**Reaction Rate Expression**

**Introduction:**

Chemical reactions are processes in which reactants are transformed into products. In some processes, the change occurs directly and the complete description of the mechanism of the reaction present can be relatively obtained. In complex processes, the reactants undergo a series of step-like changes and each step constitutes a reaction in its own right.

The overall mechanism is made up of contributions from all the reactions that are sometimes too complex to determine from the knowledge of the reactants and products alone.

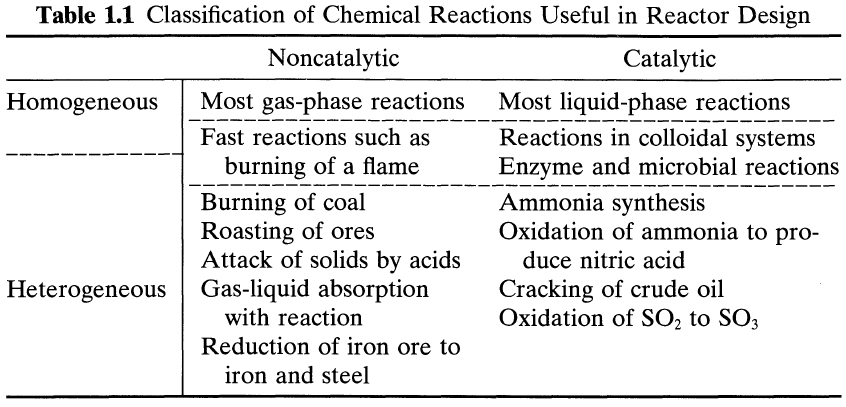
Chemical kinetics is concerned with analyzing the dynamics of chemical reactions. The raw data of chemical kinetics are the measurements of the reactions rates. The end product explains these rates in terms of a complete reaction mechanism.

**Classification of Reactions**

1. According to the number and types of phases involved:

►Homogenous reaction: takes place in one phase alone

► Heterogeneous reaction: requires the presence of at least two phases to proceed



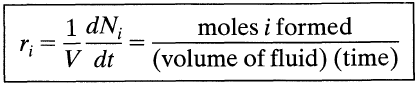
**Variables Affecting the Rate of Reaction**

Many variables may affect the rate of a chemical reaction. In homogeneous systems the temperature, pressure, and composition are obvious variables.

In heterogeneous systems more than one phase is involved; hence, the problem becomes more complex. Material may have to move from phase to phase during reaction; hence, the rate of mass transfer can become important. For example, in the burning of a coal briquette the diffusion of oxygen through the gas film surrounding the particle, and through the ash layer at the surface of the particle, can play an important role in limiting the rate of reaction. In addition, the rate of heat transfer may also become a factor.

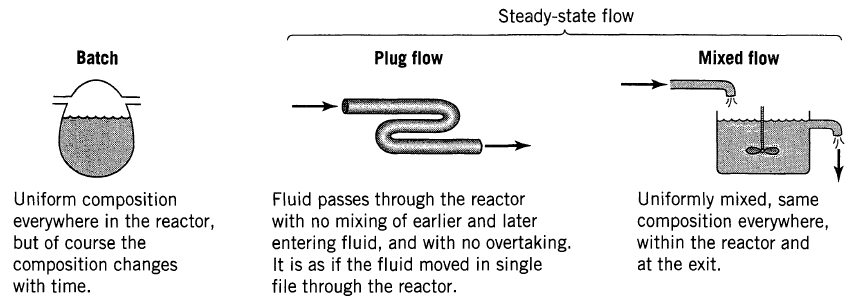
**Definition of Reaction Rate**

To define the rate of reaction first we must select one reaction component and define the rate in terms of this component *i.* If the rate of change in number of moles of this component due to reaction is *dNi/dt,* then the rate of reaction based on unit volume of reacting fluid is:



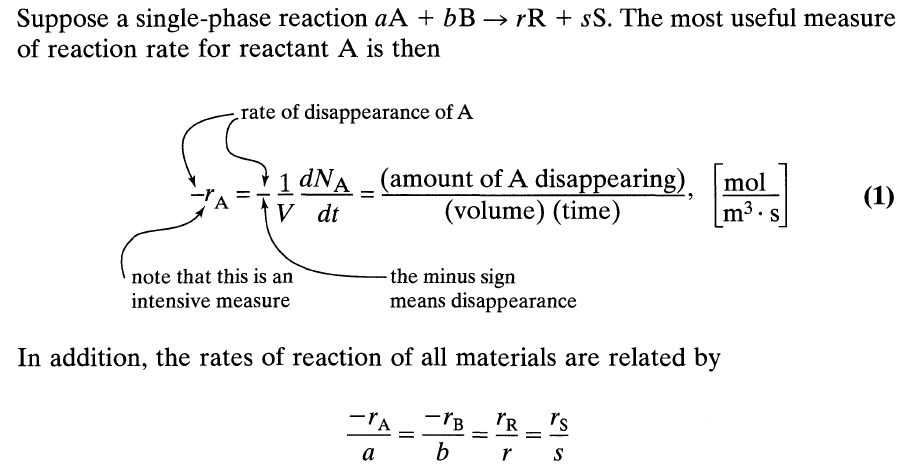
**Kinetics of Homogeneous Reactions**

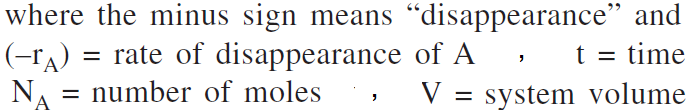
**Simple Reactor Types:**



**Reaction Rate Equation:**

The rate of a reaction is the number of units of mass of some participating reactants that is transformed into a product per unit time and per unit volume of the system.

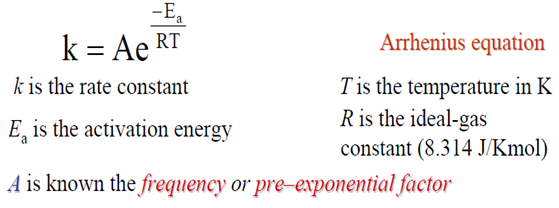


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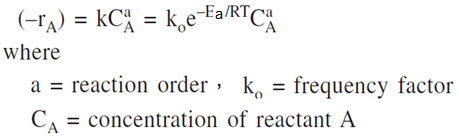
Because the reaction rate changes with time, we can use the time derivative to express the instantaneous rate of reaction since it is influenced by the composition and temperature (i.e., the energy of the material). Thus,

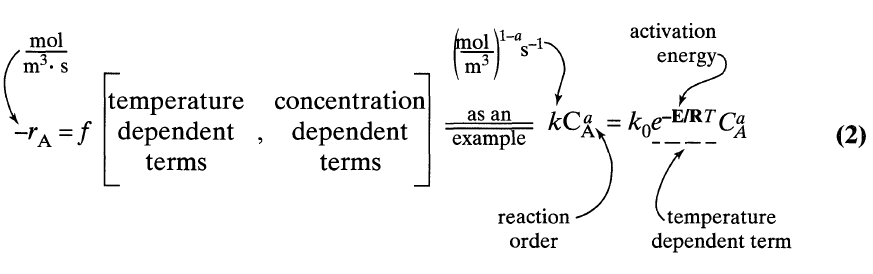


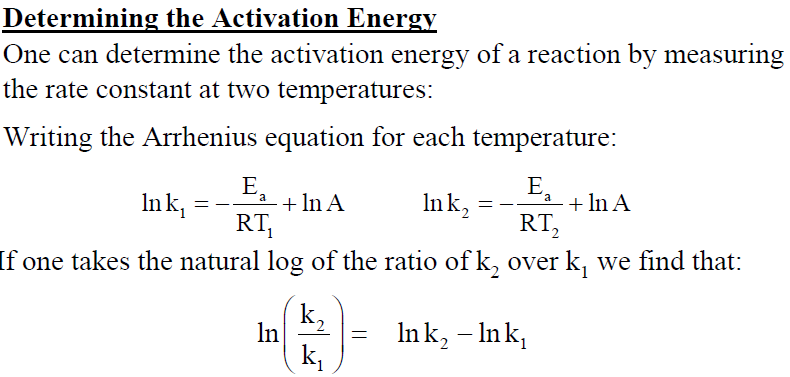
The Swedish chemist Arrhenius first suggested that the temperature dependence of the specific reaction rate k could be:

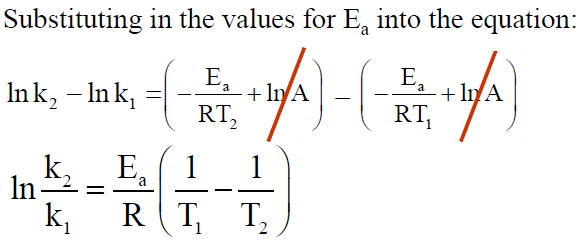


K = ko e-Ea/RT

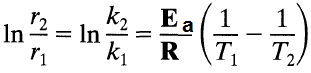


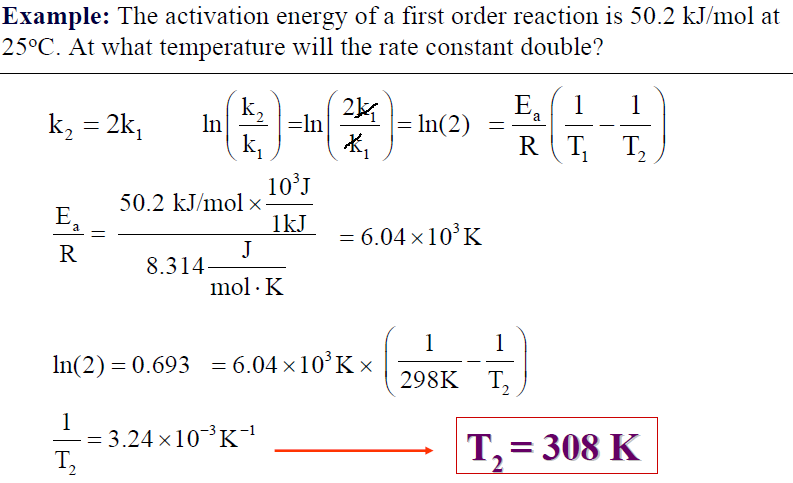






At the same concentration, but two different temperatures:





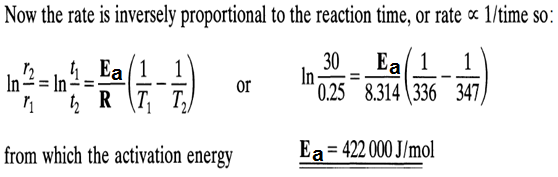
**Example:**

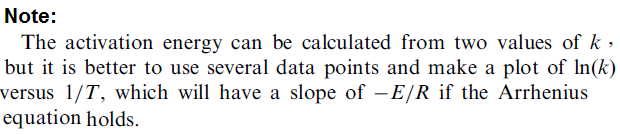
Milk is pasteurized if it is heated to 63oC for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy of this sterilization process.

**Solution:**

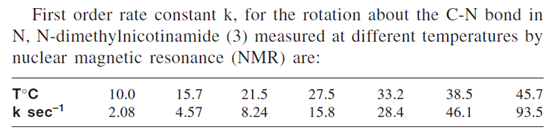
*t1* = 30 min at a *TI* = 336 K

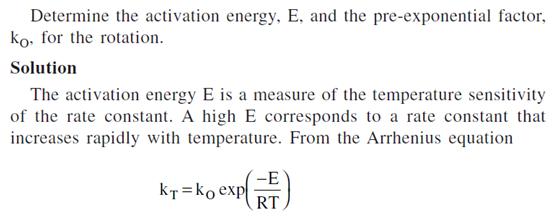
*t2* = *15* sec at a *T2* = 347 *K*

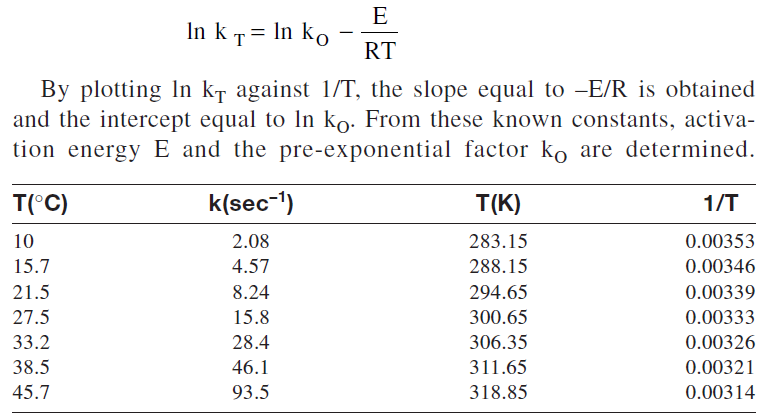


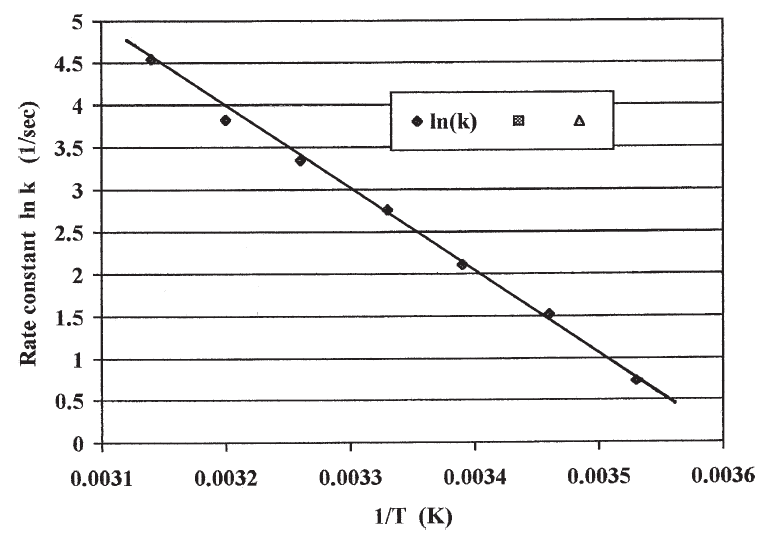


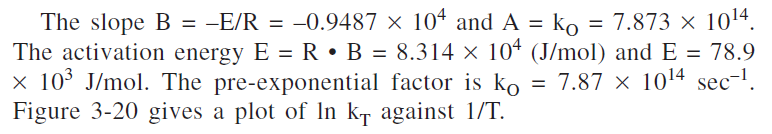
**Example:**











**Elementary and Nonelementary Reactions:**

Consider a single reaction with stoichiometric equation:



The rate of disappearance of A is given by:

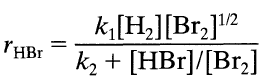


Such reactions in which the rate equation corresponds to a stoichiometric equation are called ***elementary reactions****.*

When there is no direct correspondence between stoichiometry and rate, then we have ***nonelementary reactions****,* such as:



which has a rate expression :



**Molecularity and Order of Reaction:**

The molecularity of an elementary reaction is the number of molecules involved in the reaction, and this has been found to have the values of one, two, or occasionally three.

Often we find that the rate of progress of a reaction, involving, say, materials A, B, . . . , D, can be approximated by an expression of the following type:



We call the powers to which the concentrations are raised the order of the reaction.

**Variables influenced reaction rates:**

1. The rate of a chemical reaction depends on temperature, pressure, and composition of the system under investigation.

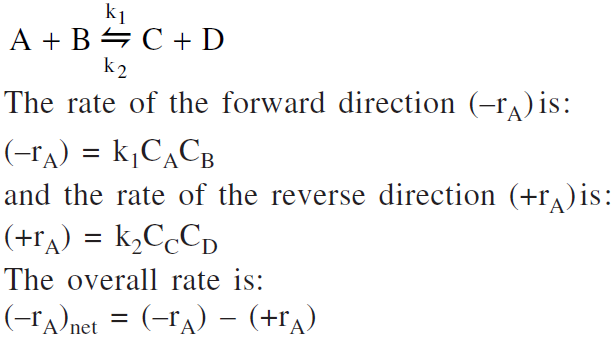
2. **Catalysts** or **inhibitors** do not appear in the stoichiometric equation for the reaction can affect the reaction rate even when they are present in only trace amounts, depending on whether they increase or decrease the reaction rate.

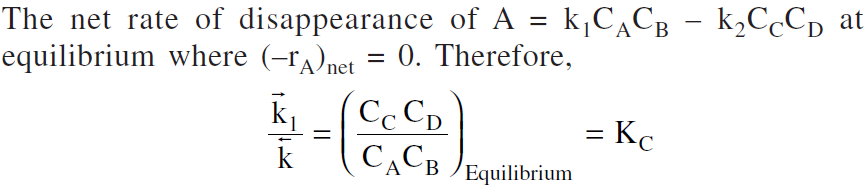
3. At a constant temperature, the rate of reaction decreases with

time or extent of the reaction.

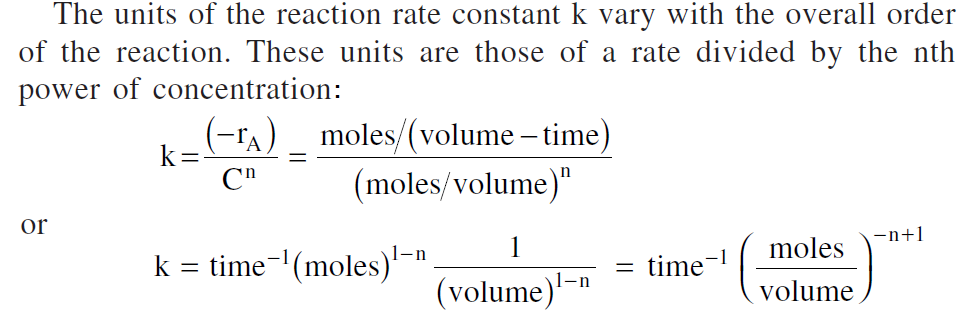
4. The rate constant k varies with the absolute temperature T of the system according to the Arrhenius law: k = koe–E/RT.

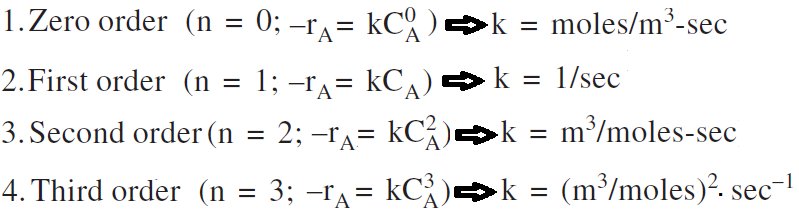
5. For a system in which both forward and reverse reactions are important, the net rate of reaction can be expressed as the difference between the rate in the forward direction and that in the opposite direction. For example:



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**Rate Constant (k):**

 Therefore:

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