Kinetics and thermodynamics are related to each other in ways that can be explained by using chemical reactions. A discussion of kinetics and thermodynamics requires an explanation of the underlying relationships between the two, through application to chemical reactions and several examples from natural processes.

Introduction

It is important to mention that a chemical reaction has kinetic and thermodynamic aspects. The quantity related to kinetics is the rate constant $k$; this constant is associated with the activation energy required for the reaction to proceed, that is, the reactivity of the reactants. The thermodynamic quantity is the energy difference resulting from the free energy ($\Delta G$) given off during a chemical reaction—the stability of the products relative to the reactants. Although kinetics describes the rates of reactions and how fast equilibrium is reached, it gives no information about conditions once the reaction equilibrates. In the same measure, thermodynamics only gives information regarding the equilibrium conditions of products after the reaction takes place, but does not explain the rate of reaction.

Kinetics Overview

The rate constant, $k$, measures how fast a chemical reaction reaches equilibrium assuming the reactants were supplied with enough activation energy to enable the reaction to proceed in the forward direction—reactants to products. This requirement for input of energy symbolizes the fact that the reactants are unreactive under certain conditions. The reaction must have some sort of energy input before it can proceed; otherwise, the reactants cannot cross the activation energy threshold and convert to products. The reaction is activated by energy supplied to the reactants by different energy sources. The rate of reaction, the rate constant, and the kinetic energy required for activation of reaction indicate how fast the reaction reaches equilibrium. See Diagram #1.

Diagram #1: Depicted in the graph below are the main points discussed in the previous paragraph. The transition state represents a threshold the reactants must pass before the reaction can proceed in the forward direction. The activation energy is the energy required to reach the transition state. Once this threshold is reached, the reaction proceed in the favorable "downhill" direction. It is important to remember that each reaction has a different transition state threshold, with different activation energies, and determined by the reactants and the conditions in which the reaction is taking place. The value of $k$ is affected by these two factors, and can be increased in the presence of a catalyst (such as an enzyme), which increases reaction rate. In chemical reactions, specifically, the catalyst can both provide more energy to the reactants and lower the transition state energy. The provider of activation energy can also be a spark, heat, or anything else that gives off energy. Regardless of what provides the activation energy, a kinetic or nonspontaneous reaction is one in which the most stable state is that of the reactants. The change in energy between the reactants and products, also known as $\Delta G$, relates to thermodynamics and will be discussed shortly.

Diagram #1 link: [http://www4.nau.edu/meteorite/Meteor...rgyDiagram.jpg](http://www4.nau.edu/meteorite/Meteor...rgyDiagram.jpg)

Example 1: Fuel

The gas in a fuel tank is not "wasted" or burnt away while the car is sitting in the parking lot. Fuel is unreactive
Thermodynamics Overview

Thermodynamics can be considered in terms of the energy stored within a reaction, a reactant, or a product. Most often, thermodynamics is thought of as the different forms of energy that are converted every time a reaction emits energy or is initiated by energy. With respect to Gibbs free energy ($\Delta G$), thermodynamics refers to either (1) the energy released during a reaction, in which case $\Delta G$ will be negative and the reaction exergonic or spontaneous, or (2) the energy consumed during a reaction, in which case $\Delta G$ will be positive and the reaction endergonic or nonspontaneous. A thermodynamic reaction favors the products, resulting in a spontaneous reaction that occurs without the need to constantly supply energy. This indicates that the reactions' most stable state is that of the products.

Thus, going back to Diagram #1, thermodynamics is what describes the free energy between the reactants and the products. Because thermodynamic values apply only after the reactants have turned into products, they are said to describe the equilibrium state. The relationship between free energy (aka, Gibbs free energy) and other thermodynamic quantities is expressed mathematically in the following equation:

\[ G = U + pV - TS \]

Because "U" is the variable representing the internal energy of a system, it is closely correlated with the free energy. Changes in internal energy change the value of the free energy, in turn affecting chemical reactions in several ways: the rate of reaction, whether the reaction is spontaneous or non-spontaneous, and even whether or not activation energy will be needed to initiate the reaction.

Example 2: Systems

The best way to understand thermodynamics is by realizing that anything that transfers, receives, or contains heat can be described as a system. Heat can enter or leave a system, which affects the amount of thermal energy it contains. Consider a kettle of water sitting on a stove. As it is heated, thermal energy is added to the system (the kettle with the water). As the stove is turned off, the kettle cools down as the heat diffuses back to the room; the kettle slowly equilibrates to room temperature. This is an example of the system losing thermal energy. To view an animated diagram of a thermodynamic system, click on 'Outside Link' number 2.

Thermodynamics vs. Kinetics

As mentioned above, the most stable states of a kinetic reaction are those of the reactants, in which an input of energy...
is required to move the reaction from a state of stability, to that of reacting and converting itself to products. **Kinetics is related to reactivity.** In contrast, the most stable state of a thermodynamically favorable reaction is the products, because the reaction occurs spontaneously, without the need for energy to be added. **Thermodynamics is related to stability.**

Therefore, something that is unreactive will desire to stay in the form of reactants, which will require an input of energy to cause the reaction to go forward, converting reactants into products. This is illustrated in example #3 below. A reactive species does not require an input of energy to be converted from reactants to products, because its most stable and preferred state is that of the products. Instead, a thermodynamically favorable reaction requires energy to be converted from products back to reactants. An energy source moves the reaction forward (kinetics corresponds to movement). The same is for thermodynamically favorable reactions, except that the reaction must be stimulated backward from products to reactants.

**Example 3: ATP**

Adenosine triphosphate, also known as ATP, provides the energy cells require in order to maintain metabolic pathways, DNA synthesis and repair, and any other cellular function necessary for survival. ATP itself is a reactive molecule that has three phosphate groups. Molecules tend toward stable states, converting to states of lower energies. Thus, ATP, a high-energy molecule, tends to lose a phosphate group and become adenosine diphosphate, ADP. In order for this to happen, an enzyme strips one phosphate group off of ATP, converting it to the more stable molecule ADP. This enzyme provides the energy of activation that enables ATP to become ADP, indicating that ATP is kinetically stable.

**Example 4: Water and Sugar**

The following example involves solvents and polarity: consider a simple situation, a spoonful of sugar is added to a cup of water. If the two are left to react, over time the sugar dissolves in the water, becoming the product of sugar+water. The natural charges and polarity of water causes the sugar molecules to react with it, eventually dissolving within the water. There is no required input of energy, indicating that this reaction is thermodynamically favorable, and therefore spontaneous. Clearly, the two reactants prefer to react and maintain stability as products.

Note: although this is a thermodynamically favorable or spontaneous reaction and does not require energy input, the use of kinetic energy will force this reaction to happen faster. If sugar is added to the cup of water and the system is heated, the kinetic energy of the reactants is increased by the thermal energy of the heat, which causes the molecules to react with one another at a much faster rate than if they been left alone at room temperature. This is an example of how thermodynamics and kinetics are closely related.

**Outside links**

2. **Thermodynamic System:** [http://upload.wikimedia.org/wikipedia/commons/8/8a/Triple_expansion_engine_animation.gif](http://upload.wikimedia.org/wikipedia/commons/8/8a/Triple_expansion_engine_animation.gif)
3. **Nonspontaneous Reaction (compare with Diagram #1):** [http://www.biology.arizona.edu/biochemistry/problem_sets/](http://www.biology.arizona.edu/biochemistry/problem_sets/)
5. Demonstration of two kinetically-stable elements in a mixture, after given enough energy of activation: http://www.metacafe.com/watch/908325...fuel_ignition/

References
2. Thermodynamic stability and crystal structure of lanthanide complexes with di-2-pyridyl ketone. S. Dominguez a; J. Torres b; J. Gonzalez c; M. Hummert d; H. Schumann - e; C. Kremer b
3. Role of Solvation Barriers in Protein Kinetic Stability. RODRIGUEZ-LARREA David ; MINNING Stefan ; BORCHERT Torben V. ; SANCHEZ-RUIZ Jose M.

Problems
1. Is it possible that graphite is thermodynamically stable and diamond is less reactive under standard conditions?
2. Explain how kinetics relate to thermodynamics. Use the terms 'energy of motion', 'energy of heat', and an example from the module in your answer.
3. Why would it be beneficial for a thermodynamically-stable reaction to use an energy input in the form of an enzyme or a catalyst even if it does not require energy to proceed?
4. How come gas does not spontaneously combust inside a fuel tank?
5. How is the rate constant k related to equilibrium? How does the rate constant change if heat is added to the reaction?
6. If the difference in energy between the reactants and products is negative, is the reaction spontaneous or nonspontaneous?

Answers
1. Yes. Their different structures will differentiate their polarity and charge, and will cause the two compounds to act differently. Thus, one can be thermodynamically stable, while the other can be less reactive.
2. The energy of motion is related to kinetics, which determines how fast the reaction will reach equilibrium, related to thermodynamics. The energy of motion (kinetics) added to a reaction causes the reaction to happen faster, using energy of heat as a way by which to accelerate the reaction. An example of this is the cup of water with the sugar while it is being heated. The heat energy converts into kinetic energy (energy of motion), accelerating the reaction between the water molecules and the sugar crystals.
3. A catalyst or enzyme will still be beneficial in a thermodynamically-favorable reaction because it will simply accelerate it.
4. Fuel is unreactive to standard conditions and regular atmosphere, which means it'll require an energy input in order
to react. The energy input is the spark caused by the ignition of the car.

5. The rate constant $k$ is related to equilibrium in that it tells us about how fast the reaction reaches equilibrium. If heat is added to a reaction, its rate will increase due to increased kinetic energy.

6. The reaction will be spontaneous, thermodynamically favorable. This is because the energy is given-off, not consumed by the reaction.

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