

**Unit 4: Thermochemistry and Nuclear Chemistry****Chapter 6: Thermochemistry**

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2. Heat is the transfer of energy between two bodies that are of different temperature. Thermal energy on the other hand is the energy associated with the random motion of atoms and molecules. When thermal energy flows between objects of different temperatures, we get heat. Heat is transferred from an open or closed system that is hot to an open or closed system that is cold.
3. We commonly use J or kJ for energy units in chemistry
7. Thermochemistry: - the study of heat changes in chemical reactions.  
Exothermic Process: - processes that give off heat to the surroundings.  
Endothermic Process: - processes that absorb heat from the surroundings.
8. Thermochemistry is based on the law of conservation of energy.
9. Answers may vary. Examples of exothermic process are condensation of steam to water and burning hydrocarbons. Examples of endothermic process are melting of ice into water and photosynthesis.
10. Combination reactions or formation reactions tend to be exothermic because most compounds are at a lower energy states compared to their elemental reactants. That is why we see more chemicals in compound forms compared to pure elemental forms. Decomposition reactions are the reverse process of combination reactions. Hence, they will involve an input of energy (endothermic) as the stable compounds are forced to break apart into their elements.
11. The first law of thermodynamics is based on the law of conservation of energy. In the equation,  $\Delta E = q + w$ ,  $\Delta E$  stands for total internal energy of a system (+ means the system gained energy; - means the system lost energy).  $q$  stands for heat (+ means endothermic change on the system; - means exothermic change on the system).  $w$  stands for work (+ means work is done on the system, volume of the system decreased; - means work is done by the system, volume of the system increased).
13. (a) If pressure remains constant, then an expansion of gas will constitute work done on the surrounding.  
(b) Because temperature remains constant, there is no change in kinetic energy of the gas. There is probably no potential energy change either considered phase change was not involved. Hence, under these conditions, there is no heat flow in or out of the system.  
(c)  $\Delta E = \Delta H - P\Delta V$ . Since  $\Delta V > 0$  with constant  $P$  and  $\Delta H = 0$ ,  $\Delta E < 0$ . The internal energy of the system would decrease.
14. At constant pressure, (a) and (c) are changes that will result in work done by the system on the surrounding. At constant pressure, (b) is a change that will result in work done by the surrounding on the system. Reaction (d) will have no work done on either the surrounding or the system.
15. (a) 0 J            (b)  $-3.0 \times 10^2$  J            (c)  $-1.4 \times 10^3$  J
17. -198 J
19.  $-1.04 \times 10^3$  J
21. Enthalpy ( $H$ ) is a thermodynamic quantity used to describe heat changes taking place at constant temperature, pressure and volume. Enthalpy of Reaction ( $\Delta H$ ) is the difference between the enthalpies of the products and the enthalpy of the reactants. The heat of the reaction will equal to the enthalpy change when no work is done on or by the system (that is the system is at constant volume and pressure).  $\Delta E = q + w$ . For  $w = -P\Delta V$  and  $\Delta V = 0$ ,  $\Delta E = q = \Delta H$ .
24. (a) If the equation is multiplied by 2,  $\Delta H = -2905.6$  kJ.  
(b) If the direction of the reaction is reversed,  $\Delta H = 1452.8$  kJ.  
(c) If water vapour instead of liquid water is formed as the product,  $\Delta H = -1290.2$  kJ.  
(For water,  $\Delta H_{\text{vap}} = 40.65$  kJ/mol and since water vapour has a higher energy state,  $\Delta H = -1452.8 + 4 \text{ mol} (40.65 \text{ kJ/mol}) = -1290.2$  kJ)

25.  $-1.57 \times 10^4$  kJ
27. 480. kJ
29. Specific Heat ( $s$ ) is the amount of heat energy required to raise the temperature of one gram of substance by one degree Celsius. The units for specific heat are  $J/(g \cdot ^\circ C)$  or  $kJ/(kg \cdot ^\circ C)$ . It is an intensive property. Heat Capacity ( $C$ ) is the amount of heat required to raise the temperature of a given quantity of substance by one degree Celsius. The units for specific heat are  $J/^\circ C$  or  $kJ/^\circ C$ . It is an extensive property.
30. It would take more time to heat A instead of B because A has a larger specific heat capacity. More heat is required to raise A's temperature by  $1^\circ C$ .
31. Calorimetry is a method to measure heat change. A calorimeter is a device that measure heat change of a system. There are two types of calorimeter. The constant-volume calorimeter is also referred to as a bomb calorimeter. A sample is ignited and the heat gained by the calorimeter (container and water) is calculated by  $C\Delta T$  (heat capacity of the calorimeter time difference in temperature of the water). We use  $C$  because it takes into account of the gain in heat by the calorimeter container itself and therefore will be more accurate. The value of heat capacity is determined by using a reference reaction with known heat change and divided by the  $\Delta T$  of the water (that is,  $C = \frac{\Delta H}{\Delta T}$ ). The other calorimeter is the constant-pressure calorimeter, which is commonly called the Styrofoam calorimeter. In this case, we ignore the gain in heat by the container, and we use the formula  $q = ms\Delta T$  to calculate heat change of the system.
32. Choice (d) will take place when the two metals are brought into contact. Heat will flow from Cu to Al because Cu is at a higher temperature. The definition of heat is the transfer of thermal energy between two bodies that are at different temperatures.
33.  $0.237 J/g \cdot ^\circ C$
35.  $-3.31$  kJ
37.  $24.76$  kJ/g;  $601.9$  kJ/mol
39. The standard state condition is at  $25^\circ C$  and  $1$  atm.
40. In cases where the compounds can be directly synthesized from their elements at standard condition, we perform a calorimetry experiment to find out their  $\Delta H^\circ_f$ . For compounds that cannot be directly synthesized from their elements, we use a series of reactions with Hess's law (adding  $\Delta H^\circ_{rxn}$  from these reactions) or the extended Hess's law,  $\Delta H^\circ_{rxn} = \Sigma H^\circ_{products} - \Sigma H^\circ_{reactants}$ , using known  $\Delta H^\circ_f$ .
41. Standard enthalpy of reactions refers to the molar change of enthalpy of reaction at standard conditions.
42.  $\Delta H^\circ_{rxn} = \Sigma H^\circ_{products} - \Sigma H^\circ_{reactants}$   
 $\Delta H^\circ_{rxn} =$  Standard Enthalpy of Reactions  
 $\Sigma H^\circ_{products} =$  Sum of  $\Delta H^\circ_f$  of all products =  $n\Delta H^\circ_{f, product 1} + n\Delta H^\circ_{f, product 2} + n\Delta H^\circ_{f, product 3} + \dots$   
 $\Sigma H^\circ_{reactants} =$  Sum of  $\Delta H^\circ_f$  of all reactants =  $n\Delta H^\circ_{f, reactant 1} + n\Delta H^\circ_{f, reactant 2} + n\Delta H^\circ_{f, reactant 3} + \dots$
45.  $CH_4(g)$  and  $H(g)$ . All the other choices are elements in their most stable form ( $\Delta H^\circ_f = 0$ ). The most stable form of hydrogen is  $H_2(g)$ .
47.  $\Delta H^\circ_f$  of  $H_2O(l)$  is more negative since  $\Delta H^\circ_{rxn} > 0$ .
49.  $2 H_2O_2(l) \rightarrow 2 H_2O(l) + O_2(g)$ . Because  $H_2O(l)$  has a more negative  $\Delta H^\circ_f$  than  $H_2O_2(l)$ .
51.  $177.8$  kJ/mol
55. (a)  $-724$  kJ/mol      (b)  $-1.37 \times 10^3$  kJ/mol      (c)  $-2.01 \times 10^3$  kJ/mol
61.  $0.30$  kJ/mol
63.  $-238.7$  kJ/mol
66. In order to dissolve an ionic compound in water, one must break the lattice structure of the crystal. This involves an input of energy that has a positive energy notation. The hydration of ions involves forming ion-dipole bonds between the ions and the solvent molecules. Forming bonds releases energy and thereby it has a negative energy notation.

67. Compound A will be more stable because it has larger lattice energy. This means that it is more difficult to break the lattice structure before hydration can occur.
68.  $\text{Mg}^{2+}$  will have larger hydration energy because it has a smaller radius and twice the charge compared to  $\text{Na}^+$ . This is due to the equation  $E = \frac{kQ_1Q_2}{r}$ .
70. The main reason why we should not add water to concentrated sulfuric acid because it can be highly exothermic. In addition, as water hit the surface of the concentrated acid, splashes of acid could injure someone. Hence, mixing acids should always be done in an Erlenmeyer flask or volumetric flask.
73.  $-44.35 \text{ kJ/mol}$
77. (a) Although we cannot directly calculate  $\Delta H^\circ_{\text{rxn}}$  for this reaction, the reverse process, is the combustion of glucose. We could easily calculate  $\Delta H^\circ_{\text{rxn}}$  for this combustion in a bomb calorimeter by measuring mass of glucose and water used, along with the initial and final temperatures. After calculating  $\Delta H^\circ_{\text{rxn}}$  of the combustion of glucose, we can simply reverse the sign for the  $\Delta H^\circ_{\text{rxn}}$  of the photosynthesis of glucose.
- $$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$$
- (b)  $1.1 \times 10^{19} \text{ kJ}$
81.  $-238.7 \text{ kJ/mol}$

pg. 496 to 499 (from Chapter 11)

62. Molar Heat of Vaporization is the amount of energy to vaporize one mole of a substance at its normal boiling point. Molar Heat of Fusion is the amount of energy to melt one mole of a substance at its normal freezing point. Molar Heat of Sublimation is the amount of energy to sublime one mole of a substance. All of which have a unit of  $\text{kJ/mol}$ .
63. According to Hess's Law,  $\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$
67. At the boiling point, energy input is used to break the intermolecular forces (London-dispersion, dipole-dipole, and/or hydrogen bonding) between molecules. The energy is not used to make the molecules any faster. Hence, temperature remains constant during boiling.
75. 1 mole of steam to 1 mole of water at  $100^\circ\text{C}$  would transfer more energy than freezing 1 mole of water to 1 mole of ice at  $0^\circ\text{C}$ . This is because for water,  $\Delta H^\circ_{\text{vap}} = -40.65 \text{ kJ/mol}$  gives off more energy than  $\Delta H^\circ_{\text{fus}} = -6.01 \text{ kJ/mol}$
77.  $169 \text{ kJ}$
83. The solid ice turns to vapor (sublimation). The temperature is too low for melting to occur.
129. The advantages of cooking vegetable like broccoli with steam instead of water are that steam produces extra heat when it condenses at  $100^\circ\text{C}$ . In addition, it avoids extraction of ingredients by boiling in water.
135. Ethanol mixes well with water. The mixture has a lower surface tension and readily flows out of the ear channel.
137. The two main reasons for spraying the trees with water to protect the fruits from frost are:  
 (a) As water freezes, heat is released. ( $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$   $\Delta H_{\text{fus}} = -6.01 \text{ kJ/mol}$ ) The heat released protects the fruit. Of course, spraying the trees with warm water is even more helpful.  
 (b) The ice forms an insulating layer to protect the fruit.

### Chapter 18: Spontaneity, Entropy and Free Energy

pg. 810 to 813

1. A spontaneous process is a reaction that does occur under the given set of conditions. Two examples of a spontaneous process are the diffusion of gases and matter falling due to gravity. Two examples of non-spontaneous process are heat flows from cold system to a warm system and water decomposing into hydrogen and oxygen on its own with no input of energy.

2. (a) and (c) are spontaneous processes, and (b) and (d) are non-spontaneous processes.
3. (b) is a spontaneous processes, and (a) and (c) are non-spontaneous processes.
4. Entropy is a measure of the disorder or randomness in a system. The unit of entropy is J/K or molar entropy has a unit of J/(K • mol).
5. (a)  $\Delta S > 0$  (b)  $\Delta S < 0$  (c)  $\Delta S > 0$  (d)  $\Delta S < 0$  (e)  $\Delta S < 0$  (f)  $\Delta S > 0$  (g)  $\Delta S > 0$
7. The Second Law of Thermodynamics states that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.  
Spontaneous Process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$   
At Equilibrium:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$
8. The Third Law of Thermodynamics states that the entropy of a perfect crystalline substance is zero at the absolute zero of temperature. This means that starting at absolute zero, we can calculate the absolute entropy of a substance from its temperature change and the heat capacity, plus any heat associated with any phase changes.
9. (a) The liquid form of any substance always has greater entropy than the solid form (more microstates or positional probability).  
(b) At first glance there may seem to be no apparent difference between the two substances that might affect the entropy (molecular formulas identical). However, the first has the –O–H structural feature which allows it to participate in hydrogen bonding with other molecules. This allows a more ordered arrangement of molecules in the liquid state. Hence, the standard entropy of  $\text{CH}_3\text{OCH}_3$  is larger.  
(c) Both Ar and Xe are monatomic species. However, Xe atom has a greater molar mass than Ar. Xenon has the higher standard entropy.  
(d) Same argument as part (c).  $\text{CO}_2(\text{g})$  has the higher standard entropy (see Appendix 3).  
(e)  $\text{O}_3$  has a greater molar mass than  $\text{O}_2$  and thus has the higher standard entropy.  
(f) Using the same argument as part (c), one mole of  $\text{N}_2\text{O}_4$  has a larger standard entropy than one mole of  $\text{NO}_2$ .
11. (a) 11.6 J/K • mol (b) 174.7 J/K • mol
13. All parts of this problem rest on two principles. First, the entropy of a solid is always less than the entropy of a liquid, and the entropy of a liquid is always much smaller than the entropy of a gas. Second, in comparing systems in the same phase, the one with the most complex particles has the higher entropy.  
(a) Positive entropy change (increase). One of the products is in the gas phase (more microstate).  
(b) Negative entropy change (decrease). Liquids have lower entropies than gases.  
(c) Positive. Same as (a).  
(d) Positive. There are two gas-phase species on the product side and only one on the reactant side.
15. Free Energy is the energy available to do work (after taking into account enthalpy, entropy and temperature). The unit of free energy is kJ or kJ/mol for molar free energy.
16. For spontaneous reactions,  $\Delta S_{\text{univ}} > 0$  or  $\Delta G < 0$ . It is more convenient to use  $\Delta G$  because it refers to the free energy available in the system and not the universe. In addition, we associate the negative sign as decreasing the system's overall energy which is always a natural process.
17. (a) 173.4 kJ/mol (b) 8.6 kJ/mol (c) –2470 kJ/mol
19. Reaction A: spontaneous at 350 K; Reaction B:  $\Delta G = 35.5$  kJ/mol at 298 K.
51. At absolute zero. A substance can never have negative entropy.
57. (a)  $\Delta S > 0$  (b)  $\Delta S < 0$  (c)  $\Delta S > 0$  (d)  $\Delta S > 0$
59. Boiling Point = 352°C. Because we use the enthalpies and entropies values at standard conditions, the assumption we have to make is that the conditions are at 25.0°C and 1.00 atm. As we calculate the boiling point of mercury at 352°C, there would be some error
61. There is no connection between the spontaneity of a reaction predicted by  $\Delta G$  and the rate at which the reaction occurs. A negative free energy change tells us that a reaction has the potential to happen, but gives no indication of the rate.

**Chapter 23: Nuclear Chemistry**

pg. 994 to 998

- Ordinary chemical reactions involve electrons in the valence energy level of the atoms. Nuclear reactions deal with changes of nucleons (neutrons and protons) in the nucleus of an atom.
- All the atomic numbers (bottom numbers of the notation) on either side has to be equalled. All the mass numbers (top numbers of the notation) on either side has to be equalled.
- There is no difference between  ${}_{-1}^0e$  and  ${}_{-1}^0\beta$ . Both mean an electron or beta particle.
- An electron is a fundamental particle of an atom. It has a charge of  $-1$  and a mass of  $9.11 \times 10^{-31}$  kg (about 1800 times lighter than a proton). A positron is antimatter of an electron. It has the same mass as an electron, but it has a  $+1$  charge.
- (a)  ${}_{11}^{23}\text{Na}$       (b)  ${}_{1}^1\text{H}$  or  ${}_{1}^1p$       (c)  ${}_{26}^{56}\text{Fe}$       (d)  ${}_{0}^1n$       (e)  ${}_{-1}^0e$
- Generally, nuclei that have an even number of protons and an even number of neutrons are the most stable.
- The belt of stability is a region of a graph (that of number of neutrons versus the number of protons of all isotopes) where the nuclei are considered stable.
- $E = mc^2$  is really  $\Delta E_{\text{bind}} = -\Delta mc^2$ . It states that the mass defect (the difference in mass resulting from when the nucleons binding together compared to when they exist individually) can be converted to pure energy responsible for the nuclear force needed to hold the nucleus together.
- Since heavier nuclei will naturally have more nucleons, they will have a bigger binding energy overall. By comparing binding energy per nucleon for different isotopes, we can see which isotope is more stable despite their different mass number. The more binding energy each nucleon in an isotope has, the more stable is its nuclei. The most stable nucleus in the periodic table is iron-56.
- (a)  $6.30 \times 10^{-12}$  J/nucleus and  $9.00 \times 10^{-13}$  J/nucleon  
(b)  $4.92 \times 10^{-11}$  J/nucleus and  $1.41 \times 10^{-12}$  J/nucleon
- Nuclear decay usually occurs with heavier nuclei where the  $n/p$  ratios are not ideal. If the  $n/p$  ratio is smaller than the belt of stability, then the nuclei will likely go through beta decay. If the  $n/p$  ratio is larger than the belt of stability, then the nuclei will likely go through a positron emission or an electron capture. Very large nuclei will likely undergo alpha decay to lower its overall size.
- (a)  ${}_{90}^{232}\text{Th} \xrightarrow{\alpha} {}_{88}^{228}\text{Ra} \xrightarrow{\beta} {}_{89}^{228}\text{Ac} \xrightarrow{\beta} {}_{90}^{228}\text{Th}$   
(b)  ${}_{92}^{235}\text{U} \xrightarrow{\alpha} {}_{90}^{231}\text{Th} \xrightarrow{\beta} {}_{91}^{231}\text{Pa} \xrightarrow{\alpha} {}_{89}^{227}\text{Ac}$   
(c)  ${}_{93}^{237}\text{Np} \xrightarrow{\alpha} {}_{91}^{233}\text{Pa} \xrightarrow{\beta} {}_{92}^{233}\text{U} \xrightarrow{\alpha} {}_{90}^{229}\text{Th}$
- $4.89 \times 10^{19}$  atoms
- 65.2 years
- In the shorthand notation for nuclear reactions, the first symbol inside the parentheses is the "bombarding" particle (reactant) and the second symbol is the "ejected" particle (product).  
(a)  ${}_{7}^{15}\text{N} + {}_{1}^1p$  (or  ${}_{1}^1\text{H}$ )  $\rightarrow$   ${}_{6}^{12}\text{C} + {}_{2}^4\alpha$       X is  ${}_{7}^{15}\text{N}$   
(b)  ${}_{13}^{27}\text{Al} + {}_{1}^2d$  (or  ${}_{1}^2\text{H}$ )  $\rightarrow$   ${}_{12}^{25}\text{Mg} + {}_{2}^4\alpha$       X is  ${}_{12}^{25}\text{Mg}$   
(c)  ${}_{25}^{55}\text{Mn} + {}_{0}^1n \rightarrow {}_{25}^{56}\text{Mn} + {}_{0}^0\gamma$       X is  ${}_{25}^{56}\text{Mn}$
- ${}_{83}^{209}\text{Bi} + {}_{2}^4\text{He} \rightarrow {}_{85}^{213}\text{At} \rightarrow {}_{85}^{212}\text{At} + {}_{0}^1n \rightarrow {}_{85}^{211}\text{At} + {}_{0}^1n$
- Any isotopes higher have a higher mass number and atomic number than iron-56 can undergo fission.
- A control rod is a device that can be lowered to absorb neutrons generated in a nuclear fission. When it is raised, the same fission reaction can take place in a nuclear reactor. A moderator is a material surrounding the fuel rods that also absorbs neutrons. However, it cannot be raised up and down like a control rod.

41. A light-water reactor uses U-235 as fuel because regular water moderator used is a good neutron absorber. A heavy-water reactor uses U-238 as fuel because deuterium (heavy) water is used as moderator and it does not absorb neutron as well as regular water. A breeder reactor converts some of the unused uranium fuel into plutonium which serves as an alternate fuel for the fission reaction.
44. Iron-56 is an isotope that has the highest binding energy per nucleon in its nucleus. Elements heavier than Fe-56 undergo fission because they have break up into smaller pieces to be like Fe-56. Elements lighter than Fe-56 undergo fusion because they have to combine to become a bigger piece to be like Fe-56.
45. A hydrogen bomb first initiates by setting off a fission bomb. This will generate enough heat to set off the fusion material in the bomb.
46. A fusion reactor does not produce radioactive wastes that have long half-lives. However, fusion reaction requires extremely high temperature to initialize the reaction. This presents various technical difficulties such as generating the hot plasma using higher power lasers and having to contain it in a safe manner.
55. (a)  ${}_{92}^{235}\text{U} + {}_0^1n \rightarrow {}_{56}^{140}\text{Ba} + {}_{36}^{93}\text{Kr} + 3{}_0^1n$       (b)  ${}_{92}^{235}\text{U} + {}_0^1n \rightarrow {}_{55}^{144}\text{Cs} + {}_{37}^{90}\text{Rb} + 2{}_0^1n$   
(c)  ${}_{92}^{235}\text{U} + {}_0^1n \rightarrow {}_{35}^{87}\text{Br} + {}_{57}^{146}\text{La} + 3{}_0^1n$       (d)  ${}_{92}^{235}\text{U} + {}_0^1n \rightarrow {}_{62}^{160}\text{Sm} + {}_{30}^{72}\text{Zn} + 4{}_0^1n$
67. Percent of C-14 left = 0.24%
85. 53.0 g of Zn