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Activation energy

FIELDS OF STUDY

Physical Chemistry; Inorganic Chemistry; Biochemistry

SUMMARY

The activation energy of a process is defined, and its importance in chemical processes is elaborated. Activation energy is a widely variable quantity in different reactions but is nevertheless characteristic of any specific reaction process.

PRINCIPAL TERMS

- **Arrhenius equation:** a mathematical function that relates the rate of a reaction to the energy required to initiate the reaction and the absolute temperature at which it is carried out.
- **catalyst:** a chemical species that initiates or speeds up a chemical reaction but is not itself consumed in the reaction.
- **chemical reaction:** a process in which the molecules of two or more chemical species interact with each other in a way that causes the electrons in the bonds between atoms to be rearranged,
- **resulting:** in changes to the chemical identities of the materials.
- **reaction rate:** how much of a particular reaction or reaction step occurs per unit time.
- **transition state:** an unstable structure formed during a chemical reaction at the peak of its potential energy that cannot be isolated and ultimately breaks down, either forming the products of the reaction or reverting back to the original reactants.

Activation Energy in Chemical Reactions

Activation energy can be thought of as a barrier that the reactants in a chemical reaction must overcome if the reaction is to proceed to the formation of products. The molecules that are involved must rearrange to form either a transition state or an intermediate that is higher in energy than the starting materials. An intermediate is a stable chemical structure formed during a reaction process that can often be captured and isolated by chemical means. Once this structure is formed, the reaction process can either progress to form products or revert back to the original reactants.

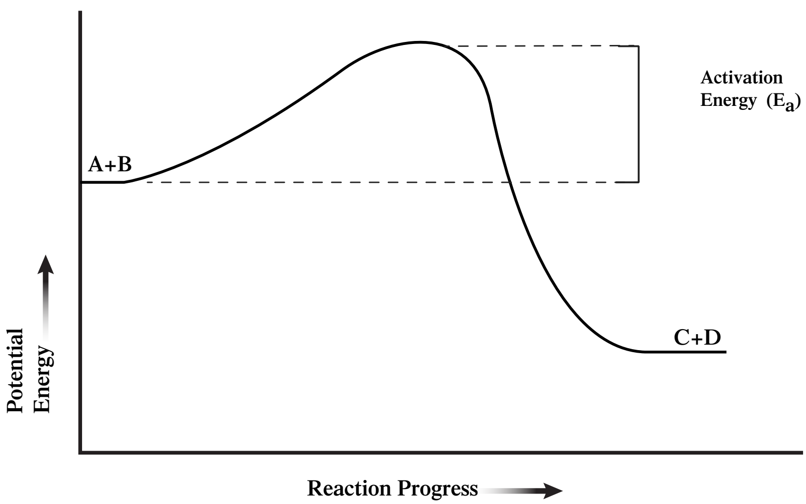
Activation energy is the energy required for a specific chemical reaction to occur. In a reaction, two reactant molecules contact each other with the energy of their ambient states.(The ambient state of a material can be thought of as its "default" state—the state it takes at one atmosphere of pressure and what is commonly considered to be room temperature.) In the case of a spontaneous reaction, the energy of the collision is sufficient to initiate the formation of the transition state or intermediate. In a nonspontaneous reaction, the energy of the molecular collision is not sufficient, and the two molecules will not interact. The input of some additional energy is required to drive the two molecules together so that the transition state or intermediate is formed and the reaction can proceed. The energy released in the transformation of reactants into products is generally sufficient to drive the reactions of other molecules in the reaction mixture.

Another way to look at activation energy is to think of it as the minimum amount of energy that two interacting molecules must gain in order to weaken bonds between atoms in both molecules so that those bonds can be rearranged. Since chemical reactions are essentially processes of breaking and making bonds, having sufficient energy to overcome the strength of the appropriate bonds is essential if there is to be any reaction between the two molecules.

Activation Energy and Reaction Rates

Reaction rates can be related directly to their activation energies. This relationship is defined by the Arrhenius equation, formulated in 1884 by the Swedish scientist Svante Arrhenius (1859–1927), who received the Nobel Prize in Chemistry in 1903.The

ACTIVATION ENERGY DIAGRAM



Arrhenius equation relates the rate constant of a reaction to its activation energy and the absolute temperature and has the form

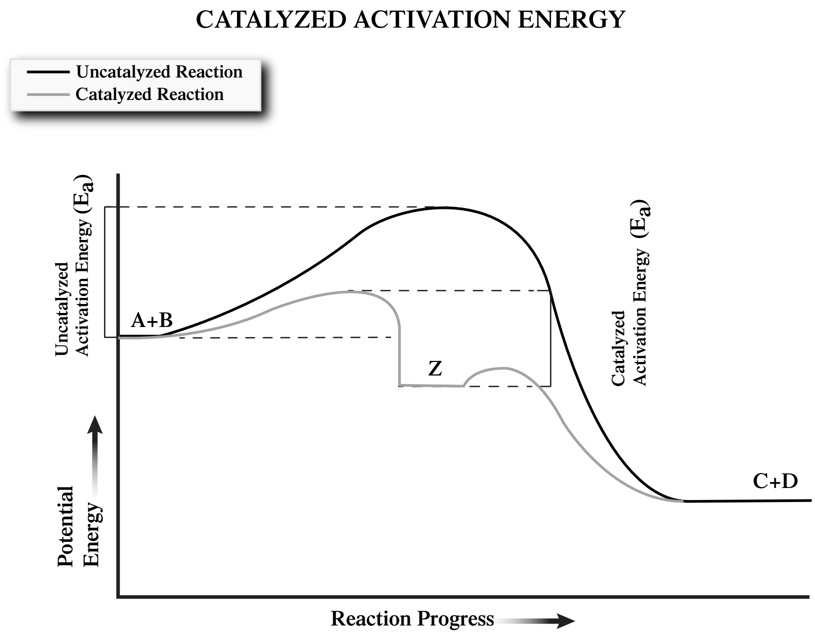
$$k = Ae{-}E/RT$$

where k is the rate constant for the reaction or process; A is the pre-exponential factor, also known in some cases as the frequency factor; E (or E_a) is the activation energy for the reaction or process; R is the gas constant; T is the absolute temperature; and the mathematical constant e is the base of the natural logarithm, so that the natural logarithm (ln) of e is equal to 1.The Arrhenius equation has been found to apply not only to chemical reactions but to physical processes as well. T he relationship can be most clearly seen by plotting experimentally determined logarithmic values of k against the inverse of the absolute temperature, $1/T$. This results in a straight line plot, from which the activation energy of the reaction or process can be calculated. The pre-exponential factor A is identified as the value that the specific rate constant k would have if the activation energy E were zero (a spontaneous reaction).In that special case, the exponent $-E/RT$ would also be equal to zero, making e$-E/RT$ equal 1 and thus causing the value of k to be equal to A. For different specific reactions, the value of A ranges over several orders of magnitude, but the rate constant k is determined almost solely by the value of e$-E/RT$, which can range over several hundred orders of magnitude, depending on the relative values of E and T.

The course of a reaction depends on the relative difference between the energy of the reactants and that of the products. The greater this difference is, the more impetus there is for the reaction to proceed to the formation of products. This is typically illustrated in a plot of energy versus the reaction coordinate, a symbolic representation of the progress of a reaction. In the plot, the energy level of the reactants, on the left, is either higher or lower than that of the products, on the right. In between, a curved line rises from the energy level of the reactants to a maximum value before falling to the energy level of the products. The difference between the energy level of the reactants and this peak energy value represents the activation energy for the reaction, while the difference between the energy levels of the reactants and the products represents the energy released in the reaction, also called its enthalpy.

The specific rate of any individual reaction is determined by its activation energy. However, in mass quantities, the energy differences between reactants and products in the system also play a role. This can be understood by considering the Boltzmann fraction e$-E/RT$, which describes the fraction of molecules in the system having energy greater than E. As energy is released from several reactions, the fraction of molecules present at any given time with sufficient energy to react increases, and more reactions can occur in any given time period. Each reaction requires the same activation energy, and the amount of energy that is available in the system to permit reactions to occur may be anything from “barely enough” to “excessive.”

The activation energy of a reaction can be greatly reduced by the inclusion of a catalyst, a material that takes part in the reaction mechanism but is not consumed in the reaction. Catalysts function by forming an activated complex with the reactants, typically



constraining the reactant molecules in an orientation that they would otherwise have to achieve through collision with each other. This reduces the energy necessary to achieve that particular orientation—that is, the activation energy—so that the reaction can proceed. When the reactant molecules are constrained in the activated complex with the catalyst, bonds between certain atoms are weakened and the orientations of atomic and molecular orbitals that must interact are often brought into the proper alignment, or trajectory, for the new bonds to form between atoms.

Activation Energy in Action

The activation energy of a reaction can range from exceedingly small to very large. Two examples serve to illustrate this point. For the first, consider the addition of two parts hydrogen gas (H_2) to one part oxygen gas (O_2).This is an explosive mixture of gases, yet the two mixed gases are quite happy to coexist quietly in the same container, no matter how much is present. The introduction of an initiator such as an electrical spark, however, results in an almost instantaneous reaction to form water (H_2O), accompanied by the release of a great deal of energy. The activation energy of the reaction between hydrogen and oxygen is very low, and the amount of energy released by one reaction is more than sufficient to drive many instances of the reaction in the gas mixture, with each subsequent occurrence releasing an equal amount of energy as the enthalpy of reaction.

The second example is the so-called thermite reaction, in which iron oxide and aluminum metal react to produce aluminum oxide and iron metal. This is a spectacular reaction often demonstrated for chemistry exhibitions. Because the activation energy of the thermite reaction is very high, the reaction is very difficult to initiate and must typically be ignited by a burning piece of magnesium metal; once it has begun, however, it is essentially impossible to stop it due to the amount of energy that is released. Typically, the iron metal falls out of the reaction mixture as a white-hot liquid.

Activation Energy in Biological Systems

Activation energy applies to biochemical processes as well as to physical processes. The chirping of crickets, for example, is dependent on temperature in a manner that is in complete accord with the Arrhenius equation. In biological systems, the activation energy of processes is made a great deal lower by the catalytic action of protein molecules called enzymes. Enzymes have well-defined three-dimensional structural shapes that allow them to coordinate with other molecules in specific ways, rather like the way a key works with a lock. The coordination normally alters the three-dimensional shape of the substrate molecule or otherwise interacts with it so that specific bonds are weakened and the molecular geometry is changed such that reaction is highly favored.

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ACTIVATION ENERGY SAMPLE PROBLEM

Use the Arrhenius equation to determine the activation energy at 0°C for a reaction having a specific rate constant (*k*) of 0.023 moles per liter per second and a pre-exponential factor (*A*) of 2,303 moles per liter per second. Use the gas constant.

$$R = 8.314 \frac{\text{J}}{\text{mol K}}$$

Answer:

Convert the temperature from degrees Celsius to kelvins, given that K = °C + 273.15:

$$\text{K} = 0 + 273.15 = 273.15$$

The Arrhenius equation is

$$k = Ae{-}E/RT$$

Rearrange the equation using natural logarithmic (ln) relationships:

$$\ln k = \ln A + \ln(e^{-E/RT})$$

$$\ln k = \ln A - \frac{E}{RT}$$

$$\frac{E}{RT} = \ln A - \ln k$$

$$E = RT(\ln A - \ln k)$$

Substitute in the values of $R\,(8.314 \frac{\text{J}}{\text{mol K}})$, T (temperature), A (pre-exponential factor), and k (rate constant). Calculate, paying attention to the units throughout:

$$E = RT(\ln A - \ln k)$$

$$E = (8.314 \frac{\text{J}}{\text{mol K}} \times 273.15\ \text{K})(\ln 2303 - \ln 0.023)$$

$$E = (8.314 \frac{\text{J}}{\text{mol K}} \times 273.15\ \text{K})[7.742 - (-3.772)]$$

$$E = 26147.938 \frac{\text{J}}{\text{mol}}$$

ACTIVE TRANSPORT

FIELDS OF STUDY

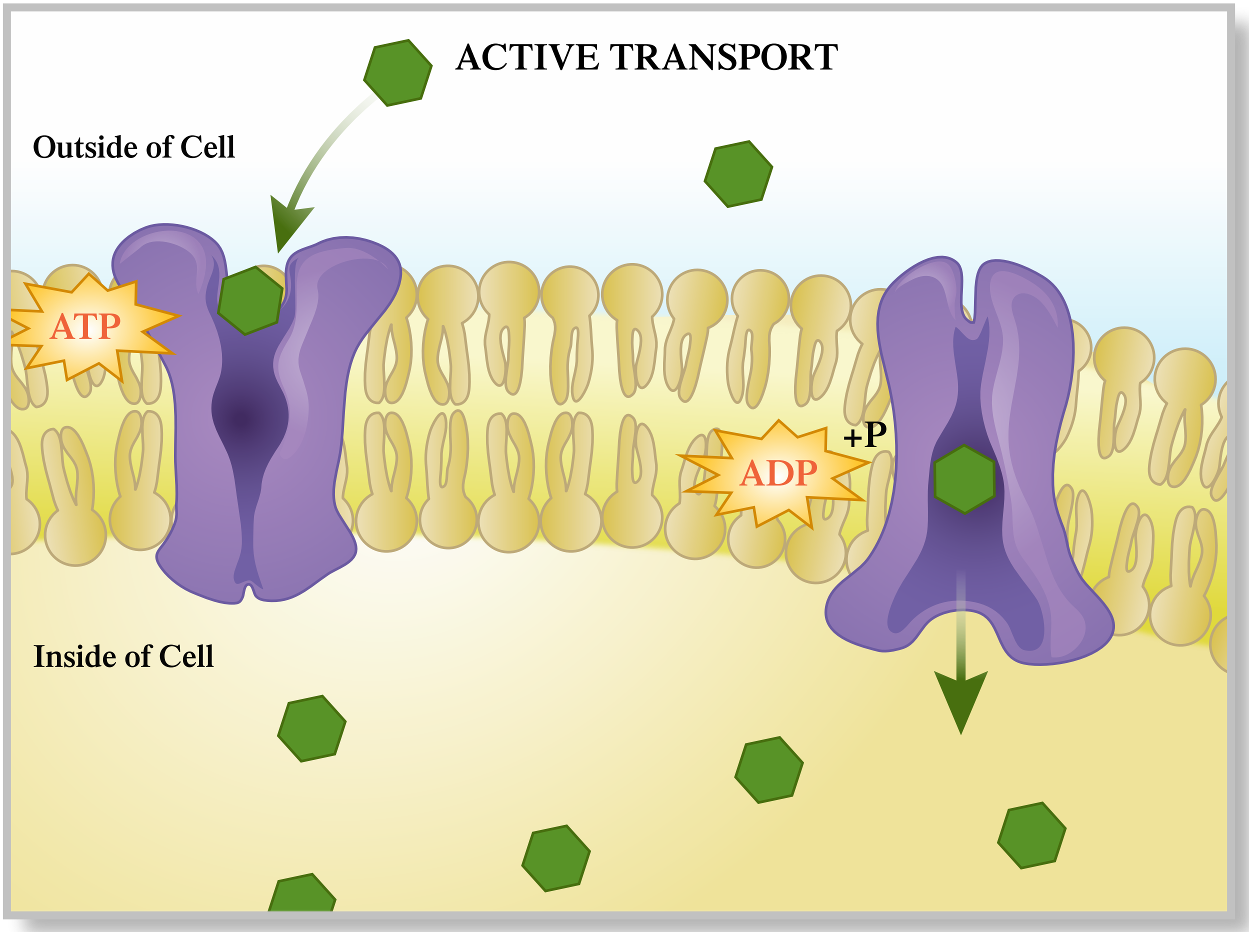
Biochemistry; Molecular Biology; Genetics

SUMMARY

The process of active transport is defined, and its importance in biochemical processes is elaborated. Active transport is an essential feature of the biochemistry of living systems and helps maintain the necessary concentrations of various biochemical components and electrolytes for the proper functioning of cellular metabolism.

PRINCIPAL TERMS

- **adenosine triphosphate (ATP):** a molecule consisting of adenine, ribose, and a triphosphate chain that is used to transfer the energy needed to carry out numerous cellular processes.
- **cell membrane:** a biological membrane that forms a semipermeable barrier separating the interior of a cell from the exterior.
- **concentration gradient:** the gradual change in the concentration of solutes in a solution across a specific distance.



- **diffusion:** the process by which different particles, such as atoms and molecules, gradually become intermingled due to random motion caused by thermal energy.
- **passive transport:** the passage of materials through a membrane with no input of energy required.

The Mechanics of Active Transport

In living cells, biochemical processes transport materials necessary for a properly functioning metabolism through cell membranes. Passive transport does not require an input of energy to move materials across cell walls because it operates in the same direction as the concentration gradient, moving the materials from an area of high pressure to one of low pressure. Active transport can be thought of as a "shuttle service" for ions and other polar materials that cannot pass through a cell membrane by diffusion, a kind of passive transport. Instead, those entities must be physically transported across membranes by various mechanisms collectively termed pumps. A pump is a type of mediated transport system that functions to conduct ions, amino acids, glucose, and other polar compounds through the nonionic lipid bilayer, the highly nonpolar material that makes up the cell wall. Pumps always work against the concentration gradient to move materials out of regions of low concentration and into regions of higher concentration, using energy derived from biochemical reactions. The transported material is subsequently used in other biochemical reactions that return the energy used during transport.

Cell Walls and Lipid Bilayers

Long-chain fatty acids are organic molecules whose molecular structure consists of a single hydrocarbon chain terminated by a carboxylic acid functional group (–COOH). The carboxyl group is highly polar and hydrophilic, while the hydrocarbon moiety, or portion, of the molecule is very nonpolar and hydrophobic. Carboxylic acids are converted to esters by enzyme-mediated reactions with alcohols. In an ester, the carboxyl functional group retains the highly polar character that it had in its free carboxylic acid form, giving the long-chain esters, called lipids, a polar-nonpolar structure similar to that of the free carboxylic acids. When carboxylic acids are esterified with glycerol, which has three hydroxyl (–OH) functional groups, the resulting triesters are called triglycerides. Lipids and triglycerides are the principal forms in which long-chain fatty acids are found in biological systems.

The hydrocarbon chains and the carboxyl-based portions of fatty acids and their esters do not interact with each other due to their different hydrophilicities—that is, the degrees to which they attract and interact with water and other polar molecules—but they are quite capable of interacting with the corresponding portions of other molecules. The hydrocarbon chains associate preferentially with each other, as do the carboxyl portions. The basic structure of the lipid bilayer results from the hydrocarbon portions of the acids of two layers of such molecules intermingling and essentially dissolving each other. The carboxyl functions on the other ends of the one on either side of the very hydrophobic interior layer. The resulting structure is a lipid bilayer.

The walls of all animal cells are formed of lipid bilayers, allowing them to interact with water-based fluids while isolating the sensitive materials and processes that take place within each cell. The fluid inside of each cell is also water based, which necessitates some means of transporting vital polar materials from the exterior of the cell to the interior and moving extraneous materials and metabolites in the opposite direction for elimination. This movement is accomplished by active transport.

Functions of Active-Transport Systems

Active-transport systems serve a variety of functions in the biochemistry of living systems. Their principal function is to allow the organism to extract "fuels" and other essential materials for use in the metabolic functions that occur within cells. This is a very important function, and the nature of active transport allows cells to retain a relatively high concentration of such materials even when their concentrations outside of the cell are quite low. A second important function of active-transport systems is to regulate and maintain the organism's metabolic steady state, a balanced state in which the material and energy that the organism removes from its environment through living functions is equal to the energy and materials that it returns to the environment through those same functions. The biochemical processes of metabolism use energy and materials taken from the environment. Anabolic processes remove materials from the environment and use energy from reactions involving those materials to build and support the life of the organism. Catabolic processes remove used materials from the organism and return them to the environment, releasing the energy stored in those materials.

Active transport maintains a constant optimal amount of various inorganic elements within the living cells of an organism. Potassium ions, for example, are essential to the proper functioning of many intracellular processes. An active-transport system produces potassium-ion channels in cell walls of nerves and muscles, including the cardiac muscles. Potassium ions are delivered into the cytoplasm of the cell via these channels to replace ejected sodium ions, thus maintaining a constant ionic concentration within the cell. The system maintains a relatively high concentration of potassium ions in most aerobic cells, between 100 and 150 millimolars (mM), whether they are plant, animal, or microbial in nature and regardless of the concentration outside of the cells. (A 1 mM solution has a concentration of 0.001 moles per liter.) The potassium ions that are pumped into the cell also serve to maintain the electric potential across the cell membrane, a factor that affects the free-energy change in reactions involved in active-transport systems.

Active Transport in Action

The transfer of ions across a membrane or against a concentration gradient by active transport is accompanied by a free-energy change (ΔG) that can be calculated by one of two equations. The first equation represents the free-energy change for the transfer of neutral materials against a concentration gradient. This is described by the following equations:

$$\Delta G = RT \ln \frac{c_2}{c_1}$$

$$8.314 \frac{\text{J}}{\text{mol K}}$$

where R is the gas constant and T is the absolute temperature in kelvins, ln is the natural logarithm function, and c_1 and c_2 are concentrations on either side of the membrane in molars, or moles per liter (M), with c_2 being greater than c_1.

The second equation, which represents the free-energy change for the transfer of electrically charged materials, needs to account for the charge on the material being transported and the difference in electric potential across the membrane. The latter is determined by the neutral nature of the lipid bilayer, which causes it to act as a capacitor, or energy-storage device, and the presence of charge as maintained by the potassium ions in the cytosol. The free-energy expression for the transport of charged species across a cell membrane is given by the following equation:

$$\Delta G = RT \ln \frac{c_2}{c_1} + ZF\Delta\Psi$$

where Z is the charge on the ion, F is the Faraday constant (96,485.3365 coulombs per mole, the electric charge on one mole of electrons), and is the difference in electric potential across the membrane in volts.

ATP and Active Transport

The energy used in active-transport systems is obtained through enzyme-mediated reactions of adenosine triphosphate (ATP). ATP molecules consist of a molecule of the nucleobase adenine that is bonded to a molecule of ribose sugar, which in turn is bonded to a triphosphate ion. A magnesium ion coordinates and stabilizes the second and third segments of the triphosphate moiety. Energy is derived from the structure by the enzymatic cleavage of the third phosphate segment from the triphosphate moiety, transforming the molecule into adensosine diphosphate (ADP), and it is restored by concatenating, or joining, a third phosphate ion to ADP to re-form ATP.

The function of muscle cells depends on the active transport of calcium ions and sodium ions, a process termed the calcium ion pump or Ca^{2+} pump. The calcium ion pump works in an organelle of muscle cells called the sarcoplasmic reticulum and is powered by ATP hydrolysis reactions mediated by the enzyme calcium adenosine triphosphatase. This process is critical to the contraction and relaxation of muscle fibers, especially heart muscles. The sarcoplasmic reticulum is a cell structure that stores and releases calcium ions to aid in this contraction and relaxation. In muscle cells, the rapid release of calcium ions from the sarcoplasmic reticulum into the cytosol, the cellular fluid outside of the organelles, triggers contraction of the muscle, while rapid removal of calcium ions from the cytosol and back into the sarcoplasmic reticulum triggers relaxation of the muscle.

The normal concentration of free calcium ions in the cytosol is between 0.1 and 0.2 micromolar (μM, or 10^{-6} moles per liter), increasing when the muscle contracts and returning to the normal value when it relaxes.

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ACTIVE TRANSPORT SAMPLE PROBLEM

Use the free-energy equation for active transport against a concentration gradient to determine the free energy associated with transporting neutral amino-acid molecules across a membrane from a concentration of 20 μM to one of 43 μM. Assume normal body temperature of 37°C. Use.

$$R = 8.314 \frac{\text{J}}{\text{mol K}}$$

Answer:

The materials being transported are electrically neutral. Therefore, use the equation

$$\Delta G = RT \ln \frac{c_2}{c_1}$$

Convert the temperature from °C to K:

$$\text{K} = °\text{C} + 273.15$$

$$\text{K} = 37 + 273.15 = 310.15$$

Convert the concentration values from micromolars to molars:

$$c_1 = 20\ \mu\text{M} = 20 \times 10^{-6}\ \text{M} = 0.00002\ \text{M}$$

$$c_2 = 43\ \mu\text{M} = 43 \times 10^{-6}\ \text{M} = 0.000043\ \text{M}$$

Substitute in the values of R, T, c_1, and c_2 and calculate, paying attention to the units throughout:

$$\Delta G = RT \ln \frac{c_2}{c_1}$$

$$\Delta G = (8.314 \frac{\text{J}}{\text{mol K}})(310.15\ \text{K}) \ln \frac{0.000043}{0.00002}$$

$$\Delta G = 1973.8 \frac{\text{J}}{\text{mol}}$$

The free energy of active transport of neutral amino acids across a concentration gradient from 20 μM to 43 μM is 1973.8 joules per mole, or 1.9738 kilojoules per mole.

AGING

FIELDS OF STUDY

Anatomy, cell biology, developmental biology, genetics, neurobiology, pathology, physiology

SUMMARY

Aging is the process of progressive and irreversible change common to all living organisms. There are striking similarities in the physical process of aging among all animal species.

PRINCIPAL TERMS

- **aging:** a process common to all living organisms, eventually resulting in death or conclusion of the life cycle
- **cognition:** ability to perceive or understand death: the cessation of all body and brain functions
- **function:** ability, capacity, performance
- **life span:** length of life from birth to death
- **longevity:** length of life

BASIC PRINCIPLES

Progressive and irreversible change has been called the single common property of all aging systems. When change is reversible or self-maintaining, such as one would see in a forest, for example, the effects of aging are often not observable. Growth of the forest is evident, but with the right conditions, trees within the forest may grow for hundreds of years in the absence of disease. Certain conditions of the forest system help to regenerate, renew, and reverse changes that happen within that system.

However, in animals some change is not reversible. The changes in the cells of the body accumulate over time and result in a steady downward trend. The end point of this trend is the death of the organism. Aging is a normal part of the life cycle. This is known to be true because aging changes within populations are rather predictable. The changes associated with aging that are seen in all animal species may occur for similar reasons. These may include chemical aging, extracellular aging, intracellular aging, and aging of cells.