

Teaching Entropy Analysis in the First-Year High School Course and Beyond



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Entropy analysis is a powerful fundamental method for analyzing the thermodynamics of chemical reactions. I have developed two entropy-analysis laboratory activities (1, 2). The majority of high school chemistry teachers know little or nothing about entropy analysis, as their background has been more traditional. Understandably, this leaves them reluctant to teach entropy analysis, much less to use activities dealing with it. The goal of this article is to assist teachers in the incorporation of entropy analysis in their curricula by educating and empowering them, and by providing an entropy-analysis unit that can be used in classrooms.

Entropy analysis is used to assess the spontaneity of physicochemical processes. The technique focuses on the entropy contributions and evaluates them based on the second law of thermodynamics. Historically, Henry Bent extensively developed the basic approach, later known as the global approach or global formulation (3, 4).¹ In the past 16 years, Norman Craig has promoted this approach and introduced the terminology, *entropy analysis*, which involves “showing all the contributions to the total entropy change” (5–8).

Traditionally, the concept of spontaneity has been approached through the use of the Gibbs energy function. It has been argued that a true understanding of spontaneity is pedagogically compromised and limited by using the Gibbs free energy (3, 9–11a).

I have taught entropy analysis to first-year high school chemistry classes for 15 years. After the first couple of years it became obvious that the entropy concept of “disorder” did not fit with entropy analysis. There were too many inconsistencies. Consequently, I abandoned the idea of “disorder” and embraced the idea of “energy dispersal”. This was difficult because the concept of “disorder” is so firmly entrenched.² Nonetheless, *the focus must be on energy*; this is the key.

Others also have experienced difficulties with the “disorder” concept of entropy (12–17). Lambert³ provides excellent arguments as to why entropy should not be taught using messy desks, disorderly dorm rooms, and shuffled cards (12). He also gives the history of how entropy became erroneously linked to “disorder” (13). Ten examples are presented of how “disorder” cannot represent entropy. He appropriately describes disorder as a “cracked crutch” for entropy. More recently, Lambert discusses entropy and the dispersal of energy from a molecular point of view through quantum microstates (17).

Entropy-Analysis Unit

The entropy-analysis unit has been used successfully for many years with high school students in beginning chemistry. The unit takes the concept of entropy and the second law of thermodynamics and uses them to develop more sophisticated ideas such as spontaneity, the heat death of the universe, the arrow of time, extent of reaction, thermodynamic equilibrium, and coupling of spontaneous and non-spontaneous reactions. The unit extends over 16, 50-minute class periods. I believe the entropy unit is the most important unit in the entire chemistry curriculum and perhaps in science, giving some justification for the length of the unit. The large number of references within should not overwhelm instructors, as they are intended for those wanting to delve further into the material.

Before the unit, students learn kinetics. More importantly, they learn how kinetic energy⁴ and potential energy are applied to molecules, collisions, and chemical reactions. The students also learn calorimetry, specific heat capacity (18, 19), reaction enthalpy, and standard states. All of these concepts provide a strong basis for the entropy unit, as entropy and entropy analysis are based upon *energy*.

Instructors may select to use only a portion of the curriculum based upon the abilities of their students and the teacher’s level of comfort with the material. The unit may be extended to more advanced high-school courses or classes and to the college level. The unit is presented day-by-day.

Day 1: Destiny

The movement or transformation of energy, its storage and release, and its involvement in spontaneous and nonspontaneous processes is an important foundation. To begin discussion, students should have an opportunity to explore a series of linked events that involve the movement or flow of energy (transformation) under several different scenarios (Table 1). The following activity, *Destiny*,⁵ does this. Each of the six scenarios starts with a prescribed event, and the students determine and follow the flow of energy back in time to a prescribed previous event. Students understand that this “retro analysis” is a thought process rather than what actually happens in nature. Although students solve the problem in the nonspontaneous retro direction, they present their solutions in the forward spontaneous direction. This retro

approach is patterned after the retrosynthetic analysis used in organic chemistry and pioneered by E. J. Corey. In five of the six scenarios, students follow the energy flow back to the Sun (i.e., Earth's primary source of energy).

Many different solutions are possible for each scenario. The following is an example of a solution to Scenario 2:

Light energy comes from the light bulb, which was produced by heating, which came from electrical energy, which was produced by the generator, which came from mechanical energy of the moving parts of the bicycle, which was provided by the action of the child, which came from chemical energy, which was provided by consuming food, which came from stored chemical energy in plants, which was provided by photosynthesis, which came from the Sun's light energy, which was provided by nuclear fusion.

The Destiny activity achieves many additional outcomes. Students explore retro analysis (working backwards), use pictorial presentations that allow for greater artistic and creative expression,⁶ engage in cooperative learning, present ideas to a large group, recognize that devices or processes are involved in the transformation of energy, and gain a better understanding of the types of energies.

Day 2: Spontaneity

Students learn the ideas associated with the concept of spontaneity. It is important for students to have a firm understanding of the meaning of "spontaneous". A process is said to be spontaneous if it can occur naturally, such as, a gas expanding into a vacuum, ice melting above 0 °C, wood combusting, water moving downhill, sugar dissolving in water, a piece of iron rusting, nuclear fusion on the Sun, or a piece of hot metal cooling to its surroundings. The reverse process of each of the above is not spontaneous and requires work to be done on it in order for it to occur. More precisely, a process moves or is capable of moving in the direction that results in a net increase in the entropy of the universe.

Spontaneous processes may cause nonspontaneous processes to happen. Students see this when examining the schemes derived from the Destiny activity. For example, the Sun shining (nuclear fusion) is a spontaneous event, but the synthesis of food (carbohydrate) is not. However, the synthesis of food is caused to happen by the Sun through a green plant (photosynthesis). An electric generator in a hydroelectric dam does not spontaneously produce electricity unless it couples with water flowing spontaneously downhill. These illustrate that spontaneous processes can be used to cause nonspontaneous processes to happen. All of these schemes in the Destiny activity consist of coupled spontaneous and nonspontaneous processes.

Day 3: Entropy

Students learn the concept of entropy. *Entropy is a measure of the extent of energy dispersal.* As energy disperses or spreads out, entropy increases. It is the natural tendency for energy to disperse. Potential energy represents nondispersed energy with zero entropy. Thermal energy⁷ represents dis-

Table 1. The Six Scenarios for the Destiny Activity

Number	Scenario
1	A toaster is on. Start with the browned bread and end with the Sun. You must involve a coal-burning power plant at some point.
2	A child is pedaling a bicycle with a small electrical generator and light. Start with the shining light and end with the Sun.
3	A front-wheel drive automobile is motoring down the highway with the radio blaring. Start with the sound from the radio and end with the Sun.
4	A nuclear-powered submarine is moving through the ocean depths. Start with a moving propeller and end with uranium from the Earth.
5	A professional soccer player kicks a soccer ball into the air. Start with the ball at its highest point and end with the Sun.
6	A light bulb is shining onto the pages of a chemistry book. Start with the page and end with the Sun. You must use a hydroelectric dam at some point.

persed energy; it is spread over microscopic states of matter. The terminology "heat energy" is not used, because heat is not a form of an energy content (21, 22). "Heat" is better thought of as "heat effect" or "heating" because "heat" is an action involving the transfer or transformation of energy. Thermal energy is defined operationally as the energy that is associated with a temperature change in either the system or surroundings (21).

Linking Entropy and Spontaneity

Students see the connection between entropy and spontaneity. The Destiny activity illustrates the flow and conversion of energy and the directionality of the flow. The activity also illustrates that spontaneous processes are required to cause nonspontaneous processes to happen. Is there a way to predict whether a process is spontaneous? The second law of thermodynamics predicts how energy flows spontaneously towards dispersal. Entropy, being a measure of the extent of energy dispersal (or the extent to which energy is spread out), will always increase in the universe when a spontaneous process happens. That is, the entropy of the universe becomes necessarily greater as a result of a spontaneous process.

Arrow of Time and Heat Death

Students examine the "arrow of time" (23)⁸ and a possible fate of the universe, Helmholtz's "heat death" of the universe (24). "Heat death" emphasizes the nature of energy movement, that is, the necessary transformation of energy into thermal energy.

Advanced Students

For more advanced students or classes, quantum theory determines more precisely the extent to which energy becomes dispersed. In other words, entropy relates to the number of possible microstates⁹ (microscopic states). As the number of accessible microstates increases, energy becomes more dis-

persed, representing greater entropy (4a). Historically, the Boltzmann relation has been used in statistical mechanics to evaluate entropy,

$$S = k_B \ln W \quad (1)$$

where S is entropy, k_B is the Boltzmann constant¹⁰ (ratio of the universal gas constant and Avogadro's number), and W is the number of ways of realizing the distribution of energy for the most probable microstate. A variation, eq 2, relates entropy directly to the number of distinct microstates, Ω or multiplicity that are equally possible. Ω is the sum of the W_i values.

$$S = k_B \ln \Omega \quad (2)$$

The actual calculation of entropies is not as simple as eq 2 suggests because expressions for Ω are hard to write and to evaluate (26).

Simple quantum mechanical models of this idea have been used to illustrate eq 2. Bent (4b) elegantly illustrates the distribution of energy of vibrating atoms within a solid, and Lowe (27) deals with the distribution of translational energies of molecules in a one-dimensional box.

Wright succinctly captures the two approaches to entropy, thermal energy and accessible microstates, in the following quotation: "Entropy 'is' a function S such that $dS = dq_{\text{rev}}/T$; or the quantity $k \log_e W$; and not a name given to disorder" (16).¹¹ For a detailed discussion of microstates and the Boltzmann equation see the Supplemental Material (microstates under Day 3).¹²

Day 4: Entropy and the Natural Logarithm

Students see the mathematics used to determine entropy changes quantitatively for both isothermal and non-isothermal processes. Consider that for a given surroundings (assume the surroundings to be a vast thermal reservoir in contact with a system, and isothermally) how the quantity of thermal energy increases as a consequence of a heat effect. What is the change in entropy for the surroundings? Instead of giving the students the equation, they are led through a qualitative development of the equation. The entropy change correlates with the change in thermal energy in the surroundings. The more thermal energy dispersed into the surroundings (or the increase in the thermal energy content of the surroundings through heating), the greater the entropy change. Temperature is a second factor that is important. There is a greater change in entropy of the surroundings for a given energy input, if the temperature is lower. This is an inverse relationship. Students readily accept eq 3,

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} \quad (3)$$

where S is entropy,¹² q_{surr} is the heat effect in the surroundings, and T is the temperature in Kelvin. The heat effect in the surroundings (q_{surr}) is opposite to the heat effect in the system (q_{sys}), meaning $q_{\text{surr}} = -q_{\text{sys}}$. Alternatively, the change in the internal energy of the surroundings, ΔE_{surr} (4) or ΔU_{surr} , may be used in place of q_{surr} in eq 3. (For more discussion of eq 3, see the section below titled More Detailed Discussion of Eq 3.)

Equation 3 only applies to large thermal reservoirs in which the temperature changes little.¹³ The equation is applicable only to reactive systems that behave accordingly, and then the sys label replaces the surr label. Examples of such systems include the heating or cooling of a substance and the melting (or freezing) or vaporization (or condensation) of a substance at its normal transition point.¹⁴

What about processes involving a change in temperature? The following problem illustrates this situation:

What is the change in entropy of a 0.00100-kg bar of metal, if its temperature increases from 1.00 K to 11.00 K? Assume the specific heat capacity of the metal is 500.0 J kg⁻¹ K⁻¹ and temperature independent.

The solution to this problem is not clear-cut because the process is not isothermal. It requires the use of the natural logarithm function. Beginning classes are given the general relationship in eq 4,

$$\Delta S = cm \ln \left(\frac{T_2}{T_1} \right) \quad (4)$$

where c is specific heat capacity, m is mass, T_2 is the final temperature (Kelvin) and T_1 is the initial temperature (Kelvin). Substitution into eq 4 gives an entropy change of 1.20 J/K, as shown below:

$$\begin{aligned} \Delta S &= cm \ln \left(\frac{T_2}{T_1} \right) \\ &= \left(500.0 \frac{\text{J}}{\text{kg K}} \right) (0.00100 \text{ kg}) \ln \left(\frac{11.00}{1.00} \right) \\ &= 1.20 \frac{\text{J}}{\text{K}} \end{aligned} \quad (5)$$

Advanced Students

For more advanced students, eq 4 is shown to be derived from calculus. More specifically, the temperature interval is subdivided into successively smaller intervals until the temperature intervals are infinitesimally small:

$$\Delta S = \int_{T_1}^{T_2} \frac{cm}{T} dT = cm \ln \left(\frac{T_2}{T_1} \right) \quad (6)$$

Then, the entropies for the infinitesimally small temperature intervals are summed by integration to give an entropy change of 1.20 J/K.

More Detailed Discussion of Equation 3

The following discussion is directed towards the surroundings in contact with a system and the resulting effects. Consider a system in thermal equilibrium with its surroundings at temperature T . As a consequence, both the system and surroundings are at the same temperature, T . Assume that something happens in the system that produces energy, such as an enthalpy change, $\Delta H_{\text{sys}} < 0$, and this energy transfers as a heat effect to the surroundings. The entropy change in the surroundings can be represented as $\Delta S = q_{\text{surr}}/T_{\text{surr}}$. During the process, the energy lost by the system is gained by the surroundings, $-q_{\text{sys}} = q_{\text{surr}}$. Substitution

gives $\Delta S_{\text{surr}} = -q_{\text{sys}}/T_{\text{surr}}$. Because the system and the surroundings remain in thermal equilibrium with each other, $T_{\text{surr}} = T_{\text{sys}} = T$, a new equation results, $\Delta S_{\text{surr}} = -q_{\text{sys}}/T$. Substitution of $q_{\text{sys}} = \Delta H_{\text{sys}}$ into this latter equation gives $\Delta S_{\text{surr}} = (-\Delta H_{\text{sys}}/T) > 0$.

An example of the above is liquid water freezing at a temperature below its normal freezing point. When the liquid water becomes ice it releases energy (an exothermic process) to the surroundings, causing the entropy of the surroundings to increase.

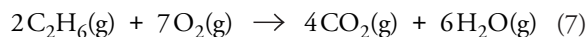
An example of a situation where energy moves in the reverse direction is ice melting at a temperature higher than its normal melting point. As the ice melts (an endothermic process), energy moves from the surroundings to the system, resulting in a decrease in the thermal energy content of the surroundings, and consequently, a decrease in the entropy of the surroundings.

At the normal melting point, ice and liquid water coexist in equilibrium. At equilibrium, ΔS_{univ} is zero, which means ΔS_{surr} equals $-\Delta S_{\text{sys}}$. In other words, the decrease in entropy experienced by the surroundings when ice melts is exactly the same as the increase in entropy experienced by the system.

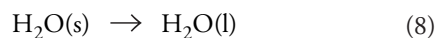
Day 5: Qualitative Treatment

Students learn entropy analysis; that is, students determine all of the entropy changes that occur during a process (chemical reaction or phase change) and then determine whether it is spontaneous or not as a result of the entropy analysis.

The skill in analyzing situations qualitatively is important to a good conceptual understanding. This can be demonstrated by assessing whether the reactions shown in eqs 7 and 8 are spontaneous. [Note, in the qualitative treatment, only the signs (positive, negative) or zero represents the various entropies. Signs are easier for students to use rather than the concepts of greater than zero and less than zero.]



$$\Delta_r H^\circ = (-)$$



$$\Delta_r H^\circ = (+)$$

Because eq 7 is exothermic, $\Delta_r H^\circ = (-)$, heating occurs in the surroundings, causing the thermal energy content to increase, resulting in an increase in the entropy of the surroundings. The reaction does not involve a phase change, but the number of moles of gas increases from 9 moles to 10 moles. Thus, owing to a greater dispersal of energy among more particles, this represents an increase in the entropy of the system. Because both the surroundings and system experience an increase in entropy, the universe experiences a net increase in entropy $\Delta S_{\text{univ}} = (+)$. The conclusion is that the combustion of ethane is spontaneous at standard-state conditions.

$$\begin{array}{l} \Delta_r H^\circ = (-) \quad \Delta S_{\text{surr}} = (+) \\ \Delta S_{\text{sys}} = (+) \\ \hline \Delta S_{\text{univ}} = (+) \end{array}$$

Table 2. Thermodynamic Calculations for Equations 9–16, 20–22^a

Eq	$\Delta_r H^\circ /$ (kJ/mol rxn)	$\Delta S_{\text{surr}} /$ [J/(K mol rxn)] ^b	$\Delta_r S_{\text{sys}}^\circ /$ [J/(K mol rxn)] ^c	$\Delta S_{\text{univ}} /$ [J/(K mol rxn)] ^d	Spont ^e
9	-164.9	553 (+)	-172.6 (-)	380 (?)	yes (?)
10	-92.2	309 (+)	-198.7 (-)	111 (?)	yes (?)
11	-571.6	1920 (+)	-326.7 (-)	1590 (?)	yes (?)
12	176.2	-591 (-)	284.8 (+)	-306 (?)	no (?)
13	41.4	-139 (-)	25.9 0	-113 (-)	no (no)
14	-137	460 (+)	-120.7 (-)	339 (?)	yes (?)
15	-1666.0	5590 (+)	273.8 (+)	5860 (+)	yes (yes)
16	133.6	-448 (-)	424.2 (+)	-24 (?)	no (?)
20	218.7	-734	20.9	-713	no
21	-218.7	734	-20.9	713	yes
22	44.0	-148	118.9	-29	no

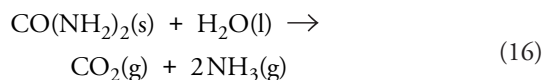
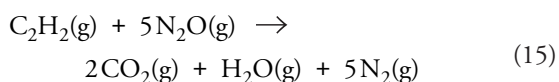
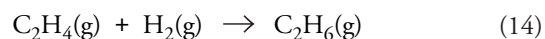
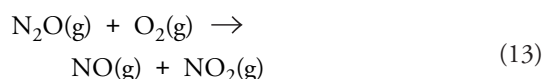
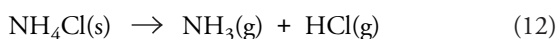
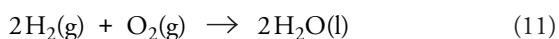
^aQualitative results are in parentheses. ^bCalculated using eq 17. ^cCalculated using eq 18. ^dCalculated using eq 19. ^eAnswers the question, "Is the reaction spontaneous at 298 K?"

Equation 8 is endothermic, $\Delta_r H^\circ = (+)$. The entropy of the surroundings decreases, and the entropy of the system increases (change to a more mobile phase), resulting in an inconclusive result for the change in entropy of the universe ($\Delta S_{\text{univ}} = ?$).¹⁵

$$\begin{array}{r} \Delta_r H^\circ = (+) \quad \Delta S_{\text{surr}} = (-) \\ \Delta S_{\text{sys}} = (+) \\ \hline \Delta S_{\text{univ}} = ? \end{array}$$

However, if the temperature of the surroundings is not high (below 0 °C), then the entropy decrease in the surroundings (eq 3) is large enough for the sum of the entropies of the surroundings and system to be negative. Under these conditions water freezes.

Students perform qualitative entropy analyses on the following chemical equations, eqs 9–16. The changes in enthalpy are calculated from standard enthalpies of formation. The results of the analyses are shown in Table 2.



Day 6: Quantitative Treatment

Instruction in the quantitative treatment begins after the qualitative treatment is mastered. The change in entropy of the surroundings is equal to q_{surr}/T (isothermal). For a chemical reaction at standard conditions, $q_{\text{surr}} = -q_{\text{sys}} = -\Delta_r H^\circ$, which gives eq 17.

$$\Delta S_{\text{surr}} = \frac{-\Delta_r H^\circ}{T} \quad (17)$$

Students calculate the change in entropy of the chemical system, ΔS_{sys} , using eq 18, where the ν represent the molar coefficients and the S_m° represent the standard-state molar entropies, which are derived from the third law of thermodynamics.

$$\Delta_r S_{\text{sys}}^\circ = \Delta_r S^\circ = \sum_{\text{products}} \nu_i S_{m,i}^\circ - \sum_{\text{reactants}} \nu_i S_{m,i}^\circ \quad (18)$$

Students calculate the entropy change in the universe by summing the entropy changes within the surroundings and the system, eq 19.

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta_r S_{\text{sys}}^\circ \quad (19)$$

For example, eq 9 illustrates that a localized decrease in entropy occurs in the system; however, this is more than offset by the entropy change in the surroundings to give a net increase in the entropy of the universe. The entropy of the universe today is greater than yesterday, and tomorrow it will be even greater! When surroundings and system are included, at no time does the entropy of the universe ever decrease.

Example: Equation 9

$$\Delta_r H^\circ = \sum_{\text{products}} \nu_i H_{f,i}^\circ - \sum_{\text{reactants}} \nu_i H_{f,i}^\circ$$

$$\begin{aligned} \Delta_r H^\circ &= \left[\left(1 \frac{\text{mol}}{\text{mol rxn}} \right) \left(-74.8 \frac{\text{kJ}}{\text{mol}} \right) \right. \\ &\quad \left. + \left(2 \frac{\text{mol}}{\text{mol rxn}} \right) \left(-241.8 \frac{\text{kJ}}{\text{mol}} \right) \right] \\ &\quad - \left[\left(1 \frac{\text{mol}}{\text{mol rxn}} \right) \left(-393.5 \frac{\text{kJ}}{\text{mol}} \right) \right. \\ &\quad \left. + \left(4 \frac{\text{mol}}{\text{mol rxn}} \right) \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] \\ &= -164.9 \frac{\text{kJ}}{\text{mol rxn}} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{surr}} &= \frac{- \left(-164.9 \frac{\text{kJ}}{\text{mol rxn}} \right) \left(1000 \frac{\text{J}}{\text{kJ}} \right)}{298 \text{ K}} \\ &= 553 \frac{\text{J}}{\text{K mol rxn}} \end{aligned}$$

$$\begin{aligned} \Delta_r S_{\text{sys}}^\circ &= \left[\left(1 \frac{\text{mol}}{\text{mol rxn}} \right) \left(186.3 \frac{\text{J}}{\text{K mol}} \right) \right. \\ &\quad \left. + \left(2 \frac{\text{mol}}{\text{mol rxn}} \right) \left(188.8 \frac{\text{J}}{\text{K mol}} \right) \right] \\ &\quad - \left[\left(1 \frac{\text{mol}}{\text{mol rxn}} \right) \left(213.7 \frac{\text{J}}{\text{K mol}} \right) \right. \\ &\quad \left. + \left(4 \frac{\text{mol}}{\text{mol rxn}} \right) \left(130.7 \frac{\text{J}}{\text{K mol}} \right) \right] \\ &= -172.6 \frac{\text{J}}{\text{K mol rxn}} \end{aligned}$$

$$\begin{aligned}\Delta S_{\text{univ}} &= 553 \frac{\text{J}}{\text{K mol rxn}} + \left(-172.6 \frac{\text{J}}{\text{K mol rxn}} \right) \\ &= 380 \frac{\text{J}}{\text{K mol rxn}}\end{aligned}$$

Students perform quantitative entropy analyses on eqs 10–16. The author has not yet explored the use of entropy diagrams but intends to do so soon (7). See the Supplemental Material for entropy calculations for the freezing of water at various temperatures.^W

Day 7: Practice

Students continue work on eqs 10–16. Also, eqs 1–6 are assigned for homework from *Solution-Phase Thermodynamics: A Spontaneity Activity (1)*. There have been some changes since the activity was published. Equations 20 and 21 represent new reactions, giving the activity more variety.



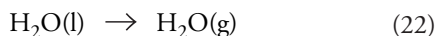
Day 8: To Be or Not To Be

Students perform the spontaneity activity (1). Students monitor temperature changes using a thermometer to measure the enthalpy of reaction. (Note that there is an error in the activity: ΔH_f° for $\text{Ca}^{2+}(\text{aq})$ should be -543 kJ mol^{-1} .)

Day 9: Extent of Reaction

This day's lesson revolves around two important questions: (i) "What does a standard-state calculation really mean?" and (ii) "Does the magnitude of ΔS_{univ} have any significance?" The lesson starts with the following problem.

Does liquid water at 25 °C in a closed system have the capacity to evaporate? Calculate $\Delta S_{\text{univ}}^\circ$ for eq 22 and determine the spontaneity.



A calculation of ΔS_{univ} gives a value of $-29 \text{ J/(K mol rxn)}$ (see Table 2), meaning the reaction is not spontaneous under standard-state conditions. This is an interesting dilemma, for students know that water does in fact evaporate at room temperature, yet the calculation reveals that this evaporation is not a spontaneous process! The solution to the dilemma lies in understanding the conditions of the calculation. The calculation is for standard-state conditions, meaning that the pure gaseous water is at a pressure of 1 atmosphere (760 torr) and 25 °C. In other words, the calculation is for the production of 1 mole of gaseous water, having a vapor pressure of 1 atmosphere. The vapor pressure of water at 25 °C is only 23.8 torr or 3.169 kPa (29).

If the specified process is not spontaneous, does this mean nothing will happen? No. For instance, consider opening an evacuated sealed container, in a room under standard

conditions. Will *all* of the air in the room move spontaneously into the bottle? No, this will never occur by itself. Does this mean that nothing will take place spontaneously? No, in fact, some portion of the air will move into the bottle until the pressure inside is equal to the pressure outside. This hypothetical situation leads to the realization that all processes (reactions) will go spontaneously to some extent.

The sign and magnitude of ΔS_{univ} determine the extent of reaction. Equation 23 relates ΔS_{univ} to the thermodynamic equilibrium constant, K (1, 5, 7):

$$\Delta S_{\text{univ}} = R \ln K \quad (23)$$

The universal gas constant, R (8.31 J/K mol), and k_B are related by eq 24, where N_A is Avogadro's constant:

$$\frac{R}{N_A} = k_B \quad (24)$$

An application of eq 23 to the evaporation of water to give the equilibrium pressure at 25 °C is presented in the Supplemental Material (Day 9), as well as an advanced thermodynamic derivation of the equilibrium-constant expression.^W

P/R Ratio

Consider a hypothetical reaction in which the ΔS_{univ} is allowed to change, but the initial concentrations of the reactants remain constant. As the ΔS_{univ} increases, the equilibrium constant increases, meaning a greater extent of reaction.

Thermodynamics provides a better entry into the concept of chemical equilibrium, as opposed to the more traditional entry through kinetics. In kinetics, an approach to deriving the equilibrium-constant expression is to write rate laws for the forward reaction and the reverse reaction from the overall stoichiometry and then equating the two rate laws. Rate laws, however, cannot be written from the overall stoichiometry of a chemical reaction that has a reaction mechanism composed of more than one elementary step!

The entropy-analysis unit develops the concept of equilibrium, without the mathematical rigors associated with the equilibrium-constant expression. There is no need to use the symbol for extent of reaction, nor the definition, nor the equilibrium constant, for beginning students at this point. Instead, reference is made to a ratio of products over reactants or to the quotient of products and reactants, P/R . I prefer to call this the " P over R ratio". After the entropy-analysis unit, I teach a more traditional unit on chemical equilibrium.

Consider the chemical equations,



$$\Delta S_{\text{univ}} = R \ln \left(\frac{[\text{B}]}{[\text{A}]} \right) \quad (26)$$

where the quotient, $[\text{B}]/[\text{A}]$, represents the products over the reactants, which allows for future discussions to evolve into a development of the concept of the equilibrium constant. (Notice the simplicity of the chemical equation.) Students examine the possible scenarios for extent of reaction, assuming that the initial condition is for 1 mol/L of A (Table 3). If ΔS_{univ} is less than zero, $\Delta S_{\text{univ}} = (-)$, then the reaction pro-

Table 3. Relationship between Extent of Reaction and ΔS_{univ} for Equation 25

Extent of Reaction	[B]/[A]	$\Delta S_{\text{univ}}^\circ$
Less than 0.5 mol/L of B	Less than 1	Less than 0
Equal to 0.5 mol/L of B	1	0
Greater than 0.5 mol/L of B	Greater than 1	Greater than 0

ceeds to an extent less than 0.5 mol/L of B. As the ΔS_{univ} becomes more negative, the extent of reaction is less. If $\Delta S_{\text{univ}} = 0$, then the reaction proceeds to 0.5 mol/L of B.¹⁶ And, finally, if the ΔS_{univ} is greater than zero, $\Delta S_{\text{univ}} = (+)$, then the reaction proceeds to an extent greater than 0.5 mol/L of B. In other words, ΔS_{univ} predicts the extent of reaction! Instructors and students alike appreciate the link between this level of sophistication and the qualitative approach from the beginning of the entropy unit.

The minimum temperature for the spontaneous evaporation of water at 1 atm can be calculated in a similar manner. If eq 17 is substituted into eq 19, zero is substituted for ΔS_{univ} , and the equation is solved for T , then eq 27 results:

$$T = \frac{\Delta_r H^\circ}{\Delta_r S_{\text{sys}}^\circ} \quad (27)$$

Substitution of the tabulated values for the enthalpy of reaction and the entropy change of the system gives a temperature of 370 K. This is three degrees lower than the normal boiling point of water. If the enthalpy of reaction and the entropy change of the system are corrected for temperature, then a temperature of 373 K results.¹⁷

In preparation for the following day, for homework, students read about galvanic cells in their textbooks. Students acquire introductory knowledge about oxidation and reduction, oxidizing and reducing agents, half reactions, galvanic cells and their construction, cathode and anode, and electrode polarity.

Advanced Students

Students derive the relationship between ΔS_{univ} and the thermodynamic equilibrium constant, K , eq 23. For systems involving solutions of solute i , eq 28 relates the entropy of the solute, S_i , to the concentration in molarity of solute i , C_i (6). This equation applies to ideally dilute

$$S_i = S_i^\circ - R \ln C_i \quad (28)$$

solutions of solute. The standard state of solute i is a concentration of 1 M. If a concentration of 1 M is substituted into the eq 28 for solute i , then the result is $S_i = S_i^\circ$, meaning the entropy of solute i is equal to the standard-state entropy of solute i . Also, eq 28 shows that as the concentration of solute i decreases (perhaps as a result of either a dilution or a reaction), the entropy of solute i increases. See the Supplemental Material (Day 9, *Thermodynamic Equilibrium*

of Reactive Systems Involving Solutes) for a derivation of the equilibrium constant.¹⁸

Days 10 and 11: Galvanic Cells

Students learn the concepts involved in electrochemical cells. In preparation for the laboratory experiments on days 12 and 13, for homework, students do an *entropy analysis* of eq 1–6 from *Understanding Electrochemical Thermodynamics through Entropy Analysis* (2).

Day 12: Cell Potentials and Entropy

Students conduct the experiment from *Understanding Electrochemical Thermodynamics through Entropy Analysis* (2). Specifically, students construct six galvanic cells based on the six redox reactions in the previous day's homework. Students measure cell potentials, note cathodes, perform a graphical analysis, and do additional *entropy analyses* for eq 7–10, along with predictions of cell potentials (2).

Day 13: Validation of Cell Potential Predictions

Students construct the cells for eq 7–10 (2), measure the cell potentials, and determine the cathodes. A discussion of the results follows, leading to a fundamental understanding of how both n , the number of moles of electrons transferred, and the S_{univ}° affect electrochemical cell potentials.

Day 14: Stuck In the Middle With You (31)

Students discover the concept of thermodynamic equilibrium. There is one fundamental question, "Why does thermal energy always spontaneously transfer from a hotter object to a cooler object?" A problem is introduced to examine this concept.

Consider two identical bars of metal (same material, mass, and dimensions) each with a mass of 0.00200 kg and a specific heat capacity of 500 J kg⁻¹ K⁻¹. The left-side bar has a temperature of 1.0 K and the right-side bar has a temperature of 7.0 K, all of which is represented by the notation {1,7}. When the two bars come into physical contact, thermal energy transfers until the two bars are equal in temperature.¹⁸ How does the entropy of the two bars change during the process?

It is instructive to break the problem down into three parts and then evaluate the entropy change for each, separately. Each part has the left-side bar and the right-side bar changing by 1 Kelvin each time, until both bars are at the same temperature, 4 K. Equation 4, from day 4, calculates the entropy change for each part (Table 4 and Figure 1). The total change in entropy (total ΔS_{univ}) increases as thermal energy transfers from the right-side bar to the left-side bar, reaching a maximum when both bars are equal in temperature (Figure 1). It is always true that when thermal energy moves from a hotter body to a cooler body, there is a net increase in entropy. In the process of transferring energy, the entropy increase from the cooler body is greater than the entropy decrease from the hotter body, resulting in a net increase in entropy.¹⁹

Table 4. The Entropy Changes for Two Contacting Metal Bars Undergoing Temperature Changes

Temperatures { T_i^L, T_i^R } → { T_f^L, T_f^R } ^a /K	ΔS (left-side)/ (J K ⁻¹)	ΔS (right-side)/ (J K ⁻¹)	ΔS_{univ} / (J K ⁻¹)	Total ΔS_{univ} ^e / (J K ⁻¹)
{1,7} → {1,7} ^b	0	0	0	0
{1,7} → {2,6} ^c	0.69	-0.15	0.54 ^d	0.54
{2,6} → {3,5}	0.41	-0.18	0.23	0.77
{3,5} → {4,4}	0.29	-0.22	0.07	0.84

^a T_i^L is the initial temperature of the left side, T_i^R is the initial temperature of the right side, T_f^L is the final temperature of the left side, and T_f^R is the final temperature of the right side.

^bThis is the situation before any thermal energy transfers.

^cLeft-side metal starts at 1 K and the right-side metal starts at 7 K. The left-side metal stops at 2 K and the right-side metal stops at 6 K.

^d $\Delta S_{\text{univ}} = \Delta S$ (left-side) + ΔS (right-side) = (1 J/K)ln(T_f^L/T_i^L) + (1 J/K)ln(T_f^R/T_i^R) = (1 J/K)ln(2/1) + (1 J/K)ln(6/7).

^eTotal ΔS_{univ} represents the total entropy change in the metals since the start of the process when they were {1,7}.

Students see graphically that the thermal energy transfer (flow) causes an increase in entropy and that the transfer stops when the entropy is at a maximum value, corresponding to equal temperatures. However, each successive change results in a smaller increase in the entropy of the universe, until they are equal in temperature. The point at which the total entropy change is at a maximum (the “hilltop”) is the condition of thermodynamic equilibrium. At this point, students appreciate why reactions proceed to a certain extent and then stop (Day 9). When a reaction has reached maximum entropy or thermodynamic equilibrium, it has no more capacity for change. Brosnan has shown that a chemical reaction reaches maximum entropy (ΔS_{univ}) at a certain extent of reaction (32). Bent demonstrates that the entropy reaches a maximum at equilibrium (4c).

Day 15: Coupled Chemical Reactions

Students explore the idea of coupling²⁰ a spontaneous process to a nonspontaneous process. If a spontaneous chemical reaction produces more net entropy than a nonspontaneous

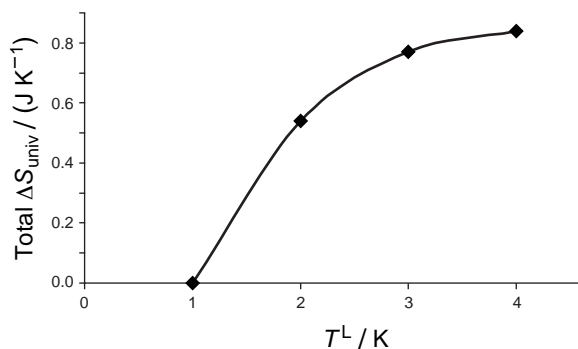


Figure 1. Entropy versus the temperature of the left-side metal (T^L).

ous chemical reaction loses and the two are chemically “coupled”, then the spontaneous reaction may cause the nonspontaneous reaction to happen. If the product of one of the reactions is used as a reactant in the other, then the two reactions are chemically “coupled”. Four examples are used to illustrate the concept: (i) hydroxide ion assisted ionization of phenolphthalein, (ii) acid assisted dissolution of calcium carbonate, (iii) carbon assisted degradation of copper(I) oxide, and (iv) carbon assisted degradation of iron(III) oxide. Demonstration of the first two reveals the necessary physical changes that accompany each successful coupled pair. These reactions are discussed in more detail in the Supplemental Material.^W

Day 16: Free Energy

The connection is made between the Gibbs free energy and entropy analysis. Students see the similarities and differences of both, after stressing that the Gibbs function is in terms of system variables only, which is a strength and a weakness. The Gibbs function is given as eq 29, and at a constant temperature it reduces to eq 30.²¹

$$G \equiv H - TS \quad (29)$$

$$\Delta G = \Delta H - T\Delta S \quad (30)$$

At constant pressure, eq 17 substitutes in eq 19, giving eq 31:

$$\Delta S_{\text{univ}} = \frac{-\Delta_r H^\circ}{T} + \Delta_r S_{\text{sys}}^\circ \quad (31)$$

Multiplying both sides by $-T$ gives eq 32:

$$-T\Delta S_{\text{univ}} = \Delta_r H^\circ - T\Delta_r S_{\text{sys}}^\circ \quad (32)$$

Substitution of eq 30 in eq 32 gives eq 33:

$$-T\Delta S_{\text{univ}} = \Delta_r G^\circ \quad (33)$$

This demonstrates the equivalency of eq 19 to eq 30. For spontaneous changes, $\Delta S_{\text{univ}} > 0$ and since $T > 0$, then $\Delta G < 0$. The product of ΔS_{univ} and $-T$ gives the change in Gibbs energy, the free energy. The free energy is directly correlated with the change in the entropy of the universe. The free energy represents the maximum quantity of available “useful” energy from a chemical reaction at constant pressure and temperature. Useful energy is all forms of interconvertible energy, such as, electrical, chemical, mechanical, light, and gravitational (see the *Destiny* activity). This excludes thermal energy and PV -related energy (energy of expansion²²) as useful energy.

If a chemical reaction is spontaneous (entropy-producing), then it is capable of transferring useful energy to an energy-demanding process or to an entropy-diminishing chemical reaction (a nonspontaneous reaction, $\Delta S_{\text{univ}} < 0$). For the latter, a spontaneous chemical reaction may transfer some or all of its useful energy to a coupled nonspontaneous chemical reaction. If enough energy is transferred, then the nonspontaneous chemical reaction takes place. If there is an excess of useful energy, then the excess will become dispersed thermal energy, resulting in an overall $\Delta S_{\text{univ}} > 0$.

If the Gibbs energy cannot be harnessed as useful energy, then the Gibbs energy represents the maximum extent of energy dispersal to the universe. The extent of the energy dispersal, of course, depends on the existing thermal energy content of the universe or the universe’s ability to disperse energy over matter. A more advanced discussion of Gibbs energy and “work effect” appears in the Supplemental Material.^u

^uSupplemental Material

Additional information pertaining to the entropy analysis is available in this issue of *JCE Online*.

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Notes

1. Planck was probably the first to do entropy analysis using $\Psi = S - (H/T)$. Strong and Haliwell proposed that $\Delta S_{\text{tu}} = -\Delta H_s/T + \Delta S_s$ be referred to as the Planck function, where ΔS_{tu} is the total change in entropy for a process that is totally unopposed (9).

2. This is most true with beginning chemistry textbooks and freshman college chemistry textbooks. The ideas continue in more advanced classes, such as physical chemistry, but with the introduction of thermal energy.

3. Web sites pertaining to the second law of thermodynamics. <http://www.secondlaw.com>, <http://www.2ndlaw.com>, <http://www.shakespeare2ndlaw.com>, and <http://www.entropysimple.com> (all accessed Aug 2004).

4. For a molecule, the kinetic energy is the energy associated with the motion (translational, vibrational, and rotational) of the molecule.

5. The song *Destiny* is played during the activity (20). The author likes to choose titles that students find entertaining.

6. The pictorial presentations work well for the time period. However, a well-written solution should not be dismissed, for writing is an important skill.

7. The incoherent motion of molecules characterizes thermal energy (11b).

8. In order for students to appreciate the unidirectional nature of the universe, one way arrows are placed in the classroom in such a way that students are directed to enter from only one entrance and must exit from a second entrance. This is done for a period of one week.

9. A given macrostate is composed of many microstates, which are referred to as microcanonical ensembles. Temperature, volume, and number measure a macroscopic state. Whereas, a microcanonical ensemble is represented by energy, volume, and number.

10. Interestingly, Planck (25) determined the value of the Boltzmann constant. Planck solved two simultaneous equations for two unknowns, k_B (Boltzmann constant) and h (Planck constant).

11. The quantity dq_{rev} refers to an infinitesimal change in the heat effect in a reversible process. A “reversible process” is a process that can be returned to its initial state without an increase or decrease in the entropy of the universe. In other words, $\Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$ for reversible processes. Ice melting at 0 °C is an example of a reversible process. Recently, Craig and Gislason argued that when a system returns to its initial state, the surroundings must also be restored to its original state (21). In other words, in the forward-and-back process, the surroundings must be unchanged.

12. There does not appear to be any rationale associated with the choice of S as the symbol for entropy (28).

13. The heat effect, q , is path dependent only with regard to the system. It is, however, a state function with regard to the thermal reservoir or surroundings (6).

14. These systems are referred to as “reversible” (rev). The change in the entropy of a reversible system at constant temperature is the quotient of the heat effect, q_{rev} , for the reversible system and temperature, T , $\Delta S_{\text{sys}} = q_{\text{rev}}/T$. The change in entropy for irreversible systems cannot be determined from the heat effect for the irreversible system, $\Delta S_{\text{sys}} \neq q_{\text{irrev}}/T$. The freezing of water at -10 °C (1 atm pressure) is irreversible, but at 0 °C (1 atm pressure) it is reversible. The ΔS_{univ} for a reversible process is zero.

15. Concrete learners require visual representations to assist in the understanding of the qualitative entropy analysis of a reversible process. Red construction paper is cut into strips to represent “thermal energy”. Five strips are placed onto a surface, representing a degree of entropy. Two strips are added to the five to represent a greater degree of entropy, and then, the seven strips are spread apart to represent even more entropy. Two bottles, one with white paper (the system of ice) and one with blue paper (the system of liquid water), are used to represent the reactive system undergoing change. Two red strips of paper are removed from the pile to represent the conversion of thermal energy into potential energy, a decrease in the entropy of the surroundings.

16. For the reaction of 1 A producing 2 B, a $\Delta S_{\text{univ}} = 0$ gives 0.61 mol/L of A and 0.78 mol/L of B, when starting with 1 mol/L of A.

17. $\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + (T_2 - T_1)\Delta_r C_p$; $C_{p,m}^\circ(\text{H}_2\text{O}, \text{g}) = 33.58 \text{ J}/(\text{K mol})$, $C_{p,m}^\circ(\text{H}_2\text{O}, \text{l}) = 75.291 \text{ J}/(\text{K mol})$; (30) $\Delta_r H^\circ(373 \text{ K}) = 40.9 \text{ kJ}/(\text{mol rxn})$; $\Delta_r S_{\text{sys}}^\circ(T_2) = \Delta_r S_{\text{sys}}^\circ(T_1) + \Delta_r C_p \ln(T_2/T_1)$; $\Delta_r S_{\text{sys}}^\circ(373 \text{ K}) = 109.6 \text{ J}/\text{K}$.

18. In an earlier draft, the problem involved the transfer of thermal energy until the temperatures flip-flop (left-side bar is at 7.0 K and the right-side bar is 1.0 K). Pedagogically, students should not determine entropy changes that do not occur.

19. See Day 4 of the Supplemental Material.^W

20. The term “coupling” replaces the more traditional terminology of “driving”. “Driving” suggests a Newtonian force underlying the concept of entropy, which is not the case.

21. The Helmholtz function, $A = U - TS$, is useful under constant volume conditions, where U represents the internal energy of the chemical system and A represents the maximum available useful energy.

22. A gaseous product expanding against the atmosphere exemplifies this.

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