Consequences of Molecular Disorder

What are the consequences of this tendency to disorder? To answer this, it is necessary to look at how molecular disorder shows itself in the everyday world. All substances and systems have their own characteristic properties, which can stay the same only if the positions and velocities of the molecules that make up the substance or system are restricted to a certain range. If that range is reduced or exceeded, the properties of the substance or system will change. For example, the molecules of a crystalline solid must remain arranged in a regular array if the crystal is to retain its hardness and rigidity. To remain in a regular array, the molecules can have only a rather restricted range of positions and velocities.

The degree of disorder depends on the number of possible combinations of position and velocity that are available to the molecules. A substance (or system) has a low degree of molecular disorder if the molecules that make it up can arrange themselves over only a relatively restricted number of positions and velocities. The degree of disorder in a crystalline solid is therefore low. In a liquid, the molecules can distribute themselves over a much greater range of positions and velocities than they can in a crystalline solid. The degree of disorder of a liquid is therefore higher than that of a crystalline solid. The molecules in a gas can spread themselves over a vast range of positions and

velocities. The degree of disorder in a gas is very high.

The natural tendency towards molecular disorder would suggest that a crystalline solid should spontaneously melt, and the liquid should then evaporate and turn into a gas. This certainly happens, but only if the temperature is sufficiently high. Energy has to be absorbed from the surroundings to overcome the forces that hold the molecules together in the solid. The loss of that energy from the surroundings reduces the molecular disorder there. The solid cannot melt until the increase in disorder resulting from its melting at least equals the decrease in disorder in the outside world that comes about by the transfer of energy from the outside to the melting solid.

How something changes, or whether it changes at all, is constrained by two factors: *the total amount of energy in the universe must stay the same*, and *the total amount of molecular disorder in the universe must increase*. The first of these constraints is a statement of the First Law of Thermodynamics, while the second is a statement of the Second Law. The Second Law was previously stated as the *entropy of the universe increases*. This implies that the *entropy is a measure of the amount of molecular disorder*.

The Relationship between Entropy and Molecular Disorder

Recall that in thermodynamics, the disorder of a system is simply the number of molecular arrangements that are consistent with the properties of that system. This number is sometimes called the thermodynamic probability of the system, and is given the symbol W .

In the nineteenth century Ludwig Boltzmann^[3c] showed that the entropy S of a system is given by

$$S = k \ln W$$

where k is a constant (Boltzmann's constant, 1.381×10^{-23} joules per Kelvin), and $\ln W$ is the **natural logarithm** of W (The natural logarithm of any number x is defined as follows: if $x = e^y$, where e is the number 2.71828... then $y = \ln x$).

A Justification of the Entropy Formula

A properly detailed discussion of the mathematical relationship between entropy and molecular disorder^[4] is beyond the scope of this article. Nonetheless, it is worth offering a brief justification of the formula for the *change* in entropy.

According to this formula, the entropy change ΔS for a reversible process at constant temperature, such as the melting of ice at 273 Kelvin at a pressure of 1 atmosphere, is given by

$$\Delta S = q/T$$

where q is the heat absorbed and T is the absolute temperature.

It is easy to see that the absorption of heat would increase molecular disorder, because the extra energy would help to overcome attractive forces that tend to keep molecules close together. Even when attractive forces are negligible, the addition of extra energy gives molecules a broader range of velocities and this makes the system more disordered.

Why is the absorbed heat divided by the absolute temperature? That implies that the same amount of energy produces a greater change in the disorder of a collection of molecules at a low temperature than it does at a higher temperature. Does that seem reasonable? Recall that collections of molecules become more *disordered* as the temperature increases. The same amount of disruption (i.e., added energy) produces a greater *change* in the degree of disorder in a group of molecules that was *less* disordered to start with than it does in one that was more disordered. The analogy with a tidy room is useful. Imagine that you go into a perfectly neat and tidy room, and you throw ten objects about and leave them where they fall. Is it obvious how the state of order in the room has changed? Now go into a really untidy room and do exactly the same thing. Pick up ten objects at random, throw them into the air and leave them where they fall. Are you aware of much difference in the tidiness of the room? The change in orderliness produced by the same amount of disruption (i.e., randomly changing the positions of ten objects) is clearly much greater in a

tidy room than in a room that was already in a mess.

It has already been stated that entropy is a state function; that is, its value does not depend on the path that was taken to arrive at the final state. That makes sense, given that entropy is basically a measure of how many arrangements of molecules are consistent with the properties of the system. A system is characterized by a particular set of state functions, all of which are independent of the path taken to get to that state. Only a certain number of arrangements of molecules is consistent with that set of state functions; there is no reason to think that that number is in any way dependent on the way in which the system came to have that particular set of state functions.

Now, temperature is also a state function, but the heat absorbed is not. The heat absorbed by a system in going from one state to another is not well defined at all. It depends on how much work was done in the process, and this clearly depends on the path taken. However, imagine that the change from one state to another is carried out infinitely slowly, in other words if it is carried out *reversibly*. Then the amount of heat absorbed is well defined, and is the maximum that is consistent with the change in internal energy. The proper definition of the entropy change is therefore

$$\Delta S = q_{rev} / T$$

What happens if the temperature is not constant during the change from one state to the next? In such a case, the process must be thought of as taking place in very small steps. The tiny amount of heat absorbed reversibly by the system during this very small step is dq_{rev} . The temperature at each step is effectively constant for that step. The value of q_{rev}/T is calculated for each step, and then all the values are added to give the entropy change. This is written as

$$\Delta S = \int_1^2 dq_{rev} / T$$

This, of course, is the formula presented in a previous section as the definition of the entropy change that takes place when a system in one state (state 1) changes to another state (state 2).

Entropy Changes in Reversible Processes at Constant Temperature

It is useful to think about entropy changes taking place at a constant temperature. This can be done if the surroundings are imagined to be some sort of huge thermostat, kept at the same temperature T .

In a reversible process, the entropy change *in the system* is given by

$$\Delta S_{system} = q_{rev} / T$$

The heat absorbed came from the surroundings, so the heat “absorbed” by the surroundings is $-q_{rev}$ (the negative sign means that heat is lost by the surroundings) and the entropy change *in the surroundings* is

$$\Delta S_{surroundings} = -q_{rev} / T$$

The entropy change in the universe is the sum of the entropy changes in the system and the surroundings:

$$\begin{aligned} \Delta S_{universe} &= \Delta S_{system} + \Delta S_{surroundings} \\ &= q_{rev} / T - q_{rev} / T \\ &= 0 \end{aligned}$$

The entropy change in the universe in a reversible process at constant temperature is therefore zero. This is consistent with the definition of a reversible process as one in which the system and its surroundings are always in equilibrium. Recall that for a system in equilibrium, the change in any state function is zero.

Entropy Changes in Real Processes

Real processes *always* occur irreversibly. The entropy changes are easily calculated if we imagine that the surroundings are at a constant temperature T , as in the previous example. First, consider the entropy change in the system. Entropy is a state function, so the entropy change in the system is exactly the same as it would have been if the change had been carried out reversibly.

$$\Delta S_{system} = q_{rev} / T$$

The heat absorbed in the real process, however, would have been *less* than q_{rev} . This is

because q_{rev} is the maximum amount of heat that can be absorbed for a given change in internal energy. The quantity of heat absorbed by the system in an irreversible process can be labeled q_{irrev} .

Now consider the entropy change in the surroundings. The heat absorbed by the system, q_{irrev} came from the surroundings, so the heat “absorbed” by the surroundings is $-q_{irrev}$ and the entropy change in the surroundings is

$$\Delta S_{surroundings} = -q_{irrev} / T$$

As previously, the entropy change in the universe is the sum of the entropy changes in the system and the surroundings:

$$\begin{aligned} \Delta S_{universe} &= \Delta S_{system} + \Delta S_{surroundings} \\ &= q_{rev} / T - q_{irrev} / T \\ &> 0 \end{aligned}$$

because q_{irrev} is always less than q_{rev} .

The entropy change in the universe in a real, irreversible process is always greater than zero.

Entropy Change in the Expansion of a Perfect Gas

Suppose one mole of a perfect gas with an initial volume V_1 and an initial temperature T_1 reversibly absorbs a small quantity of heat dq_{rev} and expands by a very small volume dV against an external pressure P . The final volume is V_2 , the final temperature T_2 . The work done by the gas will then be $dW_{rev} = PdV$

From the First Law,

$$dU = dq_{rev} - dW_{rev}$$

$$dU = dq_{rev} - P dV$$

$$dq_{rev} = dU + P dV$$

From the Equation of State of a Perfect Gas, for 1 mole of the gas $P = RT/V$

$$dq_{rev} = dU + \frac{RT dV}{V}$$

Also for 1 mole of gas, the internal energy U is given by the product of the heat capacity at constant volume C_V and the temperature T ,

$$dq_{rev} = C_V dT + \frac{RT dV}{V}$$

Dividing both sides by the temperature T

$$dq_{rev}/T = C_V dT/T + R dV/V$$

With calculus, this equation can now be integrated to give

$$\Delta S = (C_V \ln T_2 + R \ln V_2) - (C_V \ln T_1 + R \ln V_1)$$

because the integral of $dx/x = \ln x$ (the natural logarithm of x).

Since $\ln x - \ln y = \ln x/y$

$$\Delta S = C_V \ln(T_2/T_1) + R \ln(V_2/V_1)$$

This equation defines the entropy change in terms that are either constants (C_V and R) or state functions (V and T). This shows that entropy is a state function for a perfect gas.

Entropy and the Direction of Change in Isolated Systems

A. The Expansion of a Gas at Constant Temperature

The equation for the entropy change that results from the absorption of heat by a perfect gas allows one to calculate the entropy change associated with the expansion of a certain quantity of gas in an isolated system at constant temperature. As previously,

$$\Delta S = C_V \ln(T_2/T_1) + R \ln(V_2/V_1)$$

but in this case $T_2 = T_1$ so $T_2/T_1 = 1$. From the definition of the natural logarithm, $\ln 1 = 0$ and so

$$\Delta S = R \ln(V_2/V_1)$$

From this equation, if V_2 is greater than V_1 , V_2/V_1 will be greater than 1 and $\ln(V_2/V_1)$ (and consequently ΔS) will be positive. If $V_1 = V_2$, then $V_2/V_1 = 1$ and $\ln(V_2/V_1)$ (and consequently ΔS) will be zero. If V_2 is less than V_1 , then V_2/V_1 will be less than 1 and $\ln(V_2/V_1)$ (and consequently ΔS) will be negative.

In the real world, a gas in an isolated system at constant temperature always expands to fill

the maximum volume available. This corresponds to an increase in entropy. The process whereby a gas at constant temperature spontaneously collects in a small volume of such a system leaving the rest of the system empty has never been reported. Such a process would correspond to a decrease in the entropy of an isolated system.

B. Transfer of Heat between Two Objects at Different Temperatures

Suppose that an isolated system contains two separate objects, one of which is at a temperature T_1 and the other is at some different temperature T_2 . Now suppose that by some unspecified process a very small quantity of heat dq is transferred from the object of temperature T_1 to the object of temperature T_2 . The change in entropy of the first object is $-dq/T_1$ (negative, because heat is lost from the object) while the change in entropy of the second object is dq/T_2 (positive, because heat is absorbed by the object). The change in entropy for the whole system is the sum of the individual changes, that is, $dq/T_2 - dq/T_1 = dq(1/T_2 - 1/T_1)$. If T_2 is smaller than T_1 , then $1/T_2$ will be greater than $1/T_1$ and the entropy change will be positive. If T_2 equals T_1 , the entropy change will be zero. If T_2 is greater than T_1 , the entropy change for the process will be negative.

Comparing these results to what happens in the real world, one sees again that in an isolated system *the process that results in an increase in entropy happens spontaneously*. Put an object in contact with one at a lower temperature, and energy will be transferred as heat from the object at the higher temperature to that at the lower temperature. If the temperature of the two objects is the same, then they are by definition in thermal equilibrium. If a minute quantity of heat is transferred reversibly from one object to the other, the entropy change is zero. The process for which the entropy change is negative, namely the transfer of heat from an object at a lower temperature to one at a higher temperature, never happens spontaneously in an isolated system. If such a process is to occur, external work must be done to transfer the heat. This is what happens in a refrigerator, where the net effect of the work being done by the

electric motor is to cool the inside of the refrigerator and make the air outside warmer.

The Second Law Restated

The statement that “in isolated systems, processes for which the entropy change is negative are not spontaneous” is yet another form of the **Second Law of Thermodynamics**. Perhaps the most general statement of the Second Law is that “the entropy of the Universe increases”. In this instance, where the word “Universe” has a capital letter, the meaning is the conventional one: *everything there is*. This is very different from the thermodynamic meaning of the word “universe” (no capital). As indicated earlier, a thermodynamic “universe” is simply the system of interest plus its surroundings, assumed to be totally isolated from external influences.

The statement of the Second Law with reference to the Universe indicates that there is an inevitable progression in time towards a state of higher entropy *for the Universe as a whole*. When one sees a movie being played backwards, one sees a world in which the entropy of the Universe is decreasing with time. Some processes, such as the swinging of a pendulum, do not look any different. Other processes, such as the dropping of a glass of water onto the floor, look remarkably different. Randomly scattered globs of water and shards of glass miraculously re-assemble themselves into a glass of water. Why, one might ask, is that such an amazing process? Why has such an event never been reported in the entire known history of the human race? After all, on the molecular level all that has to happen is for the molecular motions that took place when the glass was shattered and the water scattered to be precisely reversed. Having stated that, it is immediately obvious why such a process would be amazing. It is not that such an event is impossible. It is just wildly improbable. Of all the ways that the molecules making up a smashed glass of water have of arranging themselves, very, very few correspond to the multitude of successive rearrangements that would have to take place to re-assemble the glass.

The Driving Force of Change

The Second Law of Thermodynamics states that for a spontaneous process, the entropy of the system and its surroundings must increase. In other words, ΔS for the system and its surroundings must be positive. Suppose a process takes place in a system for which the entropy change in the system is ΔS_{system} and the enthalpy change is ΔH_{system}

The heat evolved or absorbed by the system in the enthalpy change ΔH_{system} obviously goes into, or comes from, the surroundings. This heat will be absorbed (or lost) by the surroundings at a temperature T and the entropy of the surroundings will change by an amount $(-\Delta H_{\text{system}}/T)$. The negative sign is there because heat emitted by the system is absorbed by the surroundings.

The total entropy change for the system plus the surroundings is thus

$$\Delta S_{\text{system} + \text{surroundings}} = \Delta S_{\text{system}} - \Delta H_{\text{system}} / T$$

This equation gives the total entropy change for the system and surroundings in terms of changes in thermodynamic properties of the system alone. This is very important because it provides a way of finding out whether or not a particular process will be spontaneous, using only the calculated changes in the entropy and enthalpy of the system.

For a process to be spontaneous, the total entropy change must be positive. Now, ΔS_{system} and ΔH_{system} can be either positive or negative, but the temperature T is always positive. Multiplying the equation by T ,

$$T\Delta S_{\text{system} + \text{surroundings}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}}$$

Again, a process will be spontaneous if this quantity is positive or, equivalently, if the quantity $\Delta H - T\Delta S$ is negative.

Another State Function: the Gibbs Free Energy

The quantity $\Delta H - T\Delta S$ has the units of energy. Recall that ΔH represents the energy available after allowance has been made for the work ($P\Delta V$) done in volume changes at constant pressure. The quantity $T\Delta S$ can be thought of as the

energy that has been dispersed as random molecular motion and is therefore unavailable to do useful work. The remaining energy, $\Delta H - T\Delta S$, is referred to as the *free energy*, because it is available to perform useful work. The free energy is of such great importance that it is convenient to define a new quantity $G = H - TS$ for which, at constant temperature, (from the definition of Δ)

$$\Delta G = \Delta H - T\Delta S$$

Notice that this quantity G , being made up of the state functions H , T and S , is itself a state function. That is to say, changes in its value depend only on the state of the system before and after a process, and are independent of any intermediate states that the system might have assumed during the process. This new state function is called the **Gibbs Free Energy** (after J. Willard Gibbs).^[2b]

This, at last, is the state function that can be used to predict the direction of change in a chemical system.

At equilibrium, the Gibbs Free Energy of the reactants will equal the Gibbs Free Energy of the products. If the Gibbs Free Energy change (ΔG) for a process is *negative*, the *entropy change for the universe will be positive*, and the process will be thermodynamically spontaneous.

The sign of ΔG indicates only whether or not the process will be spontaneous. It does *not* indicate whether the transfer of energy during the process will be from the system to the surroundings, or in the opposite direction. That information is given by the sign of the *enthalpy change*, ΔH , as explained in the first article in this series.^[1] A process with a negative ΔG may result in the spontaneous transfer of energy *from the system to the surroundings* (i.e., ΔH is negative). Examples of such a process include the freezing of water in the freezer compartment of a refrigerator, and the combustion of magnesium in a burning pyrotechnic composition. On the other hand, a process having a negative ΔG might well result in the spontaneous transfer of energy *from the surroundings to the system* (i.e., ΔH is positive). Examples of such a process include the melting of ice in a

glass of water, and the decomposition of strontium carbonate in a burning red star.

The Third Law

The entropy of a system, as noted previously, is a measure of the number of molecular arrangements that are consistent with the properties of the system.

Recall that the relationship between the entropy S of a system and the number W of molecular arrangements consistent with the properties of the system was shown by Boltzmann^[3c] to be

$$S = k \ln W$$

This relationship means that the entropy of a system that is consistent with only *one* arrangement of its molecules will be zero, because for such a system $W = 1$ and the natural logarithm of 1 is zero. In other words, Boltzmann's equation implies that *the entropy of a perfectly ordered system is zero*.

If this is correct, then the entropy of a perfect crystalline solid should approach zero as the temperature approaches absolute zero. This trend has been demonstrated experimentally by measurements of heat capacities at very low temperatures.^[6] The statement that "the entropy of a perfect crystalline solid is zero at the absolute zero of temperature" is one form of the **Third Law of Thermodynamics**. The importance of this law is that it allows an absolute value to be assigned to the **molar entropy** of a substance. The molar entropy is calculated from heat capacity measurements, starting from zero at 0 K. For example, the molar entropy of a gas at room temperature would include contributions from the heat capacity of one mole of the solid from 0 K to the melting point, including any heat absorbed in any changes between different crystalline states. It would also include the latent heat of fusion of the solid, the heat capacity of the liquid from the melting point to the boiling point, the latent heat of vaporization and the heat capacity of the gas from the boiling point to room temperature. At each stage the entropy would be calculated from $dS = dq/T$ and the total molar entropy would be obtained by summing all these increments dS .

What Next?

The next article in this series will show how the Gibbs Free Energy varies with temperature and pressure, and how this affects chemical equilibrium. It will also show that a number of useful facts about chemical systems can be predicted from the thermodynamic properties of the reactants and possible products. This will be illustrated with examples from pyrotechnics.

References

Specific to Text

- 0) B. Sturman "An Introduction to Chemical Thermodynamics. Part1 – Matter, Energy and the First Law", *J. Pyrotechnics*, No. 9, 1999, pp 29–49.
- 1) H. M. Leicester, *The Historical Background of Chemistry*, reprint of 1956 ed., Dover, New York, 1971; [a] p 204; [b] pp 205–206.
- 2) J. C. Slater, *Introduction to Chemical Physics*, reprint of 1939 ed., Dover Publications, New York, 1970; [a] pp 56–57; [b] Chapter 3; [c] p 34.
- 3) B. J. McClelland, *Statistical Thermodynamics*, Chapman and Hall & Science Paperbacks, London, 1973, pp 31–44.
- 4) B. H. Mahan, *Elementary Chemical Thermodynamics*, W. A. Benjamin, Inc., New York, 1964, p 76.
- 5) W. Nernst, *The New Heat Theorem*, reprint of 1926 ed., Dover Publications, New York, 1969 p 54.

General References and Suggestions for Further Reading

This article includes information from a number of references, including the following, cited in order of publication of the work used. More recent editions of some of the books may be available; others may be out of print.

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B. J. McClelland, *Statistical Thermodynamics*, Chapman and Hall & Science Paperbacks, London, 1973.

E. B. Smith, *Basic Chemical Thermodynamics*, 3rd ed., Clarendon Press, Oxford, 1982.

Finally, anyone having even the slightest interest in the matters discussed in this article will want to read Professor Peter W. Atkin's excellent book *The 2nd Law*:

P. W. Atkins, *The 2nd Law: Energy, Chaos and Form*, W. H. Freeman and Co., New York, 1994.