

Rate Laws

Reaction rates are defined as the change in concentration of a reactant or product per unit of time. Keep in mind that chemical reactions are reversible. When reactants are first placed in the reaction vessel, initially the forward reaction is the dominant reaction. As the concentration of products increases, the reverse reaction becomes important ($\Delta_{\text{REACTANTS}} = \text{Rate}_{\text{FORWARD}} - \text{Rate}_{\text{REVERSE}}$). If conditions permit the reverse reaction to be neglected, the reaction rate depends on only the concentration of the reactants. The expression showing how the rate of the reaction depends on the concentration of the reactants is called a rate law. For the reaction $A + B \rightarrow C$, the concentration of A, [A], can be held constant while the concentration of B, [B] is changed, and the rate measured, and the concentration of B, [B], can be held constant while the concentration of A, [A] is changed, and the rate measured. This is how rate laws are determined. If doubling the concentration of A causes the reaction rate to double, while doubling the concentration of B causes it to quadruple, and doubling them both causes the reaction rate to increase eightfold, the rate law is $\text{Rate} = k[A][B]^2$. The general form of rate laws is:



Why molecules follow rate laws

$\text{Rate} = k[A]^m[B]^n$. The value of m and n can only be determined experimentally. The form of the rate law depends on the reaction mechanisms. Experimental data verifying the rate law confirms the reaction mechanism.

Single Step Reactions

Concentrations of reactants are raised to their stoichiometric coefficients based on collision theory

- for $A + B \rightarrow 2C$, where one particle of A collides with one of B to form two particles of C
 - $R = k[A][B]$
- for $2C \rightarrow A + B$, where two particles of C collide to form one of A and one of B
 - $R = k[C]^2$

Multiple Step Reactions

For the reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

- The mechanism is believed to consist of two steps
 - Step 1:** $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}_3(\text{g}) + \text{NO}(\text{g})$ slow
 - Step 2:** $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$ fast
 - Net:** $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
- The rate law is determined from the rate determining step
 - $R = k[\text{NO}_2]^2$

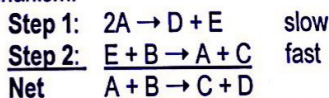
Sample Problems

For the single step reaction $A + B \rightarrow C$, what effect will tripling the concentration of both A and B have on the reaction rate?

- Write the rate law: $R = k[A][B]$
- Make a ratio of the rate laws based on the final and initial concentrations:

$$\frac{R_f}{R_i} = \frac{k[3][3]}{k[1][1]} = 9$$

For the multistep reaction $A + B \rightarrow C + D$ with the following mechanism:



What effect will doubling the concentration of A have

- Write the rate law: $R = [A]^2$
- Make a ratio of the rate laws based on the final and initial concentrations:

$$\frac{R_f}{R_i} = \frac{k[2]^2}{k[1]^2} = 4$$

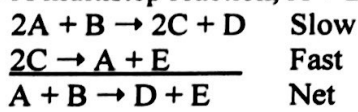
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Write the rate laws for each of the reactions below, and describe what the effect of manipulating the concentration of the reactants will be on the reaction rate.

1. A single step reaction occurs as follows: $2A + 3B \rightarrow 2C + D$

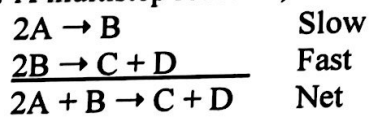
- What is the rate law?
- What is the effect of doubling both the concentrations of A and B on the reaction rate?

2. A multistep reaction, $A + B \rightarrow D + E$, occurs as follows:



- What is the rate law?
- What is the effect of doubling both the concentrations A and B on the reaction rate?

3. A multistep reaction, $2A + B \rightarrow C + D$, occurs as follows:



- What is the rate law?
- What is the effect of doubling the concentration A and tripling the concentration of B on the reaction rate?

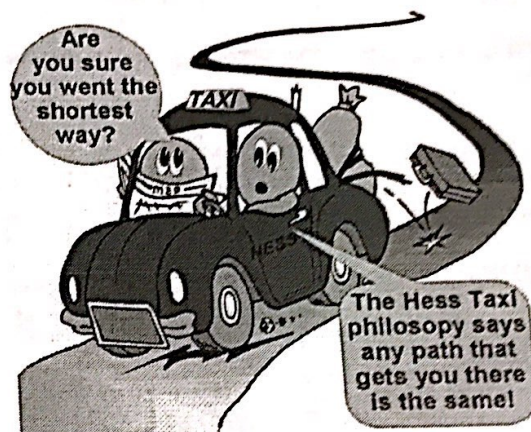
A single step reaction occurs as follows: $A \rightarrow 2C + D$

- What is the rate law?
- What is the effect of tripling the concentration of A on the reaction rate?

Applying Hess's Law

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 the 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.

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

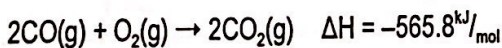
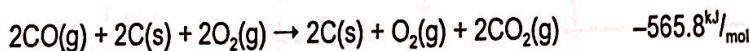
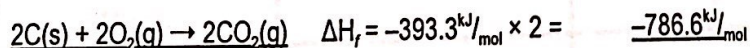
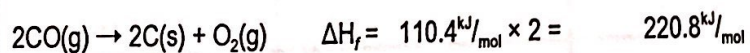


For example, under standard conditions (1 atm and 298K) the heat of formation for carbon dioxide is -393.3 kJ/mol [$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_f = -393.3 \text{ kJ/mol}$] and the heat of formation of carbon monoxide is -110.4 kJ/mol [$\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)} \quad \Delta H_f = -110.4 \text{ kJ/mol}$]. Notice the coefficient in front of the oxygen is $\frac{1}{2}$. 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 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 changed, 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 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 $2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$

Equations (from above)

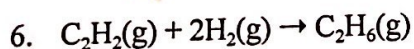
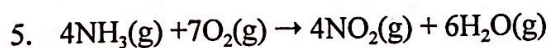
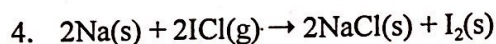
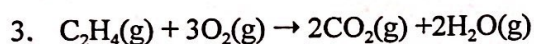
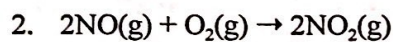
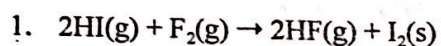


Explanation

- Reverse the reaction so CO is on the reactant side. Reverse the sign of ΔH_f . Multiply by the coefficient 2.
- Multiply by the coefficient 2.
- Add the equations and the enthalpies
- Subtract $\text{O}_2(\text{g})$ and 2C(s) from both sides

CONTINUE 

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



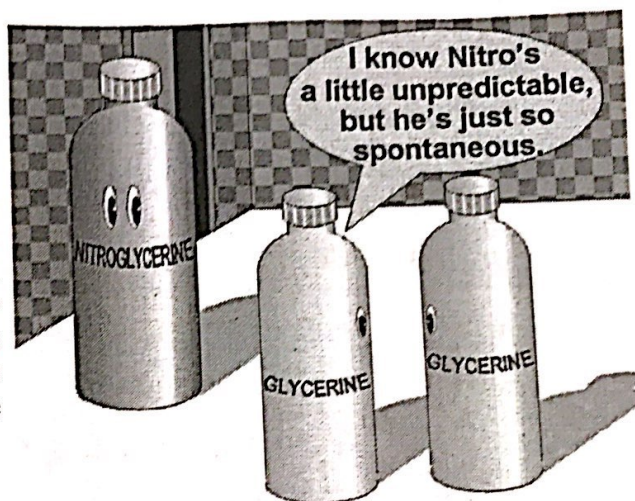
STANDARD ENERGIES OF FORMATION OF COMPOUNDS AT 1 atm AND 298 K		
Compound	Heat (Enthalpy) of Formation * kJ/mol (ΔH_f°)	Free Energy of Formation kJ/mol (ΔG_f°)
Aluminum oxide $\text{Al}_2\text{O}_3(\text{s})$	-1674.1	-1580.9
Ammonia $\text{NH}_3(\text{g})$	-46.0	-16.3
Barium sulfate $\text{BaSO}_4(\text{s})$	-1471.8	-1361.0
Calcium hydroxide $\text{Ca}(\text{OH})_2(\text{s})$	-985.2	-897.9
Carbon dioxide $\text{CO}_2(\text{g})$	-393.3	-394.2
Carbon monoxide $\text{CO}(\text{g})$	-110.4	-137.1
Copper (II) sulfate $\text{CuSO}_4(\text{s})$	-770.8	-661.3
Ethane $\text{C}_2\text{H}_6(\text{g})$	-84.4	-33.0
Ethene (ethylene) $\text{C}_2\text{H}_4(\text{g})$	52.3	68.1
Ethyne (acetylene) $\text{C}_2\text{H}_2(\text{g})$	226.6	209.0
Hydrogen fluoride $\text{HF}(\text{g})$	-270.9	-273.0
Hydrogen iodide $\text{HI}(\text{g})$	26.3	1.7
Iodine chloride $\text{ICl}(\text{g})$	18.0	-5.4
Lead (II) oxide $\text{PbO}(\text{s})$	-215.3	-188.1
Magnesium oxide $\text{MgO}(\text{s})$	-601.1	-568.9
Nitrogen monoxide $\text{NO}(\text{g})$	90.3	86.5
Nitrogen dioxide $\text{NO}_2(\text{g})$	33.0	51.4
Potassium chloride $\text{KCl}(\text{s})$	-436.4	-408.8
Sodium chloride $\text{NaCl}(\text{s})$	-410.9	-383.7
Sulfur dioxide $\text{SO}_2(\text{g})$	-296.4	-299.7
Water $\text{H}_2\text{O}(\text{g})$	-241.6	-228.2
Water $\text{H}_2\text{O}(\text{l})$	-285.5	-237.0

* Minus sign indicates an exothermic reaction.
Sample equations:
 $2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 1674.1 \text{ kJ}$
 $2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) \quad \Delta H = -1674.1 \text{ kJ/mol}$

Being Spontaneous

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 toward 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 between the energy change (ΔH) and the product of the absolute or Kelvin temperature (T) and the entropy change (ΔS)

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



Chemical dating preferences

For a system at equilibrium, $\Delta G = 0$. 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 $T\Delta S$ will be small, and ΔH will have the greatest effect on the free energy. At high temperatures, the term $T\Delta S$ 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	-	+	

Continue 

KINETICS AND EQUILIBRIUM

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?) _____

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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.

$\Delta G_f^\circ = -394.2 \text{ kJ/mol}$

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

$\Delta H_f^\circ = -393.3 \text{ kJ/mol}$

$-394.2 \text{ kJ/mol} = -393.3 \text{ kJ/mol} - 298K(\Delta S)$

$T = 298 \text{ K (see table)}$

$-0.9 \text{ kJ/mol} = -298K(\Delta S)$

$\Delta S = 0.003 \text{ kJ/mol}\cdot\text{K}$

a. Ethene

b. Water vapor