Name: _____-

Unit 9
Advanced Topics in Kinetics & Thermodynamics

- State that combustion and neutralization are exothermic processes.

- Calculate the heat energy change when the temperature of a pure substance is changed.

- Design suitable experimental procedures for measuring the heat energy changes of reactions.

- Calculate the enthalpy change for a reaction using experimental data on temperature changes, quantities of reactants and mass of water.

- Evaluate the results of experiments to determine enthalpy changes.

- Determine the enthalpy change of a reaction that is the sum of two or three reactions with known enthalpy changes.

- Define the term average bond enthalpy.

- Explain, in terms of average bond enthalpies, why some reactions are exothermic and others are endothermic.

- Outline the characteristics of chemical and physical systems in a state of equilibrium.

- Deduce the equilibrium constant expression (Kc) from the equation for a homogeneous reaction.

- Deduce the extent of a reaction from the magnitude of the equilibrium constant.

- Apply Le Chatelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant.

- State and explain the effect of a catalyst on an equilibrium reaction.

- Apply the concepts of kinetics and equilibrium to industrial processes

Gibbs Free Energy

The Way You Can Tell If A Reaction Will Be Spontaneous

Some reactions are spontaneous because they give off energy in the form of heat ($\Delta H < 0$). Others are spontaneous because they lead to an increase in the disorder of the system ($\Delta S > 0$). Calculations of ΔH and ΔS can be used to probe the driving force behind a particular reaction.

What happens when one of the potential driving forces behind a chemical reaction is favorable and the other is not? We can answer this question by defining a new quantity known as the **Gibbs free energy** (G) of the system, which reflects the balance between these forces.

The change in the free energy of a system that occurs during a reaction can be measured under any set of conditions. If the data are collected under standard-state conditions, the result is the standard-state free energy of reaction ($\Delta G°$).

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

The beauty of the equation defining the free energy of a system is its ability to determine the relative importance of the enthalpy and entropy terms as driving forces behind a particular reaction. The change in the free energy of the system that occurs during a reaction measures the balance between the two driving forces that determine whether a reaction is spontaneous. As we have seen, the enthalpy and entropy terms have different sign conventions.

> *Favorable*　　$\Delta H < 0, \Delta S > 0$
> *Unfavorable*　$\Delta H > 0, \Delta S < 0$

The entropy term is therefore subtracted from the enthalpy term when calculating ΔG for a reaction.

Because of the way the free energy of the system is defined, ΔG is negative for any reaction for which ΔH is negative and ΔS is positive. ΔG is therefore negative for any reaction that is favored by both the enthalpy and entropy terms. We can therefore conclude that any reaction for which ΔG is negative should be favorable, or spontaneous.

Spontaneous reactions: $\Delta G < 0$

Conversely, ΔG is positive for any reaction for which ΔH is positive and ΔS is negative. Any reaction for which ΔG is positive is therefore unfavorable.

Non-spontaneous reactions: $\Delta G > 0$

1. For the decomposition of $CaCO_3$ to CaO and CO_2 at 298K the ΔH is 178.5 kJ/mol and the ΔS is 161.6 J/K•mol. Is the reaction spontaneous or non-spontaneous at this temperature?

2. What three factors together determine whether a reaction is spontaneous?

3. Given the following data about a reaction, A + B → C, taking place at 298K

    $\Delta G°rxn$ = -1405 kJ ; $\Delta H°rxn$ = -1453 kJ; $\Delta S°rxn$ = -162 J/K

    Which one of the following statements is TRUE?

    (a) The reaction is spontaneous, endothermic and becoming more disordered.
    (b) The reaction is non-spontaneous, endothermic and becoming more disordered.
    (c) The reaction is spontaneous, exothermic and becoming more disordered.
    (d) The reaction is spontaneous, exothermic and becoming more ordered.
    (e) The reaction is non-spontaneous, exothermic and becoming more ordered.

4. An exothermic reaction has an increase in the amount of disorder of the reaction. Predict the signs of ΔH, ΔS, & ΔG.

    (a) ΔH=+, ΔS=+, ΔG=+
    (b) ΔH=+, ΔS=−, ΔG=+
    (c) ΔH=−, ΔS=+, ΔG=−
    (d) ΔH=−, ΔS=−, ΔG=−
    (e) ΔH=+, ΔS=−, ΔG=−

5. Which of the following represents a reaction condition that will **always** be **spontaneous** only at LOW temperatures?

    (a) ΔH = positive; ΔS = positive
    (b) ΔH = positive; ΔS = negative
    (c) ΔH = negative; ΔS = positive
    (d) ΔH = negative; ΔS = negative
    (e) ΔH = 0; ΔS = positive

6. Above what temperature (K) will the reaction below become spontaneous?

    $2Au_2O_3(s)$ → $4Au(s)$ + $3O_2(g)$
    ΔH = 19.3 kJ/mol
    ΔS = 30 J/mol•K

    (a) 275 K
    (b) 370 K
    (c) 643 K
    (d) 916 K
    (e) 1554 K

7. Complete the following table:

ΔS	ΔH	ΔG	Spontaneous?
+	−		
		+ or −	At high temperatures
	+		No
−			At low temperatures

Assignment: Gibbs Free Energy

Predicting if a Reaction is Spontaneous or Not

Whether a reaction proceeds spontaneously or not depends on the balance between two natural tendencies: [1] The drive toward greater stability (reduced potential energy); and [2] The drive toward less organization (increased entropy). In nature, systems tend towards the lowest possible energy or enthalpy (H). Exothermic reactions are favored (ΔH is negative). In nature, systems also tend toward greater randomness (disorder) or entropy (S). When entropy increases, ΔS, the change in entropy is positive. High entropy is favored by increased temperature. the Gibbs free energy change (ΔG) predicts whether or not a reaction is spontaneous. it takes into account the change in enthalpy and the change in entropy. The Gibbs free energy change is the difference tween the energy change (ΔH) and the product of the absolute or Kelvin temperature (T) and the entropy change (ΔS).

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

For a system at equilibrium, ΔG = 0. In order for a system to change spontaneously, the resulting ΔG must be negative. If the drive toward lower energy and higher entropy cannot be satisfied at the same time, the type of change that will be favored will depend on the temperature. At low temperatures, the term TΔS will be small, and ΔH will have the greatest effect on the free energy. At high temperatures, the term TΔS will be large, and ΔS will have the greatest effect on the free energy.

Based on your reading above, fill-in the table below and answer the questions that follow.

Reaction Conditions			Is the reaction spontaneous? *(Yes, No, Likely, or Unlikely)*
Temperature	ΔH	ΔS	
High	+	−	
High	+	+	
High	−	−	
High	−	+	
Low	+	−	
Low	+	+	
Low	−	−	
Low	−	+	

1. At low temperatures, water is a solid (ice), while at high temperatures, water is a gas (steam). Explain this based on the change in Gibbs free energy (ΔG).

   _____

   _____

   _____

2. Wood, a carbohydrate and a solid, burns to form water vapor and carbon dioxide, both gases.

   a) Is the reaction exothermic or endothermic? _____

   b) Is the entropy during the reaction increasing or decreasing? _____

   c) What do your answers to the previous two questions tell you about ΔG? Should the reaction be spontaneous at room temperature? _____

   _____

   d) Is the reaction spontaneous at room temperature? How do you explain this? (*Hint: What other energy considerations besides ΔG determine if a reaction will occur?*)

   _____

   _____

   _____

3. Referring to the table to the right, determine the entropy of formation in each of the examples below:

   Sample Problem
   Find the entropy of formation of carbon dioxide.
   ΔG_f° = -394.2 kJ/mol $\Delta G = \Delta H - T\Delta S$
   ΔH_f° = -393.3 kJ/mol   -394.2 kJ/mol - -393.3 kJ/mol - 298K(ΔS)
   T = 298 K (see table)   -0.9 kJ/mol = -298(ΔS)
                 ΔS = 0.003 kJ/mol•K

STANDARD ENERGIES OF FORMATION OF COMPOUNDS AT 1atm AND 298K		
Compound	Heat (Enthalpy) of formation kJ/mol (ΔH_f°)	Free Energy of Formation kJ/mol (ΔG_f°)
Ethene (ethylene) C_2H_4 (g)	52.3	68.1
Wate H_2O (g)	-241.6	-228.2

a) Ethene   b) Water vapor
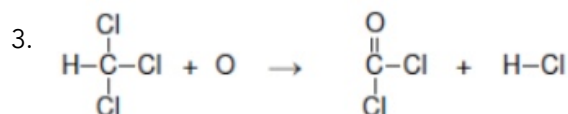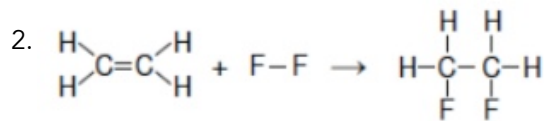
Assignment: Bond Enthalpy
Predicting if a Reaction is Endothermic or Exothermic

Bond energy is defined as the amount of energy required to break a bond. These values are positive, indicating that bond breaking is endothermic. Bond energies are reported in kilojoules per mole (kJ/mol). the energy for breaking a hydrogen-hydrogen bond is 436 kJ/mol so when a hydrogen-hydrogen bond is formed the process releases 436 kJ/mol.
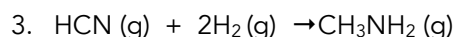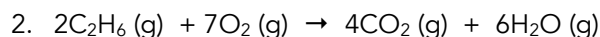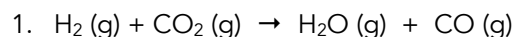
In a chemical reaction several bonds are broken and formed. For example, in the reaction below a hydrogen0hydrogen bond is broken and a fluorine-fluorine bond is broken. Two hydrogen-fluorine bonds are formed. The overall energy change for this process is calculated below.

example	H_2 (g) + F_2 (g) → 2HF

ΔH_{rxn} = [energy used for breaking bonds] – [energy formed in making bonds]

[436 kJ/mol + 155 kJ/mol] – [2(567 kJ/mol)]

= – 543 kJ/mol

Average Bond Energies (kJ/mol)

H–H	436 kJ/mol	C–H	413 kJ/mol	C=C	614 kJ/mol
H–Cl	431 kJ/mol	C–C	348 kJ/mol	C≡C	839 kJ/mol
H–F	567 kJ/mol	C–N	293 kJ/mol	C=O	799 kJ/mol
N–H	391 kJ/mol	C–O	358 kJ/mol	O=O	495 kJ/mol
N–O	201 kJ/mol	C–F	485 kJ/mol	C≡O	1072 kJ/mol
O–H	463 kJ/mol	C–Cl	328 kJ/mol	C=N	615 kJ/mol
O–O	146 kJ/mol	C–S	259 kJ/mol	N=N	418 kJ/mol
F–F	155 kJ/mol	Cl–Cl	242 kJ/mol	N≡N	941 kJ/mol
				C≡N	891 kJ/mol

Estimate the enthalpy change (ΔH_{rxn}) of the following reactions using the bond energies above.
(Attach a separate sheet to answer these questions.)

1. H–H + Cl–Cl → H–Cl + H–Cl

2.

3.

Draw Lewis structures for the reactants and products. Estimate the enthalpy change (ΔH_{rxn}) for the reactions using bond energies.

1. H_2 (g) + CO_2 (g) → H_2O (g) + CO (g)

2. $2C_2H_6$ (g) + $7O_2$ (g) → $4CO_2$ (g) + $6H_2O$ (g)

3. HCN (g) + $2H_2$ (g) → CH_3NH_2 (g)

Assignment: Hess's Law
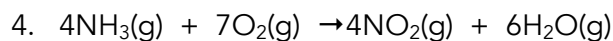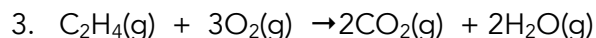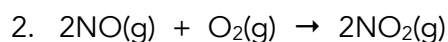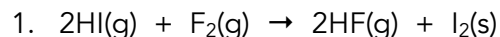*Determining ΔH for a Reaction*

Suppose you climb from the first rung of a ladder to the fifth rung of the ladder. Your potential energy has increased by the height of four rungs. Should you climb down from the first rung to the floor, climb up to the sixth rung, and down one to the fifth rung, the potential energy change is the same. The path is different, but the change in energy from the initial position to the final position is he same. This is the concept behind Hess's law. If a reaction occurs through a series of steps, the enthalpy change going from reactant to product is equal to the sum of the enthalpy changes for each of the steps.

$$\Delta H = \Delta H_A + \Delta H_B + \Delta H_C + \dots$$

For example, under standard conditions (1 atm and 298 K) the heat of formation for carbon dioxide is -393.3 kJ/mol [$C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH_f = -393.3 kJ/mol] and the heat of formation of carbon monoxide is -110.4 kJ/mol [$C(s) + 1/2 O_2(g) \rightarrow CO(g)$ ΔH_f = -110.4 kJ/mol]. Notice the coefficient in front of the oxygen is 1/2. This makes it possible to write a balanced equation in which 1 mol of product forms. This is necessary because the enthalpy is in kJ/mol. From the two equations above, it is possible to determine the heat of reaction for the oxidation of carbon monoxide to carbon dioxide by following some simple rules: [1] Manipulate the equations so they add together to give the desired results; [2] The enthalpy of formation of an element under standard conditions is zero; [3] When a reaction is reversed the sign of the enthalpy is changes, but the magnitude is the same; [4] If a balanced equation is multiplied by a coefficient, the enthalpy associated with the equation is multiplied by the same number; and [5] If the same substances are on both the product and the reactant side when the equations are added together, subtract them from both sides. See below.

Sample Problem

What is the heat of reaction (ΔH) for the reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

Equations (from above)			Explanation
$2CO(g) \rightarrow 2C(s) + O_2(g)$	$\Delta H_f = 110.4\,kJ/mol \times 2 =$	$220.8\,kJ/mol$	• Reverse the reaction so CO is on the reactant side. Reverse the sign of ΔH_f. Multiply by the coefficient 2.
$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$	$\Delta H_f = -393.3\,kJ/mol \times 2 =$	$-786.6\,kJ/mol$	• Multiply by the coefficient 2.
$2CO(g) + 2C(s) + 2O_2(g) \rightarrow 2C(s) + O_2(g) + 2CO_2(g)$		$-565.8\,kJ/mol$	• Add the equations and the enthalpies
$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\Delta H = -565.8\,kJ/mol$			• Subtract $O_2(g)$ and $2C(s)$ from both sides

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Determine the heat of reaction at 1 atm and 298 K for each of the reactions below by referring to the table to the right showing standard enthalpies of formation.

1. $2HI(g) + F_2(g) \rightarrow 2HF(g) + I_2(s)$

2. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

3. $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

4. $4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$

STANDARD ENERGIES OF FORMATION OF COMPOUNDS AT 1 atm AND 298 K

Compound	Heat (Enthalpy) of Formation * kJ/mol ($\Delta H_f°$)	Free Energy of Formation kJ/mol ($\Delta G_f°$)
Aluminum oxide $Al_2O_3(s)$	-1674.1	-1580.9
Ammonia $NH_3(g)$	-46.0	-16.3
Barium sulfate $BaSO_4(s)$	-1471.8	-1361.0
Calcium hydroxide $Ca(OH)_2(s)$	-985.2	-897.9
Carbon dioxide $CO_2(g)$	-393.3	-394.2
Carbon monoxide $CO(g)$	-110.4	-137.1
Copper (II) sulfate $CuSO_4(s)$	-770.8	-661.3
Ethane C_2H_6 (g)	-84.4	-33.0
Ethene (ethylene) $C_2H_4(g)$	52.3	68.1
Ethyne (acetylene) $C_2H_2(g)$	226.6	209.0
Hydrogen fluoride $HF(g)$	-270.9	-273.0
Hydrogen iodide $HI(g)$	26.3	1.7
Iodine chloride $ICl(g)$	18.0	-5.4
Lead (II) oxide $PbO(s)$	-215.3	-188.1
Magnesium oxide $MgO(s)$	-601.1	-568.9
Nitrogen monoxide $NO(g)$	90.3	86.5
Nitrogen dioxide $NO_2(g)$	33.0	51.4
Potassium chloride $KCl(s)$	-436.4	-408.8
Sodium chloride $NaCl(s)$	-410.9	-383.7
Sulfur dioxide $SO_2(g)$	-296.4	-299.7
Water $H_2O(g)$	-241.6	-228.2
Water $H_2O(\ell)$	-285.5	-237.0

* Minus sign indicates an exothermic reaction.
Sample equations:
$2Al(s) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s) + 1674.1$ kJ
$2Al(s) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s)$ $\Delta H = -1674.1$ kJ/mol

Assignment: Equilibrium Expression (K_eq)

Law of Chemical Equilibrium

The law of chemical equilibrium is shown in the box to the right. For the reaction $aA + bB \rightleftharpoons cC + dD$, A and B represent the reactants, C and D represent the products and *a, b, c* and *d* represent the respective coefficients. The equilibrium expression is equal to the multiple of the concentrations of the products raised to the power of their respective coefficients divided by the multiple of the reactants raised to the power of their respective coefficients.

$$\text{If } aA + bB \rightleftharpoons cC + dD$$
$$k_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

There are several things that can be done to interpret equilibrium using the law. First, since the numerator of the fraction is based on the concentration of the products, an equilibrium constant great than one ($k_{eq} > 1$) referee to a reaction that favors the formation of product, while an equilibrium constant less than one ($k_{eq} < 1$) refers to a reaction that favors the formation of the reactants [example (a)]. Second, appropriate equilibrium expressions need to be written based on the balanced equation [example (b)]. And third, mathematical problems can be done substituting values for the concentration into the equilibrium expression, either to determine if equilibrium has been reached, or to determine if the equilibrium concentration of one of the reactants or products. [examples (c) and (d)].

Sample Problems

The reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is at equilibrium at 1 atm and 298 K. The equilibrium constant for the reaction at 1 atm and 298 K is as follows: $K_{eq} = 3.5 \times 10^{-1}$

(a) Which is favored, the forward or the reverse reaction?

Answer: The reverse reaction is favored ($K_{eq} < 1$)

(b) What is the equilibrium expression?

Answer:
$$3.5 \times 10^{-1} = \frac{[HI]^2}{[H_2][I_2]}$$

(c) If the concentration of hydrogen iodide is $2.65 \times 10^{-2} M$, the concentration of hydrogen is $5.0 \times 10^{-3} M$, and the concentration of iodine is $4.0 \times 10^{-1} M$, is the reaction at equilibrium?

Answer:
$$K_{eq} = \frac{(2.65 \times 10^{-2})^2}{(5.0 \times 10^{-3})(4.0 \times 10^{-1})} = 3.5 \times 10^{-1}$$

Yes!

(d) If the reaction is at equilibrium, what is the concentration of hydrogen iodide if the concentration of hydrogen is $3.0 \times 10^{-3} M$, and the concentration of iodine is $2.5 \times 10^{-2} M$?

Answer:
$$3.5 \times 10^{-1} = \frac{[HI]^2}{(3.0 \times 10^{-3})(2.5 \times 10^{-2})}$$
$$[HI] = \sqrt{(3.5 \times 10^{-1})(3.0 \times 10^{-3})(2.5 \times 10^{-2})}$$
$$[HI] = \sqrt{2.625 \times 10^{-5}} = 5.1 \times 10^{-3} M$$

Refer to the table below to answer the questions that follow (assume all reactions are at 1 atm and 298 K).

CONSTANTS FOR VARIOUS EQUILIBRIA AT 1 atm AND 298 K	
$H_2O(l) = H^+(aq) + OH^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$H_2O(l) + H_2O(l) = H_3O^+(aq) + OH-(aq)$	$K_w = 1.0 \times 10^{-14}$
$CH_3COO^-(aq) + H_2O(l) = CH_3COOH(aq) + OH(aq)$	$K_b = 5.6 \times 10^{-10}$
$NaF(aq) + H_2O(l) = Na^+(aq) + OH^-(aq) + HF(aq)$	$K_b = 1.5 \times 10^{-11}$
$NH_3(aq) + H_2O(l) = NH_4^+(aq) + OH^-(aq)$	$K_b = 1.8 \times 10^{-5}$
$CO_3^{2-}(aq) + H_2O(l) = HCO_3^-(aq) + OH^-(aq)$	$K_b = 1.8 \times 10^{-4}$
$Ag(NH_3)_2^+(aq) = Ag^+(aq) + 2NH_3(aq)$	$K_{eq} = 8.9 \times 10^{-8}$
$N_2(g) + 3H_2(g) = 2NH_3(g)$	$K_{eq} = 6.7 \times 10^5$
$H_2(g) + I_2(g) = 2HI(g)$	$K_{eq} = 3.5 \times 10^{-1}$

Compound	K_{sp}	Compound	K_{sp}
AgBr	5.0×10^{-13}	Li_2CO_3	2.5×10^{-2}
AgCl	1.8×10^{-10}	$PbCl_2$	1.6×10^{-5}
Ag_2CrO_4	1.1×10^{-12}	$PbCO_3$	7.4×10^{-4}
AgI	8.3×10^{-17}	$PbCrO_4$	2.8×10^{-13}
$BaSO_4$	1.1×10^{-10}	PbI_2	7.1×10^{-9}
$CaSO_4$	9.1×10^{-6}	$ZnCO_3$	1.4×10^{-11}

1. A solution of ammonia is prepared [$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH-(aq)$]

   a) Which is favored, the forward or reverse reaction? _____

   b) What is the equilibrium expression?

   c) If the reaction is at equilibrium and [NH_4^+] = [OH^-] = 7.35 x 10^{-3} M, what is the concentration of $NH_3(aq)$?

2. Ammonia is prepared from it elements [$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$]

   a) Which is favored, the forward or reverse reaction? _____

   b) What is the equilibrium expression?

   c) If the reaction is at equilibrium, [N_2] = 0.500 M and [H_2} = 0.300 M, what is the concentration of $NH_3(g)$?