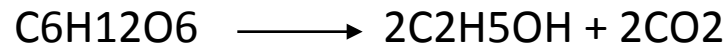
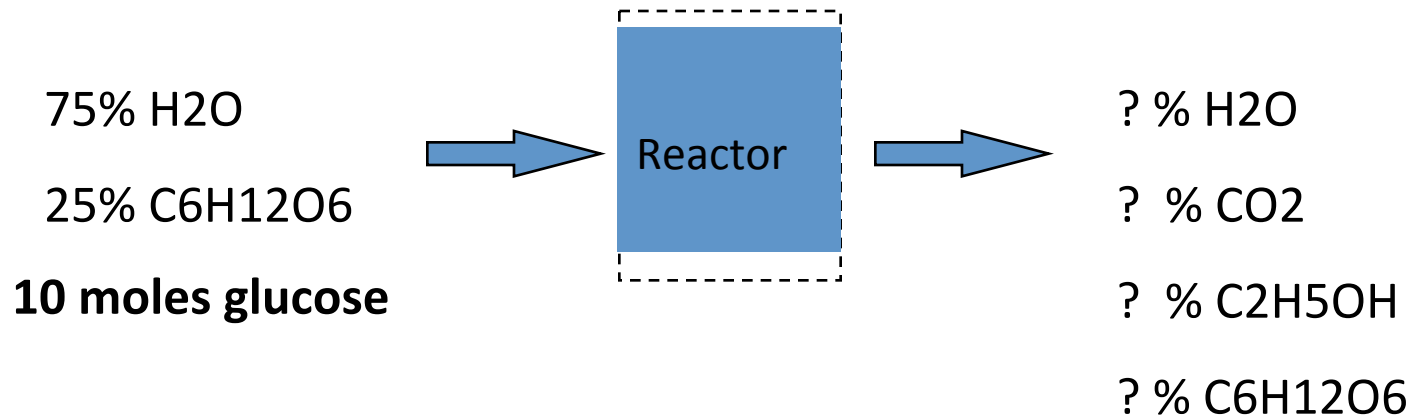


Example #1

Consider the following example:

Glucose is converted to carbon dioxide and ethanol through fermentation.



If the extent of reaction is 5, calculate the outlet composition.

Alternative calculation method

A computational method for solving this problem utilizes component material balances (CMBs). Each component has its own mass balance composed of flows in and out plus the amount reacted.

The general form of a component material balance for species i is :

$$\sum x_{ij} * Q_j + \sum \xi * \nu_i = 0$$

x_{ij} - mole fraction of i in stream j

Q_j - molar flowrate of stream j

Formulating the problem in this fashion generates one CMB equation for each component. The problem is therefore solvable if you have the same number of unknown quantities.

Applying this to our example, we have 2 two flow streams (1-**in** and 2-**out**) and 4 components: water (W), glucose (G), carbon dioxide (C) and ethanol (E).

The **in** stream is composed of 10 mols of glucose ($x_{G1}=25\%$) and 30 mols of water ($x_{W1}=75\%$), so $F1 = 40$ mols.

Because it is inert, we know that the outlet stream also contains 30 mols of water.

Putting this information into the CMB formula generates 4 CMB' s:

$$(0.25)*(40) - (x_{G2})(Q2) + (5)(-1) = 0 \quad \text{Glucose} \quad (x_{G2})(Q2) = 5$$

$$0 - (x_{E2})(Q2) + (5)(2) = 0 \quad \text{Ethanol} \quad (x_{E2})(Q2) = 10$$

$$0 - (x_{C2})(Q2) + (5)(2) = 0 \quad \text{Carbon dioxide} \quad (x_{C2})(Q2) = 10$$

$$(0.75)(40) - (x_{W2})(Q2) = 0 \quad \text{Water} \quad (x_{W2})(Q2) = 30$$

4 CMB' s and 4 unknowns (3 x_i ' s and $Q2$; remember $\sum x_i = 1$)

$$Q2 = 30+5+10+10 = 55 \text{ mols.}$$

$$x_G = 5/55 = 9.09\% \quad x_E = 10/55 = 18.18\%$$

$$x_E = 10/55 = 18.18\% \quad x_W = 30/55 = 54.54\%$$

This is the same result as previously obtained from direct calculations.

Component material balances can also be written in terms of mass rather than moles

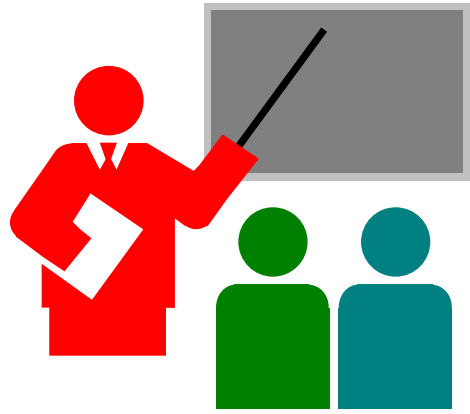
$$\sum \omega_{ij} * F_j + \sum \xi * v_i * MW_i = 0$$

ω_{ij} - mass fraction of i in stream j

F_i - mass flow rate in stream i

MW_i - molecular weight of i

The method of solution is the same, given n components and n unknowns.

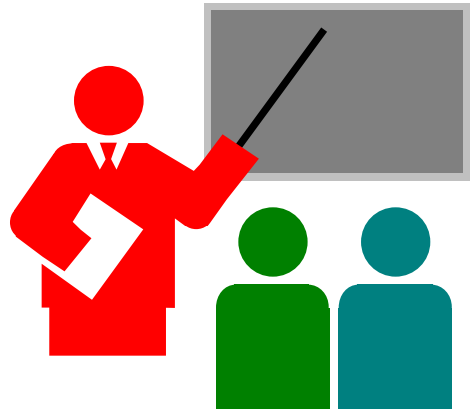


How to do Calculations

Mass Balance w/ reactions

There is a stepwise procedure you should follow to solve mass balance problems.

- Draw a picture of the process, labeling all streams and components.
- Write balanced stoichiometric equation.
- If needed, convert stream compositions to mass % and determine the molecular weights of each component.



How to do Calculations

Mass Balance w/ reactions

- Write down the component material balance equations filling in known information. Compare the number of unknowns and equations to determine if the problem can be solved.
- Solve for unknowns.
- Check answers by make sure the total masses in and out are in balance.

Concepts and Skills to Know

- Define stoichiometry and be able to apply the concept to balance stoichiometric equations.
- Define limiting and excess reactant, fractional conversion and the extent of reaction.
- Be able to determine limiting and excess reactants and conversion parameters.
- Be able to write component mass balance equations for a systems that include reactions.

Measuring how far a reaction has occurred

Concentration (C) – start at C_0 , end at C

Conversion (X) – start at 0, goes up to 1

$$X = (C_0 - C)/C_0 = 1 - C/C_0$$

Extent of reaction (ξ) – starts at 0, goes up to infinity

$$\xi = (N_{i0} - N_i)/\nu_i \quad (\text{component } i)$$

Example calculations

$2A + 3B \rightarrow C$ (assume 2 L total reaction mixture)

Starting $C_{A0} = 12 \text{ mol/L}$ ending $C_A = 3 \text{ mol/L}$

$C_{B0} = 30 \text{ mol/L}$ ending $C_B = 16.5 \text{ mol/L}$

$C_{C0} = 0 \text{ mol/L}$ ending $C_C = 4.5 \text{ mol/L}$

$\Delta C_A = -9 \text{ mol/L}$ $\Delta C_B = -13.5 \text{ mol/L}$ $\Delta C_C = +4.5 \text{ mol/L}$

$X_A, X_B?$

$\xi_A, \xi_B?$

Concentration (C)	<ul style="list-style-type: none"> • Easy to understand • Directly measurable 	<ul style="list-style-type: none"> • No limitation on numerical values • Hard to compare reactions and component amounts
Conversion (X)	<ul style="list-style-type: none"> • Easy to understand • % of initial component reacted ($0 < X < 1$) 	Different value for each component
Extent of reaction (ξ)	<ul style="list-style-type: none"> • Same value for every reactant • $\xi > 0$ 	<ul style="list-style-type: none"> • Depends on stoichiometry • No upper limit on numerical value • Depends on size of reaction amounts

Thermodynamics vs. Reaction Kinetics

Thermodynamics

- energy/mass balances
 - extent of reaction
- equilibrium

Thermodynamics
dictates the extent
(how much) of a
reaction

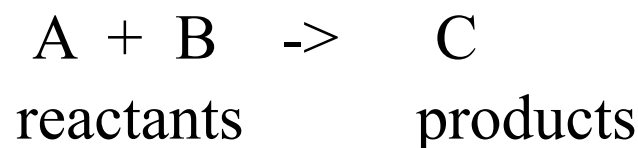
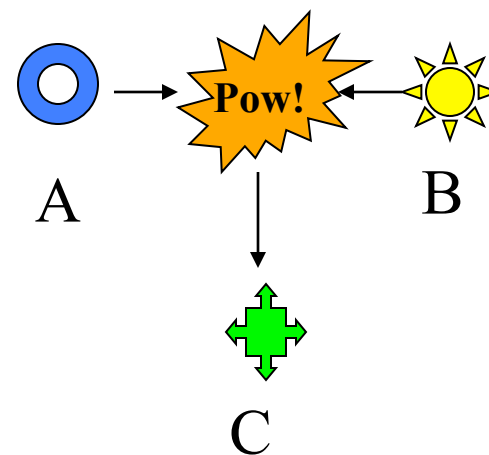
Kinetics

- rate
- mechanism
- equipment design

Kinetics determines the
speed (how fast) of a
reaction

Molecular collision theory

The classical mechanistic concept of a chemical reaction is that 2 or more molecules collide with sufficient energy to overcome their repulsive forces and form new covalent bonds. The reaction may also depend on the orientation of the molecules.



Transition state intermediate

A frequently used mechanistic concept in chemical reactions is the transition state intermediate (TSI). The TSI is high energy state, unstable intermediate state which quickly decomposes to form products.

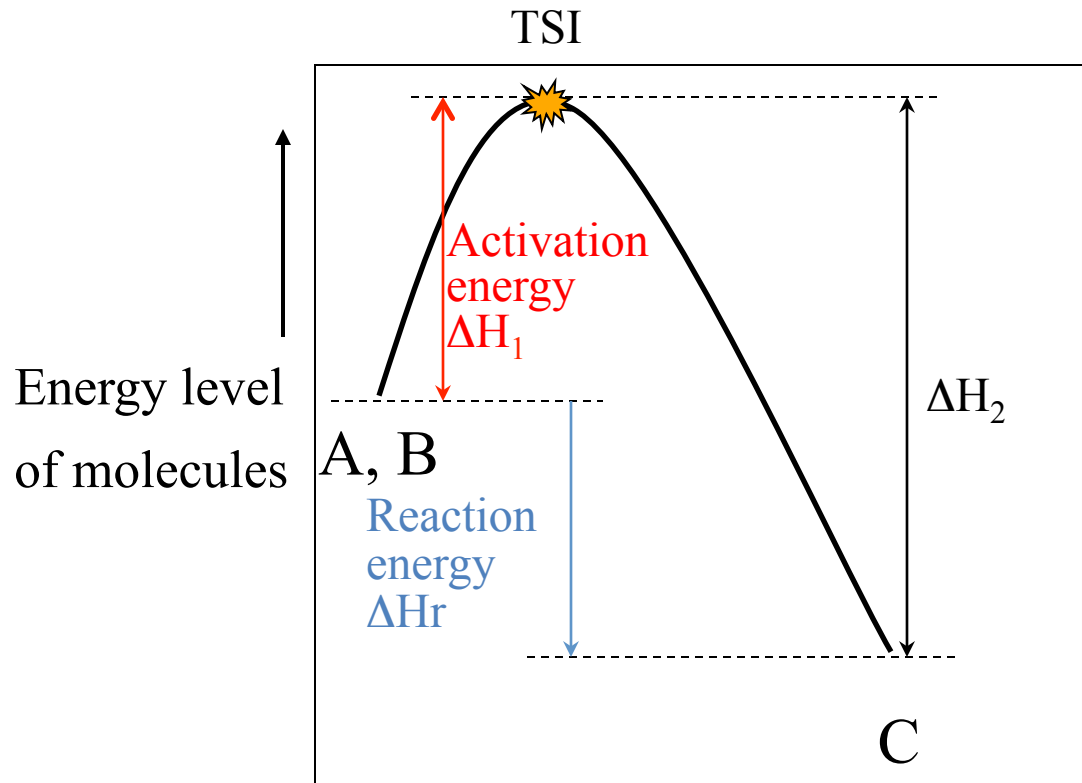


Exothermic reaction

Energetically, a
exothermic
chemical reaction
looks something
like this

$$\Delta H_1 - \Delta H_2 = \Delta H_r$$

(note that $\Delta H_r < 0$)

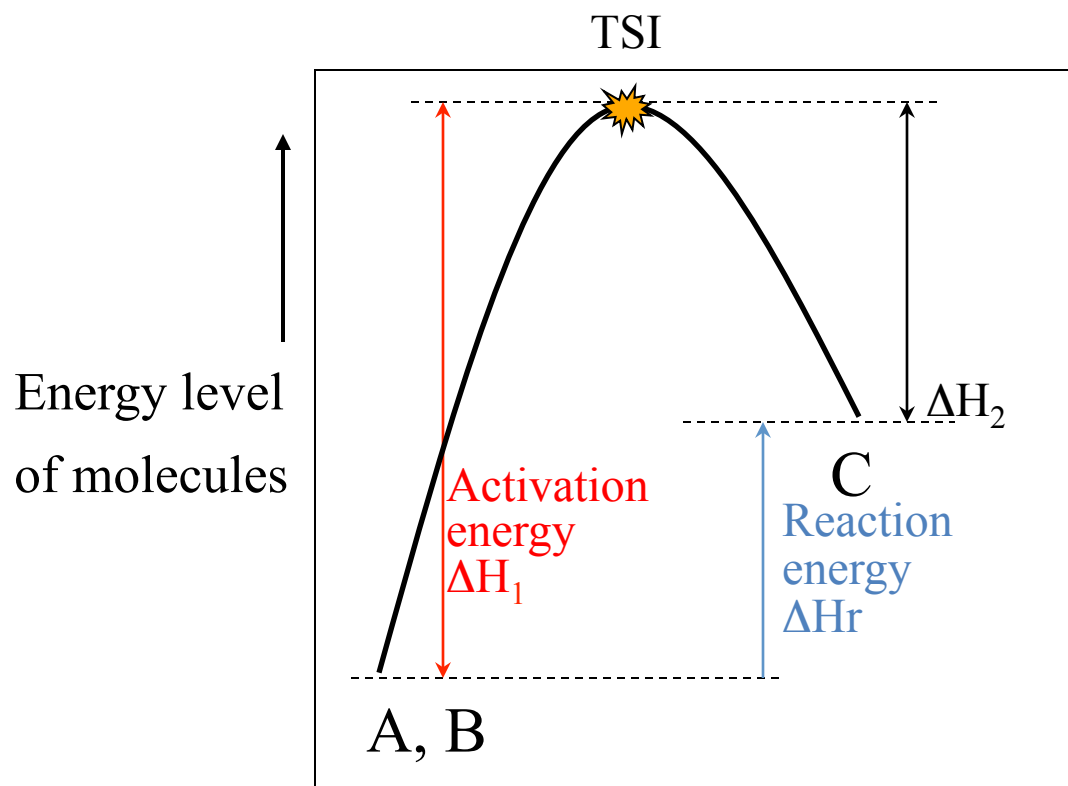


Endothermic reaction

An endothermic
chemical reaction
looks something
like this

$$\Delta H_1 - \Delta H_2 = \Delta H_r$$

(note that $\Delta H_r > 0$)



Collision theory vs. Transition theory

Two conceptual models (collision theory and transition theory) are often used to model the kinetics of reactions.

1. Collision theory uses the frequency of collision of the molecules to explain the rate of reaction. It assumes that the breakdown of the intermediate is so fast that it does not influence the overall reaction rate.
2. Transition theory assumes an activated transition intermediate is always in equilibrium with the reactants. Therefore, the overall rate of reaction is dependent primarily on the decomposition of the transition complex into products.

Units

The rate of reaction is generally defined as the number of moles or reactant/product that is consumed/produced per unit time and unit volume

$$r_i = (1/V)(dN_i/dt)$$

r_i - reaction rate

V - volume

N_i - moles of i

t - time

The Rate Equation

Suppose a single-phase reaction $aA + bB \rightarrow rR + sS$. The most useful measure of reaction rate for reactant A is then

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{(\text{amount of A disappearing})}{(\text{volume})(\text{time})}, \quad \left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right] \quad (1)$$

rate of disappearance of A

note that this is an intensive measure

the minus sign means disappearance

In addition, the rates of reaction of all materials are related by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

Consider a single reaction with stoichiometric equation



If we postulate that the rate-controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B, then the number of collisions of molecules A with B is proportional to the rate of reaction. But at a given temperature the number of collisions is proportional to the concentration of reactants in the mixture; hence, the rate of disappearance of A is given by

$$-r_A = kC_A C_B$$

Elementary reactions



An elementary reaction is one in which the rate of reaction ($-dC_A/dt = -r_A$) corresponds to the stoichiometric equation, i.e.

$$-r_A = k C_A C_B$$

k - reaction rate constant

C_A - molar concentration of A

r_A - rate of reaction

(note the negative sign in front of r , denoting reactant depletion)

Non-elementary reactions

Reaction rates are not necessarily related to stoichiometry.

Often reaction mechanisms are much more complex than might be indicated by their stoichiometric equation. For example if a complex series of intermediates are formed during a reaction, the reaction equation may be quite complex, even though the stoichiometry is very simple.



$$r_{\text{HBr}} = \frac{k_1 [\text{H}_2][\text{Br}_2]^{1/2}}{k_2 + [\text{HBr}]/[\text{Br}_2]} \quad \text{reaction rate equation}$$

Complex reactions are made up of sets of elementary reaction

- Part of reaction modeling is to develop reaction mechanisms that explain observed kinetic behavior
- Mechanisms involve sets of elementary reactions, usually with intermediate compounds
- Reaction rate equations developed by applying component material balances with assumptions (steady state, constant intermediate conc., etc.)

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:

$$-r_A = kC_A^a C_B^b \dots C_D^d, \quad a + b + \dots + d = n \quad (4)$$

where a, b, \dots, d are not necessarily related to the stoichiometric coefficients. We call the powers to which the concentrations are raised the *order of the reaction*. Thus, the reaction is

a th order with respect to A

b th order with respect to B

n th order overall

The dimensions of the rate constant k for the n th-order reaction are

$$(\text{time})^{-1}(\text{concentration})^{1-n}$$

Consider the elementary reaction



If the rate is measured in terms of B, the rate equation is

$$-r_B = k_B C_B C_D^2$$

If it refers to D, the rate equation is

$$-r_D = k_D C_B C_D^2$$

Or if it refers to the product T, then

$$r_T = k_T C_B C_D^2$$

But from the stoichiometry

$$-r_B = -\frac{1}{2} r_D = \frac{1}{3} r_T$$

hence,

$$k_B = \frac{1}{2} k_D = \frac{1}{3} k_T \quad (9)$$

- To avoid ambiguity when the stoichiometry involves different numbers of molecules of the various components, we must specify the component being considered to which the rate constant is referred.



If an elementary reaction $-r_A = k_A C_A C_B$

1st order in A, 1st order in B, overall second order

If an non-elementary reaction $-r_A = k_A C_A$

1st order in A, zero order in B, overall first order