Chapter 1 : Download Microsoft Small Basic from Official Microsoft Download Center

A training film for a mechanical fire control computer aboard Navy Ships. Amazing how problems of mathematical computation were solved so elegantly in "permanent" mechanical form, before.

History[edit] Historically, equations of motion first appeared in classical mechanics to describe the motion of massive objects , a notable application was to celestial mechanics to predict the motion of the planets as if they orbit like clockwork this was how Neptune was predicted before its discovery , and also investigate the stability of the solar system. It is important to observe that the huge body of work involving kinematics, dynamics and the mathematical models of the universe developed in baby steps â€" faltering, getting up and correcting itself â€" over three millennia and included contributions of both known names and others who have since faded from the annals of history. In antiquity, notwithstanding the success of priests , astrologers and astronomers in predicting solar and lunar eclipses , the solstices and the equinoxes of the Sun and the period of the Moon , there was nothing other than a set of algorithms to help them. Despite the great strides made in the development of geometry made by Ancient Greeks and surveys in Rome, we were to wait for another thousand years before the first equations of motion arrive. The exposure of Europe to Arabic numerals and their ease in computations encouraged first the scholars to learn them and then the merchants and invigorated the spread of knowledge throughout Europe. By the 13th century the universities of Oxford and Paris had come up, and the scholars were now studying mathematics and philosophy with lesser worries about mundane chores of lifeâ€"the fields were not as clearly demarcated as they are in the modern times. Of these, compendia and redactions, such as those of Johannes Campanus , of Euclid and Aristotle, confronted scholars with ideas about infinity and the ratio theory of elements as a means of expressing relations between various quantities involved with moving bodies. These studies led to a new body of knowledge that is now known as physics. Of these institutes Merton College sheltered a group of scholars devoted to natural science, mainly physics, astronomy and mathematics, of similar in stature to the intellectuals at the University of Paris. Thomas Bradwardine , one of those scholars, extended Aristotelian quantities such as distance and velocity, and assigned intensity and extension to them. Bradwardine suggested an exponential law involving force, resistance, distance, velocity and time. The Merton school proved that the quantity of motion of a body undergoing a uniformly accelerated motion is equal to the quantity of a uniform motion at the speed achieved halfway through the accelerated motion. For writers on kinematics before Galileo , since small time intervals could not be measured, the affinity between time and motion was obscure. They used time as a function of distance, and in free fall, greater velocity as a result of greater elevation. Discourses such as these spread throughout Europe and definitely influenced Galileo and others, and helped in laying the foundation of kinematics. The relationships between speed, distance, time and acceleration was not known at the time. Galileo was the first to show that the path of a projectile is a parabola. Galileo had an understanding of centrifugal force and gave a correct definition of momentum. This emphasis of momentum as a fundamental quantity in dynamics is of prime importance. He measured momentum by the product of velocity and weight; mass is a later concept, developed by Huygens and Newton. In the swinging of a simple pendulum, Galileo says in Discourses [6] that "every momentum acquired in the descent along an arc is equal to that which causes the same moving body to ascend through the same arc. The term "inertia" was used by Kepler who applied it to bodies at rest. The first law of motion is now often called the law of inertia. Galileo did not fully grasp the third law of motion, the law of the equality of action and reaction, though he corrected some errors of Aristotle. With Stevin and others Galileo also wrote on statics. He formulated the principle of the parallelogram of forces, but he did not fully recognize its scope. Galileo also was interested by the laws of the pendulum, his first observations of which were as a young man. In , while he was praying in the cathedral at Pisa, his attention was arrested by the motion of the great lamp lighted and left swinging, referencing his own pulse for time keeping. To him the period appeared the same, even after the motion had greatly diminished, discovering the isochronism of the pendulum. More careful experiments carried out by him later, and described in his Discourses, revealed the period of oscillation varies with the square root of length but is

independent of the mass the pendulum. Later the equations of motion also appeared in electrodynamics , when describing the motion of charged particles in electric and magnetic fields, the Lorentz force is the general equation which serves as the definition of what is meant by an electric field and magnetic field. With the advent of special relativity and general relativity , the theoretical modifications to spacetime meant the classical equations of motion were also modified to account for the finite speed of light , and curvature of spacetime. There are analogs of equations of motion in other areas of physics, for collections of physical phenomena that can be considered waves, fluids, or fields. Kinematic equations for one particle[edit] Kinematic quantities[edit] Kinematic quantities of a classical particle of mass m:

Chapter 2 : Equations of motion - Wikipedia

Get this from a library! Jasper's Basic mechanisms of the epilepsies: molecular and cellular approaches. [Antonio V Delgado-Escueta; National Institute of Neurological and Communicative Disorders and Stroke.

It is from this law that Newton was able to build up our present understanding of dynamics. When a force F is applied on an object, V, the change of the velocity of the object, increases with the length of time delta t increases; The greater the force F, the greater V; and The larger the body object is, the less easily accelerated by forces. It is convenient to write the proportionality between F t and V in the form: This constant m is refered to as the inertial mass of the body. As in which a is the acceleration of the object. As you can guess, it is harder to get the cannon ball going. If you apply a constant force F for a time t, the change in velocity is given by Equation So, to get the same v, the product F t must be greater the greater the mass m you are trying to accelerate. To throw a cannon ball from rest and give it the same final velocity as a baseball also starting from rest , we must push either harder or longer. What counts is the product F t. This product F t is the natural measure of how hard and how long we push to change a motion. It is called the impulse of the force. Since the initial value of the quantity mv is zero in each case, and since equal impulses are applied, the final values mv will be equal for the baseball and the cannon ball. Yet, because the mass of the cannon ball is much greater than the mass of the baseball, the velocity of the cannon ball will be much less than the velocity of the baseball. The product mv, then, is quite a different measure of the motion than simply v alone. We call it the momentum p of the body, and measure it in kilogram-meters per second. Newton did express his law of motion in terms of the momentum, which he called the quantity of motion. The right-hand side of the last equation can be written as the change in the momentum. The incident ball stops and the ball it hits goes off with the same velocity with which the incident ball came in. The two billiard balls have the same mass. Therefore, the momentum of the second ball after the collision is the same as that of the incident ball before collision. The incident ball has lost all its momentum, and the ball it struck has gained exactly the momentum which the incident ball lost. Figure Collision of billiard balls This phenomenon is consistent with the law of conservation of momentum which says that the total momentum is constant when two bodies interact. If you drag an object along the floor you do work in overcoming the friction between the object and the floor. In lifting an object you do work against gravity which tends to pull the object toward the earth. Steam in a locomotive cylinder does work when it expands and moves the piston against the resisting forces. Work is the product of the resistance overcome and the distance through which it is overcome. In the British system, power is expressed in foot-pounds per second. For larger measurements, the horsepower is used. This can come from having work done on it at some point in time. Generally, there are two kinds of energy in mechanical systems, potential and kinetic. Potential energy is due to the position of the object and kinetic energy is due to its movement. For example, an object set in motion can overcome a certain amount of resistance before being brought to rest, and the energy which the object has on account of its motion is used up in overcoming the resistance, bring the object to rest. Fly wheels on engines both receive and give up energy and thus cause the energy to return more smoothly throughout the stroke. Elevated weights have power to do work on account of their elevated position, as in various types of hammers, etc.

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Alzheimer's disease (AD) is the leading cause of dementia worldwide. It compromises patients' daily activities owing to progressive cognitive deterioration, which has elevated direct and indirect costs.

The Profile mandates the use of that structure, and places the following constraints on its use: While the combination of R and R below clearly imply that there may be at most one child element of the soap: Body, there is no explicit requirement in the Profile that articulates this constraint, leading to some confusion. The Profile requires that a fault be generated instead, to assure unambiguous operation. R The children of the soap: Although published errata NE05 see http: These requirements ensure that conformant artifacts have the broadest interoperability possible. Body element is unclear. Therefore, such elements are disallowed. Envelope following the soap: This requirement clarifies a mismatch between the SOAP 1. However, this introduces complexity, as this function can also be served by the use of XML Namespaces. As a result, the Profile prefers the use of literal, non-encoded XML. Therefore, only those two values are allowed. In particular, it defines rules for the processing of header blocks and the envelope body. It also defines rules related to generation of faults. The Profile places the following constraints on the processing model: Mandatory header blocks are those children of the soap: Header element bearing a soap: SOAP12 This requirement guarantees that no undesirable side effects will occur as a result of noticing a mandatory header block after processing other parts of the message. MustUnderstand" fault when an envelope contains a mandatory header block i. In request-response exchanges, a fault message will be transmitted to the sender of the request, and some application level error will be flagged to the user. It is important to realize that generation of a Fault is distinct from its transmission, which in some cases is not required. Because there are situations where the Web infrastructure changes the HTTP status code, and for general reliability, the Profile requires that they examine the envelope. A Fault is an envelope that has a single child element of the soap: Body element, that element being a soap: Body of the message has a single soap: Fault element to those elements explicitly described in SOAP 1. Fault element are local to that element, therefore namespace qualification is unnecessary. Fault element MUST be unqualified. Such children can be qualified or unqualified. The namespace of qualified attributes can be anything other than "http: As such, they may not be in a particular language, and therefore the xml: A schema without conflicts can be found at " http: Use of this mechanism to extend the meaning of the SOAP 1. Therefore, its use should be avoided, as doing so may cause interoperability issues when the same names are used in the right-hand side of the ". Alternatively, it is acceptable to define custom fault codes in a namespace controlled by the specifying authority. A number of specifications have already defined custom fault codes using the ". Despite this, their use in future specifications is discouraged. It is recommended that applications that require custom fault codes either use the SOAP1.

Introduction to Mechanisms. Yi Zhang with Susan Finger Stephannie Behrens Table of Contents. 1 Physical Principles. This chapter introduces the basic physical principles behind mechanisms as well as basic concepts and principles required for this course.

Introduction Cyclic voltammetry involves applying a voltage to an electrode immersed in an electrolyte solution, and seeing how the system responds. In CV, a linear sweeping voltage is applied to an aqueous solution containing the compound of interest. The process can then be repeated in a periodic, or cyclic manner. As an important tool for studying mechanisms and rates of oxidation and reduction processes, CV provides the capability for generating a species during the forward scan and then probing its fate with the reverse scan or subsequent cycles, all within seconds. The unique aspect of cyclic voltammetry is the three electrodes used, which consist of a working electrode, a reference electrode, and a counter electrode. The working electrode can be seen as a medium whose reductive or oxidative power can be externally adjusted by the magnitude of the applied potential--as the potential is increased or decreased linearly versus time, it becomes a stronger oxidant or reductant, respectively. The potential is measured between the reference and working electrodes, and the current is measured between the working and counter electrodes. By sweeping the voltage slowly, information may be extracted from a graph of potential versus current going through the sample. CV differs from polarography in two important ways. Firstly, the working electrode at which the reactions of interest occur has a constant area, not one which changes with time as in classical polarography. This electrode may be a solid such as graphite or platinum with a small surface area, or a stationary or hanging mercury drop. The latter type of electrode may have its surface renewed periodically. The second difference is that the potential of the working electrode is scanned rapidly over a wide potential range and then returned to its initial value using an applied potential signal which varies linearly with time between the initial value and the final value at the limit of the forward scan. Normally, this technique is applied so that currents due to reduction processes are observed during the forward scan, and those due to oxidation on the reverse scan. A typical potential against time profile applied to the working electrode and the resulting cyclic voltammogram are shown in Figure 1. Left Potential versus time program for cyclic voltammetry showing the forward and reversed linear potential ramp and Right Cyclic Voltammogram of measured current versus applied potential. Considering the initial sweep in the negative direction where reduction reactions are expected, it is clear that, if the sweep rate is sufficiently slow, the current against potential curve approaches that obtained by steady state measurements such as d. However, as v is increased, a peak develops on the i-E curve which becomes increasingly prominent Figure 1. The peak is produced from the combined effects of high mass transfer rates in the non steady state followed by progressive depletion of the reactant in the diffusion layer. Effect of potential sweep rate on the PE curves in a linear potential sweep experiment adjacent to the electrode. It should be noted that since E is a linear function of t, that the potential axis is also a time axis. Solution of this second order partial differential equation requires specification of boundary and initial conditions, and is described in textbooks on electroanalytical chemistry 1,2. If the electron transfer reaction is sufficiently fast in reaction 1 to maintain a Nernstian equilibrium at the electrode surface i. After the direction of the potential sweep is reversed, a second current peak is observed corresponding to oxidation of the product B. The method of estimating peak currents is illustrated in Figure 1. Reaction Mechanisms One of the major uses of cyclic voltammetry is in the rapid qualitative elucidation of electrode reaction mechanisms. Organic molecules often undergo a rapid chemical reaction with the solvent or some other constituent of the solution after the electron transfer process. The product of this reaction is usually reduced or oxidized at a much different potential. Hence, the above three-step mechanism is referred to as the ECE reaction mechanism. A typical current-potential curve for such a system is shown in Figure 1. In addition, a peak develops at III due to oxidation of D. Cyclic voltammogram at an intermediate sweep rate for a system with an ECE mechanism. It should also be noted that the current-potential curves on the second and successive sweeps are not the same as that observed on the first. Variation of measured current for peak I from Figure 1. Cyclic voltammetry can be applied to the analysis of

many other reaction mechanisms including those with dimerization of the product of electron transfer, with preceding chemical steps, catalytic processes, etc. It is controlled from a computer running Windows. A number of different electrochemical techniques are available in the Epsilon software, including cyclic voltammetry current vs. UCD cyclic voltammetry Instrument including potentiostat To begin an experiment, make sure that the Epsilon unit is turned on, and doubleclick the Epsilon icon on the desktop. Select New from the File menu or click the New icon. This will generate a menu that lists the available techniques. An experiment window containing an empty axis set is displayed Figure 1. Change Parameters dialog box for cyclic voltammetry. If the Apply Open Circuit Potential for Initial E box is checked, then the open circuit potential will automatically be measured and used as the Initial Potential. When the experiment is started, the cell is held at the Initial Potential for the number of seconds defined by the Quiet Time. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current Full Scale value are determined by the software. This dialog box is also used to change the analog Noise Filter Value settings from the default values set by the software. The default condition of the cell is that the cell is On i. A series of identical experiments on the same cell can be programmed using the MR Multi-Run option. Clicking the IR-COMP button activates the iR compensation option compensates for the drop in voltage due to the resistance of the solution. Clicking Exit will exit the dialog box without saving any changes made to the parameter values. Any changes can be saved by clicking Apply before exiting. Range of allowed parameter values: Once the parameters have been set, the experiment can be started by clicking Run either in this dialog box, in the Experiment menu, in the pop-up menu, on the Tool Bar, or using the F5 key. The Pt electrode should be cleaned by gently rubbing the electrode surface on fine damp paper cloth. Usually the electrode has to be cleaned when the cyclic voltammogram is no longer symmetrical and peaks are getting flat. Sometimes you have to repeat the cleaning procedure. The same method of cleaning applies to the glassy carbon electrode used in part II. The cleaning operation must be carried out under the supervision of the teaching assistant. The next step is to determine the current which flows in the presence of the ferricyanide reactant. The solution in the cell is now deoxygenated by purging with argon gas for 10 minutes. While deoxygenation is taking place, the scan parameters can be set. The working Pt electrode should be disconnected during this procedure. Use the following initial settings:

In order to re-evaluate the mechanisms of β-mediated up-regulation of HVA channels, all of the T-type Ca v channel intracellular linkers were systematically swapped with correspond- ing.

The specification is split into two sections. Those features of HTTP for which implementations are usually consistent are described in the main body of this document. Those features which have few or inconsistent implementations are listed in Appendix D. Practical information systems require more functionality than simple retrieval, including search, front-end update, and annotation. HTTP allows an open-ended set of methods to be used to indicate the purpose of a request. An entity consists of metainformation in the form of entity headers and content in the form of an entity body. These are often browsers, editors, spiders web-traversing robots , or other end user tools. Requests are serviced internally or by passing them, with possible translation, on to other servers. A proxy must interpret and, if necessary, rewrite a request message before forwarding it. Proxies are often used as client-side portals through network firewalls and as helper applications for handling requests via protocols not implemented by the user agent. Unlike a proxy, a gateway receives requests as if it were the origin server for the requested resource; the requesting client may not be aware that it is communicating with a gateway. Gateways are often used as server-side portals through network firewalls and as protocol translators for access to resources stored on non-HTTP systems. The tunnel ceases to exist when both ends of the relayed connections are closed. Tunnels are used when a portal is necessary and the intermediary cannot, or should not, interpret the relayed communication. A cache stores cachable responses in order to reduce the response time and network bandwidth consumption on future, equivalent requests. Any client or server may include a cache, though a cache cannot be used by a server while it is acting as a tunnel. Likewise, any server may act as an origin server, proxy, gateway, or tunnel, switching behavior based on the nature of each request. A client establishes a connection with a server and sends a request to the server in the form of a request method, URI, and protocol version, followed by a MIME-like message containing request modifiers, client information, and possible body content. Most HTTP communication is initiated by a user agent and consists of a request to be applied to a resource on some origin server. In the simplest case, this may be accomplished via a single connection v between the user agent UA and the origin server O. There are three common forms of intermediary: A proxy is a forwarding agent, receiving requests for a URI in its absolute form, rewriting all or parts of the message, and forwarding the reformatted request toward the server identified by the URI. A tunnel acts as a relay point between two connections without changing the messages; tunnels are used when the communication needs to pass through an intermediary such as a firewall even when the intermediary cannot understand the contents of the messages. A request or response message that travels the whole chain must pass through four separate connections. This distinction is important because some HTTP communication options may apply only to the connection with the nearest, non-tunnel neighbor, only to the end-points of the chain, or to all connections along the chain. Although the diagram is linear, each participant may be engaged in multiple, simultaneous communications. Any party to the communication which is not acting as a tunnel may employ an internal cache for handling requests. The following illustrates the resulting chain if B has a cached copy of an earlier response from O via C for a request which has not been cached by UA or A. The default port is TCP 80 [15] , but other ports can be used. This does not preclude HTTP from being implemented on top of any other protocol on the Internet, or on other networks. Except for experimental applications, current practice requires that the connection be established by the client prior to each request and closed by the server after sending the response. Both clients and servers should be aware that either party may close the connection prematurely, due to user action, automated time-out, or program failure, and should handle such closing in a predictable fashion. In any case, the closing of the connection by either or both parties always terminates the current request, regardless of its status. Appendix C describes the ways in which the context of HTTP allows for different use of Internet Media Types than is typically found in Internet mail, and gives the rationale for those differences. Implementors will need to be familiar with the notation in order to understand this specification. The augmented BNF includes

the following constructs: Whitespace is only significant in that indentation of continuation lines is used to indicate a rule definition that spans more than one line. Angle brackets are used within definitions whenever their presence will facilitate discerning the use of rule names. Unless stated otherwise, the text is case-insensitive. Thus, " elem foo bar elem " allows the token sequences "elem foo elem" and "elem bar elem". N rule Specific repetition: Wherever this construct is used, null elements are allowed, but do not contribute to the count of elements present. That is, " element , , element " is permitted, but counts as only two elements. Therefore, where at least one element is required, at least one non-null element must be present. Default values are 0 and infinity so that " element " allows any number, including zero; "1 element" requires at least one; and "1 2element" allows one or two. This is a simple way of including useful notes in parallel with the specifications. Except where noted otherwise, linear whitespace LWS can be included between any two adjacent words token or quoted-string , and between adjacent tokens and delimiters tspecials , without changing the interpretation of a field. At least one delimiter tspecials must exist between any two tokens, since they would otherwise be interpreted as a single token. However, applications should attempt to follow "common form" when generating HTTP constructs, since there exist some implementations that fail to accept anything beyond the common forms. The end-of-line marker within an Entity-Body is defined by its associated media type, as described in Section 3. All linear whitespace, including folding, has the same semantics as SP. The TEXT rule is only used for descriptive field contents and values that are not intended to be interpreted by the message parser. Hexadecimal numeric characters are used in several protocol elements. These special characters must be in a quoted string to be used within a parameter value. Comments are only allowed in fields containing "comment" as part of their field value definition. In all other fields, parentheses are considered part of the field value. The protocol versioning policy is intended to allow the sender to indicate the format of a message and its capacity for understanding further HTTP communication, rather than the features obtained via that communication. No change is made to the version number for the addition of message components which do not affect communication behavior or which only add to extensible field values. Leading zeros should be ignored by recipients and never generated by senders. This document defines both the 0. As far as HTTP is concerned, Uniform Resource Identifiers are simply formatted strings which identify--via name, location, or any other characteristic--a network resource. The two forms are differentiated by the fact that absolute URIs always begin with a scheme name followed by a colon.

Chapter 6 : Chapter Introduction to Mechanisms

Introduction Purpose Terminology Overall Operation HTTP and MIME 2. Notational Conventions and Generic Grammar Augmented BNF Basic Rules 3.

Bring fact-checked results to the top of your browser search. Comparison of selected reaction mechanisms For the following incomplete and abbreviated survey of reaction mechanisms, several mechanisms important in the development of mechanistic study have been chosen. Nucleophilic substitutions at saturated carbon centres The term substitution refers in general to the replacement of any group in a molecule by any other group. Saturated carbon centres are carbon atoms at which no multiple bonds occur, and nucleophilic substitutionsâ€"those brought about by nucleus-seeking reagentsâ€"can occur at such carbon atoms by either of two main mechanisms: Bimolecular In bimolecular nucleophilic substitution reactions in which the substrate is attacked at a saturated carbon atom, the starting material has a tetrahedral structure, and the transition state has a trigonal bipyramidal structure both of which are shown below. Each individual act of substitution produces a product of inverted i. A typical bimolecular substitution reaction is shown by the equation in which the chemical symbols represent atoms of the elements as above with Br the symbol for an atom of bromine and N the symbol for any nucleophilic agent. This equation differs from the earlier ones in that a three-dimensional representation of the structures is intended. The three-dimensional effect is achieved by considering that the bonds represented by ordinary solid lines lie in the plane of the paper, bonds represented by dashed lines project to the rear, and bonds represented by dark triangles project to the front. A further unique feature of this equation is that the representation of the transition state shows half bonds bonds in the process of being formed or broken , which are indicated by dotted lines. The resulting change in configuration of the substrate has been likened to the turning inside out of an umbrella, with the transition state representing that precise moment when the ribs are essentially vertical in the course of their passage from one side of the structure to the other. The reaction is synchronized, or synchronous, in that entry of the nucleophile and departure of the leaving group occur simultaneously. It is bimolecular in that one molecule each of substrate and nucleophile are involved in the transition state, and it is stereospecific in that the stereochemical outcome of the reaction is invariably the same. This bimolecular mechanism occurs with a wide range of structures. It often can be characterized by second-order kineticsâ€"i. The transition state is highly congested, so that effects of steric hindrance are large. Otherwise, however, structural changes produce a variable response because of the conflicting electronic requirements of the bond-forming and bond-breaking processes. Bimolecular nucleophilic substitutions with rearrangement of the bonding skeleton also are known. Unimolecular Unimolecular nucleophilic substitution reactions proceed by a two-stage mechanism in which heterolysis precedes reaction with the nucleophile. The following equation is a typical example: The significant consideration in this reaction mechanism is the initial separation of the bromide ion by way of a transition state showing partial separation of the ion to give a free positively charged organic ion carbonium ion. This step is the rate-determining step of the reaction, and, because it involves only a molecule of the substrate, the reaction is unimolecular. The second stage of the reaction is the interaction of the intermediate carbonium ion with the nucleophile to give the products of the reaction. The unimolecular reaction is characterized experimentally by first-order kineticsâ€"i. Inversion of stereochemical configuration change from one configuration to the mirror-image configuration is frequently encountered, accompanied by racemization production of both mirror images. The extent of racemization depends upon the life of the intermediate carbonium ion, with longer-lived ions leading to more extensive racemization due to the fact that the symmetrical ion is exposed to attack from either side. In an important group of structures, a group not formally involved in the overall reaction interacts with a carbonium ion centre to form an intermediate, which then reacts with the nucleophile to give a product of the same stereochemical configuration as the starting material. This behaviour can be represented by the equation In the first demonstrations of this behaviour, the participating group G was a carboxylate anion group, which can be represented in chemical symbols as Subsequent investigations revealed numerous examples involving other substituents, and the phenomenon is

now commonly described as neighbouring-group participation. A frequent consequence of reaction through intermediates having carbonium ionic character is that some of the products have rearranged skeletal structures. In this equation the symbol Cl represents a chlorine atom. The fundamental difference between the transition states in the bimolecular and unimolecular mechanisms is the degree of covalent bonding between the nucleophile and the substrate in the transition state. In the unimolecular mechanism such bonding is negligible; in the bimolecular case it has essentially reached the half-bond status. In borderline situations the matter is difficult to resolve, a number of intermediate cases being known, and there has been much controversy as to the validity of the distinction between the bimolecular and the unimolecular mechanisms. Experimentally, however, clear examples of each class have been established. Nucleophilic substitution at unsaturated carbon centres Unsaturated carbon centres—including those involving ordinary carbon-carbon double bonds and those involving the extended cyclic systems of alternate single and double bonds known as aromatic rings—are not easily attacked by nucleophilic reagents unless they have been denuded of electrons by electron-attracting substituents. A two-stage process that includes addition of the nucleophile followed by expulsion of a negatively charged anionic group is the course normally taken for substitutions at aromatic centres. An example of this type of reaction is the displacement of fluoride ion from 2,4-dinitrofluorobenzene by nucleophiles such as ethoxide ion. Substitution reactions at ordinary double bonds olefinic bonds also take place by a two-stage process. When the two stages in the reaction occur synchronously or in very quick succession, the product has the same geometrical relationship that existed in the starting material. If, however, the anionic intermediate has sufficient lifetime, rotation about the new carbon-carbon single bond can precede loss of the negatively charged group, resulting in production of two products of differing molecular geometry—that is, products in which the substituents are differently situated with respect to the double bond. If the intermediate anion takes up a hydrogen ion proton and then loses hydrogen and halogen simultaneously concerted elimination , the reaction is then said to be following an addition-elimination sequence. Examples of such reactions are known, particularly in situations in which the double bond includes an atom other than carbon. In aromatic systems the reverse situation, in which elimination occurs, followed by addition, also is found. Finally, unimolecular mechanisms of substitution also are known to take place at particularly activated unsaturated centres. Electrophilic substitution at unsaturated carbon centres Because of its wide applicability, particularly to aromatic systems, electrophilic substitution is an important reaction. Reaction by any one of several mechanisms is possible. One of the more common is shown here; reactions in this category consist of replacement of a group designated Y often a hydrogen atom in an aromatic molecule by an electrophilic agent designated E. Both substituents can be any one of various groups e. Here, Y represents a substituent on the ring; the arrow from the ring centre indicates coordination. As shown, the reaction begins with formation of a pi complex, in which the electrons associated with the aromatic ring, or other unsaturated centres pi electrons , coordinate weakly with the electrophile. This complex forms rapidly in an equilibrium preceding the rate-determining step, which itself leads to a carbonium ion intermediate and then by way of a second pi complex to the product. Examples are known in which the removal of the proton from the carbonium ion intermediate to form the second pi complex becomes rate-determining. Reactivity by this mechanism is dominated by the electrophilic character of the reagent E ; however, it also responds powerfully to changes in structure of the organic substrate. As would be expected, substituents that release electrons toward the reaction site facilitate the reaction, and those that withdraw electrons retard reaction. These effects are very specific with regard to the position at which the modifying group is introduced. Steric spatial effects generally are smaller than electronic effects in determining the characteristics of reaction by this mechanism, but they are not negligible. Direct steric hindrance and steric acceleration both have been found with suitably placed large substituents and reagents, and indirect effects arising because one group interferes with the orienting power of another also are known. Substitution with accompanying rearrangement of the double-bond system is another established reaction path. An example is shown below in which the positions of chlorine attachment and proton loss were established by isotopic labeling. Addition-elimination and indirect substitution reactions also can occur and are responsible for a number of unusual products formed in aromatic substitution reactions. Examples of these reaction sequences are shown below: Addition reactions Reactions in which a multiple

bond between two atoms becomes partly or fully saturated by covalent attachments at both centres are called addition reactions. Many mechanisms are known for such reactions; most of them are variants of four basic mechanisms, which differ chiefly in the sequence of events that occur. With initial electrophilic attack Addition reactions beginning with electrophilic attack include many additions to olefins compounds with double bonds , some additions to acetylenes compounds with triple bonds , and some additions to compounds with other multiple bonds. There is a close relationship between this mode of addition and the electrophilic substitutions discussed in the preceding section, as shown by this general representation of the reaction: In general, any nucleophile can complete the reaction. When the first stage of the reaction addition of the electrophile is rate-determining, the rate responds powerfully to electron release to the reaction centre, and this factor determines selectively the orientation of initial attack with respect to the double bond. Thus, propylene reacts with hydrogen chloride many times faster than ethylene does, and the product is exclusively 2-chloropropane, rather than 1-chloropropane, because the concentration of electrons on the terminal carbon determines that the electrophilic proton finds it easier to attack that carbon rather than the central carbon atom. Addition by this mechanism can be accompanied by substitution and by rearrangement as alternative reactions of the carbonium ionic intermediate. Characteristically, the ratios of product are kinetically controlled see above Reaction mechanisms: Reactions by this mechanism can be complicated by the intervention of intermediates that are more complicated structurally. Neighbouring-group interaction can modify the structure of the intermediate toward a bridged structure and thus determine the stereochemistry of addition. Although it is common to find that the first stage of this sequence is rate-determining, in some cases the rate-limiting transition state lies later along the reaction path. Especially in acid-catalyzed additions to carbon-oxygen and carbon-nitrogen double bonds, the first stage of the reaction can become rapidly reversible, and the mechanistic characteristics of the reaction are then appropriately modified. With initial nucleophilic attack The reverse mode of addition, in which a nucleophile initiates attack on the multiply bonded carbon atom, is less easily realized in simple systems; it does occur with acetylenes, and it also is the basis of reactions that occur when the centre of attack is denuded of electrons. For example, the formation of substances called cyanohydrins from carbonyl compounds materials with carbon-oxygen double bonds occurs as follows: Initial attack on carbon by the nucleophilic cyanide ion in this case is facilitated by the electron withdrawal by the oxygen atom shown by the curved arrow in the formula. Such electron withdrawal also can be transmitted along a series of alternate double and single bonds a conjugated system , with resultant addition to the ends of the system. Electrocyclic In a third class of additions, both portions of the attacking reagent combine simultaneously with the substrate. Reactions of this kind sometimes retain predominantly electrophilic or predominantly nucleophilic character, as can be shown by structural and environmental effects. In a number of important cases, however, quite different behaviour is observed. For example, the addition of cyclopentadiene to 1,4-benzoquinone follows second-order kinetics and proceeds at nearly the same rate in the gas phase and in solvents of widely differing polar character. In this equation the polygons represent rings of carbon atoms one at each corner , with double bonds between certain atoms as shown. Therefore, there must be little development of charge in the transition state, and the formation of the two new single bonds and the accompanying electronic movements must be well synchronized. A large number of such reactions are known; they are characterized by a remarkable stereospecificity stereochemical specificity , controlled in part by steric effects and in part by the stereo-electronic characteristics of the combining double-bond systems. Homolytic Additions by free-radical mechanisms also are well known. They replace the concomitant polar additions most easily when homolytic decomposition of a compound into two neutral atoms or radicals fission of the reagent can be readily catalyzed and when the radicals produced as intermediates sustain chain processes. Addition of hydrogen bromide to olefins falls into this class. Equations 1â€"4 describe the main part of the sequence; reactions 2 and 3 are repeated many times before reaction 4 or some other reaction intervenes to break the chain. As a result, one act of initiation results in many molecules of product. The reaction can give an orientation of substituents opposite to that found in electrophilic addition, which in the above example would produce CH3CH Br CH3, and in suitable cases it can be just as stereospecific. Elimination reactions Elimination reactions can be treated formally as the reverse of additions. The simplest examples of this class

of reactions are the olefin-forming 1,2-eliminationsâ€"that is, eliminations of substituents from adjacent carbon atomsâ€"but eliminations to give other types of double bonds are equally well known. Again, 1,3-eliminationsâ€"eliminations of substituents from carbon atoms separated by a third carbonâ€"give compounds with three-membered rings of carbon atoms cyclopropanes. Furthermore, the so-called conjugate eliminations occur when one or more double bonds are inserted between carbon atoms bearing the substituents that are eliminated; the result of such eliminations is a system of alternating double and single bonds a conjugated system. Finally, there also are fragmentation reactions, in which two small fragments are lost from the organic molecule. Of these reaction types, only the 1,2-eliminations will be discussed here, it being understood that examples of the mechanisms may be found, as appropriate, in other types of elimination reactions. Concerted, bimolecular Concerted bimolecular eliminations are characterized by second-order kinetics; they occur readily with powerful nucleophiles. A favoured stereochemical course trans-elimination involves a particular geometry, as shown, which requires that in the starting material the eliminated units be situated on opposite sides of the molecule.

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2 Naval Postgraduate School Department of Electrical & Computer Engineering Monterey, California Survey of Propagation Mechanisms (1) There are may propagation mechanisms by which signals can travel between the.

This has been fixed for Small Basic 1. Language Improvements - We made thorough reviews and updated the UI text for these languages: We also had some logged errors that were fixed in this pass: This crash is eliminated in 1. This has been fixed for 1. This is inconsistent because Small Basic v1. AddText method at the top of your program, Small Basic shows an exception thrown by the target. The exception is no longer thrown in 1. Math Object Crashes 1. The crashes were fixed for 1. Divide by Zero Produces Zero 1. Breaking Changes to v 1. There are no new breaking changes introduced in Small Basic 1. However, there are two breaking changes from Small Basic 1. Windows XP - Due to the upgrade to. We will continue to offer Small Basic 1. Extensions built on 1. Updates made in v 1. This includes blue and dark gray borders around the text boxes. And the window title font is also updated. Language Downloads - You can now directly download your language from the Download Center. See the Download Center Page. Bug Fixes made in v 1. This issue is fixed in 1. It comes installed with Windows 8 and newer. Install Instructions If you have Small Basic 1. If you previously set your web browser to block the "C: If your system does not have. Download and Install Microsoft Small Basic in your preferred language. Launch by clicking the Microsoft Small Basic program shortcut.

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As \(v\) is decreased, peak II diminishes more rapidly and peak I less rapidly than the usual v 1/2 dependence would predict because the chemical step removing species B becomes important and peak I has a contribution from reaction \(\ref{}\). In addition, a peak develops at III due to oxidation of D.

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vâ€² = v â^' u (the velocity vâ€² of a particle from the perspective of Sâ€² is slower by u than its velocity v from the perspective of S) a â€² = a (the acceleration of a particle is the same in any inertial reference frame).