

Chapter 19. Chemical Thermodynamics

Common Student Misconceptions

- Students often believe that a spontaneous process should occur very quickly. They do not appreciate the difference between kinetics and thermodynamics.
- Students have a problem distinguishing between absolute thermodynamic quantities and the change in thermodynamic quantities.
- Students often cannot tell the difference between heat and temperature.
- Students often think that only exothermic reactions can be spontaneous.
- Students often forget about the system's surroundings when evaluating changes in thermodynamic quantities, such as entropy.
- Students often do not pay attention to the states of matter (g, l, s) of substances in Appendix C.
- Students often include the temperature of 298 K as part of the standard conditions.

Teaching Tips

- Equation 19.15 is valid only when ΔH° and ΔS° do not significantly change with temperature and pressure.
- When ΔG° is negative, reactions are said to be *exergonic*; when ΔG° is positive, reactions are said to be *endergonic*.
- Students usually benefit from reviewing logarithms and graphs from Appendix A prior to starting this chapter.

Lecture Outline

19.1 Spontaneous Processes^{1,2,3,4}

- *Chemical thermodynamics* is concerned with energy relationships in chemical reactions.
 - We consider enthalpy.
 - We also consider *entropy* in the reaction.
- Recall the first law of thermodynamics: energy is conserved.

$$\Delta E = q + w$$
 - where ΔE is the change in internal energy, q is the heat absorbed by the system from the surroundings, and w is the work done.
- Any process that occurs without outside intervention is a **spontaneous** process.
 - When two eggs are dropped, they spontaneously break.
 - The reverse reaction (two eggs leaping into your hand with their shells back intact) is not spontaneous.
 - We can conclude that a spontaneous process has a direction.
- A process that is spontaneous in one direction is *nonspontaneous* in the opposite direction.
- Temperature may also affect the spontaneity of a process.

¹ “Air Bags” Animation from Instructor’s Resource CD/DVD

² “Demystifying Introductory Chemistry. Part 4: An Approach to Reaction Thermodynamics through Enthalpies, Entropies, and Free Energies of Atomization” from Further Readings

³ “A Model of Thermal Equilibrium: A Tool for the Introduction of Thermodynamics” from Further Readings

⁴ “Thermodynamics and Spontaneity” from Further Readings

Seeking a Criterion for Spontaneity

- To understand why some processes are spontaneous we must look at the ways in which the state of a system might change.
 - Temperature, internal energy, and enthalpy are state functions.
 - Heat transferred between a system and the surroundings, as well as work done on or by a system, are *not* state functions.

Reversible and Irreversible Processes^{5,6,7,8}

- A **reversible process** is one that can go back and forth between states along the same path.
 - The reverse process restores the system to its original state.
 - The path taken back to the original state is *exactly* the reverse of the forward process.
 - There is no net change in the system or the surroundings when this cycle is completed.
 - Completely reversible processes are too slow to be attained in practice.
- Consider the interconversion of ice and water at 1 atm, 0 °C.
 - Ice and water are in equilibrium.
 - We now add heat to the system from the surroundings.
 - We melt 1 mole of ice to form 1 mole of liquid water.
 - $q = \Delta H_{\text{fus}}$
 - To return to the original state, we reverse the procedure.
 - We remove the same amount of heat from the system to the surroundings.
- An **irreversible process** cannot be reversed to restore the system and surroundings back to their original state.
 - A different path (with different values of q and w) must be taken.
- Consider a gas in a cylinder with a piston.
 - Remove the partition, and the gas expands to fill the space.
 - No P - V work is done on the surroundings.
 - $w = 0$
 - Now use the piston to compress the gas back to the original state.
 - The surroundings must do work on the system.
 - $w > 0$
 - A different path is required to get the system back to its original state.
 - Note that the surroundings are NOT returned to their original conditions.
- For a system at equilibrium, reactants and products can interconvert *reversibly*.
- For a spontaneous process, the path between reactants and products is *irreversible*.
- Consider the expansion of an ideal gas.
- Consider an initial state: two 1-liter flasks connected by a closed stopcock.
 - One flask is evacuated and the other contains 1 atm of gas.
 - We open the stopcock while maintaining the system at constant temperature.
 - Initial state: an ideal gas confined to a cylinder kept at constant temperature in a water bath.
 - The process is **isothermal** at constant temperature.
 - $\Delta E = 0$ for an isothermal process.
 - Thus, $q = -w$.
- Allow the gas to expand from V_1 to V_2 .
- Pressure decreases from P_1 to P_2 .
 - The final state: two flasks connected by an open stopcock.

⁵ Figure 19.4 from Transparency Pack

⁶ Figure 19.5 from Transparency Pack

⁷ “Ice” 3-D Model from Instructor’s Resource CD/DVD

⁸ “Oxygen” 3-D Model from Instructor’s Resource CD/DVD

- Each flask contains gas at 0.5 atm.
- Therefore, the gas does no work and heat is not transferred.
- Why does the gas expand?
 - Why is the process spontaneous?
 - Why is the reverse process nonspontaneous?
 - When the gas molecules spread out into the 2 liter system there is an increase in the *randomness* or *disorder*.
 - Processes in which the disorder or entropy of the system increases tend to be spontaneous.

19.2 Entropy and the Second Law of Thermodynamics^{9,10,11,12,13,14,15}

Entropy Change

- **Entropy**, S , is a thermodynamic term that reflects the disorder, or randomness, of the system.
 - The more disordered, or random, the system is, the larger the value of S .
- Entropy is a state function.
 - It is independent of path.
 - For a system, $\Delta S = S_{\text{final}} - S_{\text{initial}}$.
- If $\Delta S > 0$ the randomness increases, if $\Delta S < 0$ the order increases.
- Suppose a system changes reversibly between state 1 and state 2.
 - Then, the change in entropy is given by:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- Where q_{rev} is the amount of heat added reversibly to the system.
 - The subscript “rev” reminds us that the path between states is reversible.
 - Example: A phase change occurs at constant temperature with the reversible addition of heat.

ΔS for Phase Changes

- Phase changes (such as melting a substance at its melting point) are isothermal processes.

$$\Delta S_{\text{fusion}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fusion}}}{T}$$

The Second Law of Thermodynamics¹⁶

- The **second law of thermodynamics**:
 - any irreversible process results in an increase in total entropy while any reversible process results in no overall change in entropy.
 - This explains why spontaneous processes have a direction.
- In any spontaneous process, the entropy of the universe increases.
- The change in entropy of the universe is the sum of the change in entropy of the system and the change in entropy of the surroundings.

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

⁹ “Teaching Entropy Analysis in the First-Year High School Course and Beyond” from Further Readings

¹⁰ “Visualizing Entropy” from Further Readings

¹¹ “Another Face of Entropy” from Further Readings

¹² “Pictorial Analogies III: Heat Flow, Thermodynamics, and Entropy” from Further Readings

¹³ “Order, Chaos, and All That!” from Further Readings

¹⁴ “Entropy: Conceptual Disorder” from Further Readings

¹⁵ “Entropy, Disorder, and Freezing” from Live Demonstrations

¹⁶ “Spontaneous Assembly of Soda Straws” from Further Readings

- For a reversible process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$
- For a spontaneous process (i.e., irreversible):

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$
 - Entropy is not conserved: ΔS_{univ} is continually increasing.
- Note that the second law states that the entropy of the universe must increase in a spontaneous process.
 - It is possible for the entropy of a system to decrease as long as the entropy of the surroundings increases.

19.3 Molecular Interpretation of Entropy

Expansion of a Gas at the Molecular Level¹⁷

- Gas expansion into a vacuum is a spontaneous process.
- Consider two flasks connected by a stopcock.
 - Track the movement of two gas molecules as they move around.
 - Before opening the stopcock: both molecules are confined to the left flask.
 - After opening the stopcock: the molecules move randomly throughout the entire apparatus.
 - Since the molecular motion is random, all four of the arrangements are equally likely.
 - The probability of finding both molecules in the left flask is $(1/2)^2$.
 - What if we had three molecules?
 - The probability of finding all three in the same flask is $(1/2)^3$.
 - What if we had a *mole* of gas molecules?
 - The probability is now $(1/2)^N$ where N is 6.02×10^{23} !
 - There is essentially zero likelihood that all of the gas molecules will be in the same flask at the same time.
 - When the gas spreads throughout the system, any given molecule can be in either flask rather than confined to the left flask.
 - The arrangement is more random or disordered than when the molecules are all confined to the left flask.

Boltzmann's Equation and Microstates^{18,19,20,21,22}

- *Statistical thermodynamics* is a field that uses statistics and probability to link the microscopic and macroscopic worlds.
 - Entropy may be connected to the behavior of atoms and molecules.
 - Envision a **microstate**: a snapshot of the positions and speeds of all molecules in a sample of a particular macroscopic state at a given point in time.
 - Consider a molecule of ideal gas at a given temperature and volume.
 - A microstate is a single possible arrangement of the positions and kinetic energies of the gas molecules.
 - Other snapshots are possible (different microstates).
- Each thermodynamic state has a characteristic number of microstates (W).

¹⁷ Figure 19.6 from Transparency Pack

¹⁸ "Derivation of the Second Law of Thermodynamics from Boltzmann's Distribution Law" from Further Readings

¹⁹ "Give Them Money: The Boltzmann Game, a Classroom or Laboratory Activity Modeling Entropy Changes and the Distribution of Energy in Chemical Systems" from Further Readings

²⁰ "The Boltzmann Distribution" from Further Readings

²¹ Figure 19.8 from Transparency Pack

²² "Mixing of Gases" Activity from Instructor's Resource CD/DVD

- The Boltzmann equation shows how entropy (S) relates to W .

$$S = k \ln W$$
, where k is Boltzmann's constant (1.38×10^{-23} J/K).
- Entropy is thus a measure of how many microstates are associated with a particular macroscopic state.
- Any change in the system that increases the number of microstates gives a positive value of ΔS and vice versa.
 - In general, the number of microstates will increase with an increase in volume, an increase in temperature, or an increase in the number of molecules because any of these changes increases the possible positions and energies of the molecules.

Molecular Motions and Energy^{23,24}

- When a substance is heated, the motion of its molecule increases.
 - The higher the temperature, the faster the molecules move.
 - Hotter systems have *broader distribution* of molecular speeds.
 - Consider a sample of ideal gas.
 - The molecules move around the container.
 - They also show three kinds of more complex motion:
 - **translational motion**
 - The moving of a molecule from one point in space to another.
 - **vibrational motion**
 - The shortening and lengthening of bonds, including the change in bond angles.
 - **rotational motion**
 - The spinning of a molecule about some axis.
 - Energy is required to get a molecule to translate, vibrate, or rotate.
 - These forms of motion are ways molecules can store energy (*motional energy*).
 - The more energy stored in translation, vibration, and rotation, the greater the entropy.
- In general:
 - The number of microstates possible for a system increases with an increase in volume, temperature, or the number of molecules.
 - Each of these changes increases the possible positions and kinetic energies of the molecules in the system.

Making Qualitative Predictions About ΔS ²⁵

- In most cases, an increase in the number of microstates (and thus entropy) parallels an increase in:
 - temperature
 - volume
 - number of independently moving particles.
- Consider the melting of ice.
 - In ice, the molecules are held rigidly in a lattice.
 - When it melts, the molecules will have more freedom to move (increases the number of degrees of freedom).
 - The molecules are more randomly distributed.
- Consider a KCl crystal dissolving in water.
 - The solid KCl has ions in a highly ordered arrangement.
 - When the crystal dissolves, the ions have more freedom.
 - They are more randomly distributed.
 - However, now the water molecules are more ordered.

²³ “Molecular Motions” Activity from Instructor’s Resource CD/DVD

²⁴ “Water” 3-D Model from Instructor’s Resource CD/DVD

²⁵ Figure 19.10 from Transparency Pack

- Some must be used to hydrate the ions.
 - Thus this example involves both ordering and disordering.
 - The disordering usually predominates (for most salts).
- Consider the reaction of $\text{NO}(g)$ with $\text{O}_2(g)$ to form $\text{NO}_2(g)$:

$$2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$$
 - The total number of gas molecules decreases.
 - Therefore, the entropy decreases.
 - How can we relate changes in entropy to changes at the molecular level?
 - Formation of the new N-O bonds “tie up” more of the atoms in the products than in the reactants.
 - The *degrees of freedom* associated with the atoms have changed.
 - The greater the freedom of movement and degrees of freedom, the greater the entropy of the system.
 - Individual molecules have degrees of freedom associated with motions within the molecule.
- In general, entropy will increase when:
 - liquids or solutions are formed from solids,
 - gases are formed from solids or liquids, or
 - the number of gas molecules increases.

The Third Law of Thermodynamics^{26,27}

- In a perfect crystal at 0 K there is no translation, rotation, or vibration of molecules.
 - Therefore, this is a state of perfect order.
 - **Third law of thermodynamics:** The entropy of a perfect pure crystal at 0 K is zero.
- Entropy will increase as we increase the temperature of the perfect crystal.
 - Molecules gain vibrational motion.
 - The degrees of freedom increase.
- As we heat a substance from absolute zero, the entropy must increase.
- The entropy changes dramatically at a phase change.
 - When a solid melts, the molecules and atoms have a large increase in freedom of movement.
 - Boiling corresponds to a much greater change in entropy than melting.

19.4 Entropy Changes in Chemical Reactions^{28,29,30,31,32,33}

- Absolute entropy can be determined from complicated measurements.
 - Values are based on a reference point of zero for a perfect crystalline solid at 0K (the 3rd law).
- **Standard molar entropy, S°** is the molar entropy of a substance in its standard state.
 - Similar in concept to ΔH° .
 - Units: J/mol-K.
 - Note that the units of ΔH are kJ/mol.
- Some observations about S° values:
 - Standard molar entropies of elements are not zero.
 - $S^\circ_{\text{gas}} > S^\circ_{\text{liquid}}$ or S°_{solid} .
 - S° tends to increase with increasing molar mass of the substance.

²⁶ “Temperature Dependence of Entropy” Activity from Instructor’s Resource CD/DVD

²⁷ Figure 19.13 from Transparency Pack

²⁸ Table 19.1 from Transparency Pack

²⁹ “Periodic Trends for the Entropy of Elements” from Further Readings

³⁰ “Estimation of Entropy Changes” Activity from Instructor’s Resource CD/DVD

³¹ “Methane” 3-D Model from Instructor’s Resource CD/DVD

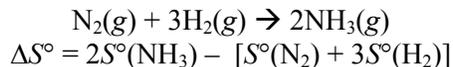
³² “Ethane” 3-D Model from Instructor’s Resource CD/DVD

³³ “Propane” 3-D Model from Instructor’s Resource CD/DVD

- S° tends to increase with the number of atoms in the formula of the substance.
- For a chemical reaction that produces n products from m reactants:

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

- Example: Consider the reaction:



Entropy Changes in the Surroundings

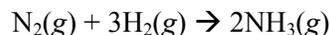
- For an isothermal process,

- $\Delta S_{\text{surr}} = \frac{q_{\text{sys}}}{T}$

- For a reaction at constant pressure,

- $q_{\text{sys}} = \Delta H$

- Example: consider the reaction:



- The entropy gained by the surroundings is greater than the entropy lost by the system.
- This is the sign of a spontaneous reaction: the overall entropy change of the universe is positive.
- $\Delta S_{\text{univ}} > 0$

19.5 Gibbs Free Energy^{34,35,36,37,38,39,40,41,42}

- For a spontaneous reaction the entropy of the universe must increase.
- Reactions with large negative ΔH values *tend* to be spontaneous.
- How can we use ΔS and ΔH to predict whether a reaction is spontaneous?
- The **Gibbs free energy**, (**free energy**), G , of a state is:

$$G = H - TS$$

- Free energy is a state function.
- For a process occurring at constant temperature, the free energy change is:

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

- Recall:

- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + [-\Delta H_{\text{sys}} / T]$

- Thus,

- $-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

- The sign of ΔG is important in predicting the spontaneity of the reaction at $T, p = \text{constant}$.
 - If $\Delta G < 0$ then the forward reaction is spontaneous.
 - If $\Delta G = 0$ then the reaction is at equilibrium and no net reaction will occur.
 - If $\Delta G > 0$ then the forward reaction is not spontaneous.
 - However, the reverse reaction is spontaneous.
 - If $\Delta G > 0$, work must be supplied from the surroundings to drive the reaction.

³⁴ “Josiah Willard Gibbs and Wilhelm Ostwald: A Contrast in Scientific Style” from Further Readings

³⁵ “J. Willard Gibbs (1839–1903): A Modern Genius” from Further Readings

³⁶ Figure 19.16 from Transparency Pack

³⁷ Figure 19.17 from Transparency Pack

³⁸ “Free Energy and Reaction Mixture” Activity from Instructor’s Resource CD/DVD

³⁹ “Formation of Water” Movie from Instructor’s Resource CD/DVD

⁴⁰ “Hydrogen” 3-D Model from Instructor’s Resource CD/DVD

⁴¹ “Nitrogen” 3-D Model from Instructor’s Resource CD/DVD

⁴² “Ammonia” 3-D Model from Instructor’s Resource CD/DVD

- The equilibrium position in a spontaneous process is given by the minimum free energy available to the system.
 - The free energy decreases until it reaches this minimum value.

Standard Free-Energy Changes

- We can tabulate **standard free energies of formation**, ΔG°_f .
 - Standard states are pure solid, pure liquid, 1 atm (gas), 1 M concentration (solution), and $\Delta G^\circ_f = 0$ for elements.
 - We most often use 25 °C (or 298 K) as the temperature.
 - The standard free-energy change for a process is given by:

$$\Delta G^\circ = \sum n\Delta G^\circ_f(\text{products}) - \sum m\Delta G^\circ_f(\text{reactants})$$

- The quantity ΔG° for a reaction tells us whether a mixture of substances will spontaneously react to produce more reactants ($\Delta G^\circ > 0$) or products ($\Delta G^\circ < 0$).

FORWARD REFERENCES

- Standard conditions (Table 19.3) will be brought up throughout Chapter 20.
- ΔG as a measure of reaction spontaneity will be linked to the cell potential in Chapter 20 (section 20.5).
- Entropy of the chelate effect will be further discussed in Chapter 23 (section 23.3).

19.6 Free Energy and Temperature⁴³

- The sign of ΔG tells us if the reaction is spontaneous, at a given temperature and pressure condition.
- Focus on $\Delta G = \Delta H - T\Delta S$.
 - If $\Delta H < 0$ and $-T\Delta S < 0$:
 - ΔG will always be < 0 .
 - Thus the reaction will be spontaneous.
 - If $\Delta H > 0$ and $-T\Delta S > 0$:
 - ΔG will always be > 0 .
 - Thus, the reaction will not be spontaneous.
 - If ΔH and $-T\Delta S$ have different signs:
 - The sign of ΔG will depend on the sign and magnitudes of the other terms.
 - Temperature will be an important factor.
 - For example, consider the following reaction:

$$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H > 0, \Delta S > 0$$
 - At a temperature less than 0 °C:
 - $\Delta H > T\Delta S$
 - $\Delta G > 0$
 - The melting of ice is not spontaneous when the temperature is less than 0 °C.
 - At a temperature greater than 0 °C:
 - $\Delta H < T\Delta S$
 - $\Delta G < 0$
 - The melting of ice is spontaneous when the temperature is greater than 0 °C.
 - At 0 °C:
 - $\Delta H = T\Delta S$
 - $\Delta G = 0$
 - Ice and water are in equilibrium at 0 °C.
- Note that we have assumed that both ΔH° and ΔS° were independent of temperature; they aren't, but the changes are negligible.
- Even though a reaction has a negative ΔG , it may occur too slowly to be observed.

⁴³ "Gibbs Free Energy" Activity from Instructor's Resource CD/DVD

- Thermodynamics gives us the direction of a spontaneous process; it does not give us the rate of the process.

19.7 Free Energy and the Equilibrium Constant^{44,45,46,47}

Free Energy Under Nonstandard Conditions

- Recall that ΔG° and K_{eq} (equilibrium constant) apply to *standard conditions*.
- Recall that ΔG and Q (equilibrium quotient) apply to *any conditions*.
- It is useful to determine whether substances will react under specific conditions:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Relationship Between ΔG° and K

- At equilibrium, $Q = K_{\text{eq}}$ and $\Delta G = 0$, so:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\therefore \Delta G^\circ = -RT \ln K$$

Thus we see a relationship between free energy and the equilibrium constant:

$$K = e^{-\Delta G^\circ / RT}$$

- From the above we can conclude:
 - If $\Delta G^\circ < 0$, then $K > 1$.
 - If $\Delta G^\circ = 0$, then $K = 1$.
 - If $\Delta G^\circ > 0$, then $K < 1$.

Driving Nonspontaneous Reactions

- If $\Delta G > 0$, work must be supplied from the surroundings to drive the reaction.
- Biological systems often use one *spontaneous* reaction to drive another *nonspontaneous* reaction.
 - These reactions are *coupled reactions*.
- The energy required to drive most nonspontaneous reactions comes from the metabolism of foods.
 - Example: Consider the oxidation of glucose:

$$\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \quad \Delta G^\circ = -2880 \text{ kJ.}$$
 - The free energy released by glucose oxidation is used to convert low energy adenosine diphosphate (ADP) and inorganic phosphate into high energy adenosine triphosphate (ATP).
 - When ATP is converted back to ADP the energy released may be used to “drive” other reactions.

FORWARD REFERENCES

- Units of Gibb’s free energy change in calculations linking ΔG with the cell potential will be discussed in Chapter 20 (section 20.5).
- Gibb’s free energy change will be used to derive the Nernst equation in Chapter 20 (section 20.6).
- Equation 19.17 will be used in Chapter 22 (section 22.5) to calculate the equilibrium constant for reactions involving oxygen.
- Energy released by $\text{ATP} \rightarrow \text{ADP}$ reaction can be used to perform mechanical work in muscle contraction and drive biochemical reactions (Chapter 22, section 22.8).

⁴⁴ “The Free Energy Prediction and the Principle of Le Châtelier” from Further Readings

⁴⁵ “Free Energy and Chemical Equilibrium” Activity from Instructor’s Resource CD/DVD

⁴⁶ “The Conversion of Chemical Energy. Part 2: Biochemical Examples” from Further Readings

⁴⁷ “Sodium Chloride (1 × 1 Unit Cell)” 3-D Model from Instructor’s Resource CD/DVD

Further Readings:

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14. Travis Thoms, "Periodic Trends for the Entropy of Elements," *J. Chem. Educ.*, Vol. 72, **1995**, 16.
15. Sidney Rosen, "J. Willard Gibbs (1839–1903): A Modern Genius," *J. Chem. Educ.*, Vol. 60, **1983**, 593–594.
16. Robert J. Deltete and David L. Thorsell, "Josiah Willard Gibbs and Wilhelm Ostwald: A Contrast in Scientific Style," *J. Chem. Educ.*, Vol. 73, **1996**, 289–295.
17. Zheng Xianmin, "The Free Energy Prediction and the Principle of Le Châtelier," *J. Chem. Educ.*, Vol. 66, **1989**, 401–402.
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Live Demonstrations:

1. Lee R. Summerlin, Christie L. Borgford, and Julie B. Ealy, “A Chemical Hand Warmer,” *Chemical Demonstrations: A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society, **1988**), pp. 99–100.
2. Brian B. Laird, “Entropy, Disorder, and Freezing,” *J. Chem. Educ.*, Vol. 76, **1999**, 1388–1390.