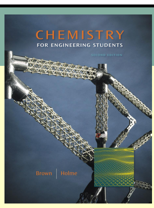

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Chapter 10
Entropy and the Second Law of Thermodynamics

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Chapter Objectives

- Describe the scientific and economic obstacles to more widespread recycling of plastics.
- Explain the concept of entropy in your own words.
- Deduce the sign of ΔS for many chemical reactions by examining the physical state of the reactants and products.
- State the second law of thermodynamics in words and equations and use it to predict spontaneity.
- State the third law of thermodynamics.

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Chapter Objectives

- Use tabulated data to calculate the entropy change in a chemical reaction.
- Derive the relationship between the free energy change of a system and the entropy change of the universe.
- Use tabulated data to calculate the free energy change in a chemical reaction.
- Explain the role of temperature in determining whether a reaction is spontaneous.
- Use tabulated data to determine the temperature range for which a reaction will be spontaneous.

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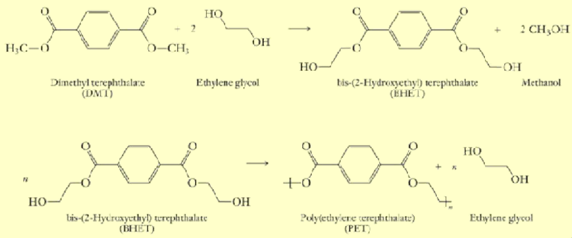
Recycling of Plastics

- Standard plastic soft drink bottles are made from poly(ethylene terephthalate) or PET/PETE.
  - PET is manufactured in a two step process starting with ethylene glycol and dimethyl terephthalate.



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Recycling of Plastics

- Soft drink bottles manufactured from PET can be recycled.
  - The PET plastic bottles are separated from other plastic types and crushed.
  - The crushed PET is washed, dried, and cut into small flakes.
  - The PET flakes are melted and extruded into spaghetti-like strands that are cut into smaller pellets, which are sold to manufacturers to make items such as fiberfill for sleeping bags and coats, fleece fabrics for outdoor wear, carpeting, and industrial strapping.

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Recycling of Plastics

- Recycled PET is not used in the manufacture of new soda bottles for economic and legal restrictions.
  - Cheaper to manufacture virgin PET than to use recycled PET.
  - Recycled PET not allowed into food and beverage containers due to possible contamination fears.
- During the recycling process, PET polymer degrades.
  - The length of the polymer chain decreases.
  - If PET were recycled into soda bottles, the resulting bottles would be thicker and heavier than bottles manufactured from virgin PET.

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Spontaneity: Natures Arrow

- Some processes or reactions proceed in only one direction.
  - Gasoline reacts spontaneously with oxygen to form carbon dioxide and water, but water and carbon dioxide never spontaneously react to reform gasoline.
- A spontaneous process takes place without continuous intervention, according to thermodynamics.
  - Spontaneous processes are not necessarily rapid processes.
  - The combustion of diamond is thermodynamically spontaneous, but diamonds are considered to last forever.

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Spontaneous Processes

- Some spontaneous reactions only occur once they are initiated.
  - The combustion of gasoline is a spontaneous reaction but only occurs when the reaction is initiated with a spark.
- Nonspontaneous reactions only occur with a continual input of energy.

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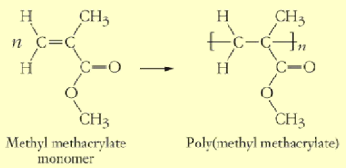
Spontaneous Processes



- Once initiated, the spontaneous reaction between methyl methacrylate monomer to produce poly(methyl methacrylate), PMMA, polymer occurs rapidly.
- The reverse reaction, production of methyl methacrylate monomer, only occurs with a continual input of heat energy.

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Enthalpy and Spontaneity

- Exothermic reactions are generally preferred over endothermic reactions.
  - Melting ice is an endothermic process but occurs spontaneously.
  - Enthalpy is not the exclusive determinant of spontaneity.

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Entropy

- Entropy is a state function and was first introduced in considering the efficiency of steam engines.
  - The Carnot cycle uses a combination of adiabatic processes (no heat is exchanged) and isothermal processes (temperature is constant).

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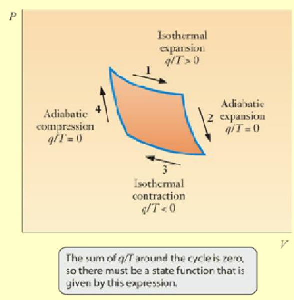
Entropy



- For the Carnot cycle, the sum of q/T around the closed path is equal to zero and therefore defines the state function.
  - The state function is entropy.

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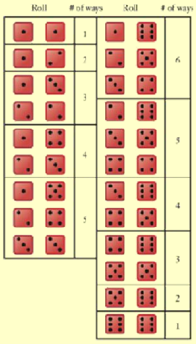
Probability and Spontaneous Change

- Probability has important uses in chemistry.
  - The fundamentals of probability explained using the rolling of dice.
  - The probability of rolling a 4 for one die is 1 in 6.



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Probability and Spontaneous Change

- As the number of dice increases, the probabilities of a set of fours increases.

$$\text{Probability} = \left(\frac{1}{6}\right)^{N}$$

  - N is the number of dice being thrown.
- The chance of a highly specified arrangement in a collection of molecules with ~10^{23} particles is phenomenally small.

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Definition of Entropy

- Entropy can be tentatively defined as a measurement of the randomness, or disorder, of a system.
  - For large numbers of particles, probability favors random arrangements.
  - Statistical mechanics or statistical thermodynamics provides a quantitative basis and molecular perspective to entropy using probability.

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Definition of Entropy

- For entropy, the probability for the number of ways in which particles can achieve the same energy is used.
  - The way by which a collection of particles can assume a given energy is a microstate.
  - The number of possible microstates is designated by Ω.
  - The number of microstates increases as the "randomness" of the system increases.

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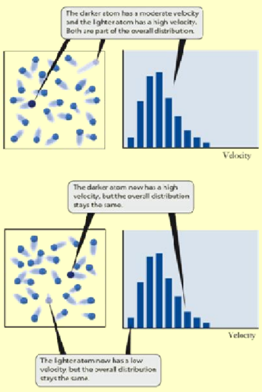
Defining Entropy



- The Maxwell-Boltzmann distribution indicates the overall collection of molecular speeds but not the speed of individual particles.
- Energy is exchanged during molecular collisions, without disrupting the overall distribution of speeds.

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Definition of Entropy

- As the number of microstates for a system increases, the entropy of the system increases. This relationship is defined by the equation:

$$S = k_b \ln \Omega$$

  - S is entropy
  - k_b is the Boltzmann constant.
  - Ω is the number of microstates.

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Judging Entropy Changes in Processes

- Certain types of changes will result in increased entropy.
  - Certain phase changes.
  - An increase in the number of particles present.
  - An increase in the temperature of a substance.

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Judging Entropy Changes in Processes

- When a solid melts to form a liquid, entropy increases.
  - In solids, the particles are held in place rigidly, limiting the number of ways a specific energy can be obtained.
  - In liquids, the particles move past each other, increasing the number of ways a specific energy can be obtained.
  - The number of microstates increases during melting.

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Judging Entropy Changes in Processes

- A chemical reaction that generates two moles of gas when only one mole of gas was initially present will increase the entropy of a sample.
  - The number of possible microstates increases as the number of particles increases.
- When a sample is heated, the temperature of the sample increases.
  - As temperature increases, the number of possible velocities increases.
  - The number of ways to distribute the kinetic energy of the sample increases, resulting in an increase in the number of microstates.

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The Second Law of Thermodynamics

- Whenever energy is converted from one form to another, some energy is "lost" or "wasted".
  - Not all of the energy available is directed into the desired process.
  - Entropy provides the key to understanding that "loss" of useful energy is inevitable.

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The Second Law

- The second law of thermodynamics: in any spontaneous process, the total entropy of the universe is positive
  - ($\Delta S_u > 0$).

$$\Delta S_u = \Delta S_{sys} + \Delta S_{surr}$$

  - ΔS_u = entropy of the universe
  - ΔS_{sys} = entropy of the system
  - ΔS_{surr} = entropy of the surroundings

  - It is impossible to convert heat completely to work, since work is a process that involves moving random motions into more ordered ones.

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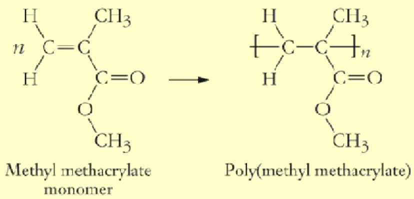
Implications and Applications



- The formation of poly(methyl methacrylate), PMMA, is a spontaneous process.
  - The formation of PMMA is exothermic, which favors spontaneity.
  - The entropy change for the formation of PMMA is negative, which does not favor spontaneity.

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Implications and Applications

- The entropy change for the surroundings can be calculated from the heat flow from the system, which is equal to $-\Delta H$.

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

  - For an exothermic reaction, the entropy of the surroundings increases.

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Implications and Applications

- For the formation of PMMA, ΔS_u is greater than zero only if the ΔS_{surr} is greater than the absolute value of ΔS_{sys}.

$$\Delta S_u = \Delta S + \Delta S_{surr} > 0$$

  - Above some temperature T, the ΔS_u is less than zero, and the formation of PMMA becomes nonspontaneous.
    - The reverse reaction, the thermolysis of PMMA back into monomer, will be spontaneous.
    - The thermolysis of PMMA is one method to recycle PMMA.

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The Third Law of Thermodynamics

- The third law of thermodynamics states that the entropy of a perfect crystal of any pure substance approaches zero as the temperature approaches absolute zero.
- The entropy of one mole of a chemical substance under standard conditions is the standard molar entropy, $S°$.
- The entropy change for a reaction can be calculated from the standard molar entropies of the reactants and products. This law allows for the quantification of entropy.

$$\Delta S^{o} = \sum_i v_i \Delta S^{o}(\text{products})_i - \sum_j v_j \Delta S^{o}(\text{reactants})_j$$

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The Third Law of Thermodynamics

Table 10.1

Standard molar entropies ($S°$) for selected substances. A much larger listing appears in Appendix E. Values for many compounds can also be found online in the NIST Chemistry WebBook at http://webbook.nist.gov/chemistry.

Compound	$S°$ ($J\ mol^{-1}\ K^{-1}$)	Compound	$S°$ ($J\ mol^{-1}\ K^{-1}$)
$H_2(g)$	130.6	$CO_2(g)$	213.6
$O_2(g)$	205.0	$C_4H_{10}(g)$	310.03
$H_2O(\ell)$	69.91	$CH_4(g)$	186.2
$H_2O(g)$	188.7	$C_2H_4(g)$	219.5
$NH_3(g)$	192.3	$C_3H_3N(\ell)$	178.91

- Standard molar entropies for selected substances.

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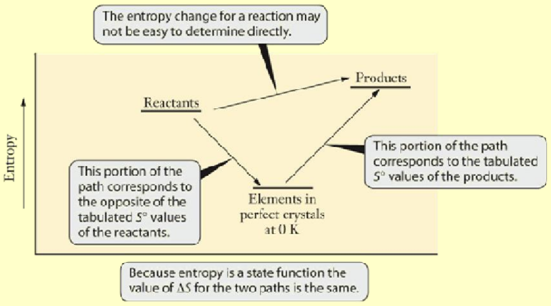
The Third Law of Thermodynamics



- Entropy is a state function, so the value of ΔS must be independent of the path taken from reactants to products.

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Example Problem 10.1

- Use data from Table 10.1 to calculate ΔS for this reaction.

$$2C_2H_4(g) + H_2(g) \rightarrow C_4H_{10}(g)$$

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Gibbs Free Energy

- The Gibbs free energy function, G, is defined as:

$$G = H - TS$$

- Changes in this function can predict whether or not a process is spontaneous under conditions of constant pressure and temperature.

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

$$\Delta G = -T\Delta S_u$$

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Free Energy and Spontaneous Change

- For a spontaneous reaction, the Gibbs free energy change must be negative.

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

- For a negative ΔH and a positive ΔS, the ΔG will always be negative and the reaction spontaneous.
- For a positive ΔH and a negative ΔS, the ΔG will always be positive and the reaction nonspontaneous.

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Free Energy and Spontaneous Change

- For a positive ΔH and a positive ΔS, the value for ΔG depends on the temperature.
- For a negative ΔH and a negative ΔS, the value for ΔG depends on the temperature.
  - The temperature at which a reaction changes from spontaneous to nonspontaneous can be calculated.

$$T = \frac{\Delta H}{\Delta S}$$

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Free Energy and Spontaneous Change

Table 10.2

The four possible combinations for the signs of ΔH and ΔS

Sign of ΔH	Sign of ΔS	Implications for Spontaneity
−	+	Spontaneous at all temperatures
+	−	Never spontaneous
−	−	Spontaneous only at low temperatures
+	+	Spontaneous only at high temperatures

- The four possible combinations for the signs of ΔH and ΔS used to determine spontaneity for a chemical reaction.

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Free Energy and Spontaneous Change

- For a spontaneous reaction with a negative ΔH and a negative ΔS, the reaction only occurs at low temperature.
  - These reactions are referred to as enthalpy driven because the negative value for the enthalpy is responsible for the negative value of the Gibbs free energy change.
- For a spontaneous reaction with a positive ΔH and a positive ΔS, the reaction only occurs at high temperature.
  - These reactions are referred to as entropy driven because the product of the positive entropy change and the absolute temperature is responsible for the negative value of the Gibbs free energy change.

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Example Problem 10.2

- Use the signs of ΔH and ΔS to explain why ice spontaneously melts at room temperature but not outside on a freezing winter day.

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Example Problem 10.3

- The heat of fusion of polyethylene is approximately 7.7 kJ/mol, and the corresponding entropy is 19 J/mol K. Use these data to estimate the melting point of polyethylene.

Free Energy and Work

- It can be shown that the Gibbs free energy change is equal to the maximum useful work done by the system.

$$\Delta G = -w_{\max}$$

  - Work is not a state function.
  - Maximum work realized only if the reaction or process is carried out along a very specific path.

Free Energy and Work

- A reversible path is the specific path required for maximum useful work.
  - For systems with a reversible path, the system is near equilibrium and a small incremental change in a variable will bring the system back to its initial state.
- In an irreversible change, a small incremental change in any variable does not restore the initial state.
  - The amount of work available is always less than maximum for an irreversible change.

Free Energy and Work

- The Gibbs free energy change establishes the upper bound to the amount of work obtained from a given process.
  - Actual work produced in any real application may be considerably less.
- Reactant mixtures are generally very far from equilibrium.
  - Systems that are far from equilibrium often change rapidly, and rapid changes tend to be irreversible.

Free Energy and Chemical Reactions

- The standard Gibbs free energy change, ΔG^o, can be calculated from Gibbs free energies of formation, ΔG_f^o.
  - ΔG_f^o = 0 for elements in their free standard state.

$$\Delta G^o = \sum_i \nu_i \Delta G_f^o(\text{products})_i - \sum_j \nu_j \Delta G_f^o(\text{reactants})_j$$

  - This equation provides an alternative method to calculate ΔG, without entropy or enthalpy.

Free Energy and Chemical Reactions

Table 10.3

Values of the free energy change of formation, ΔG_f°, for selected compounds. A much larger list appears in Appendix E.

Compound	ΔG_f° (kJ mol^{-1})	Compound	ΔG_f° (kJ mol^{-1})
H_2(g)	0	CO_2(g)	–394.4
O_2(g)	0	C_4H_{10}(g)	–15.71
H_2O(ℓ)	–237.2	CH_4(g)	–50.75
H_2O(g)	–228.6	C_2H_4(g)	68.12
NH_3(g)	–16.5	C_3H_6(g)	62.75

- Values of the free energy change of formation, ΔG_f^o, for selected compounds.

Example Problem 10.4

- Confirm that the reaction below would be spontaneous by calculating the standard free energy change using values from Table 10.3.

$$2C_2H_4(g) + H_2(g) \rightarrow C_4H_{10}(g)$$

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Implications of Gº for a Reaction

- Gibbs free energy changes indicate the spontaneity of a chemical reaction.
- For the formation of PMMA at 298 K, ΔH^o = –56 kJ and ΔS^o = –117 J/K.
  - ΔG^o = –21 kJ at 298K for the formation of PMMA.
  - The negative value indicates that the formation of PMMA is spontaneous at 298 K.

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Implications of ΔGº for a Reaction

- The reverse reaction, the thermolysis of PMMA to form methyl methacrylate monomer, has a ΔG^o = +21 kJ at 298 K.
  - The positive value indicates that the thermolysis of PMMA is nonspontaneous at 298 K.
- The temperature at which the thermolysis of PMMA becomes spontaneous is 480 K.
  - The thermolysis of PMMA above 480 K is an entropy driven process.

$$T = \frac{\Delta H}{\Delta S} = \frac{-56 \text{ kJ}}{-0.117 \text{ kJ K}^{-1}} = 480 \text{ K}$$

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The Economics of Recycling

- Almost 50% of all aluminum cans were recycled in 2001 compared to 22% of all PET bottles.
- The difference in recycling rates is based in economics.
- When an aluminum can is recycled, the paint and other coatings are removed and the aluminum can melted down to make new cans.
  - The energy required to recycle 4 aluminum cans equals the energy required to produce 1 can from aluminum ore.

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The Economics of Recycling

- When plastic bottles are recycled, the different types of plastic must be hand sorted.
  - Hand sorting increases the cost of recycling plastics.
- The recycling process leads to a degraded polymer.
  - Recycled plastics have shorter polymer chain lengths than virgin materials and different physical properties.
  - Recycled aluminum has the same physical properties as aluminum extracted from ore.

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The Economics of Recycling

- The cost of producing virgin plastics is lower than costs associated with recycled plastics.
- Recycling of plastics are economically favored when the cost of producing virgin plastics increases, the cost of recycling plastics decreases, or both.

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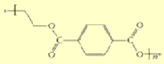
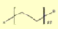
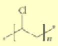
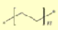
The Economics of Recycling

Table 10.4

Symbols, structures, sources, and uses for various recycled plastics

Symbol	Polymer	Repeat Unit	Sources	Recycled Products
1 PETE	Polyethylene terephthalate		Soda bottles, peanut butter jars, vegetable oil bottles	Fiber, tote bags, clothing, film and sheet, food and beverage containers, carpet, fleece wear
2 HDPE	High-density polyethylene		Milk and water jugs, juice and bleach bottles	Bottles for laundry detergent, shampoo, and motor oil; pipe, buckets, crates, flower pots, garden edging, film and sheet, recycling bins, benches, dog houses, plastic lumber
3 PVC	Polyvinyl chloride		Detergent / cleanser bottles, pipes	Packaging, loose-leaf binders, decking, paneling, gutters, mud flaps, film and sheet, floor tiles and mats, resilient flooring, electrical boxes, cables, traffic cones, garden hose
4 LDPE	Low-density polyethylene		Six-pack rings, bread bags, sandwich bags	Shipping envelopes, garbage can liners, floor tile, furniture, film and sheet, compost bins, paneling, trash cans, landscape timber, lumber

- Symbols, structures, sources, and uses for various recycled plastics.

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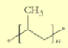
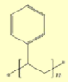
The Economics of Recycling

Table 10.4

Symbols, structures, sources, and uses for various recycled plastics

Symbol	Polymer	Repeat Unit	Sources	Recycled Products
5 PP	Polypropylene		Margarine tubs, straws, screw-on lids	Automobile battery cases, signal lights, battery cables, brooms, brushes, ice scrapers, oil funnels, bicycle racks, rakes, bins, pallets, sheeting, trays
6 PS	Polystyrene		Styrofoam, packing peanuts, egg cartons, foam cups	Thermometers, light switch plates, thermal insulation, egg cartons, vents, desk trays, rulers, license plate frames, foam packing, foam plates, cups, utensils
7 Other	Miscellaneous and multilayer plastics	N/A	Squeezable ketchup and syrup bottles	Bottles, plastic lumber

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