**Extent of Reaction**

Extent of reaction: ξ = (Ni - Ni,0)/vi

Fractional conversion: fi = (Ni,0 - Ni)/Ni,0

* Ni = number of moles present
* Ni,0 = number of moles initially present
* vi = stoichiometric coefficient of balanced equation
  + Positive for products
  + Negative for reactants

**Component Material Balances**

Molar basis: ∑xij\*Qj + ∑ξ\*vi = 0

* xij = mole fraction of i in stream j
* Qj = molar flow rate of stream j

Mass basis: ∑ωij\*Fj + ∑ξ\*vi\*MWi = 0

* ωij = mass fraction of i in stream j
* Fi = mass flow rate in stream j
* MWi = molecular weight of i

**Mass Balance with Reactions**

* Draw a picture of the process and label all streams and components
* Write a balanced stoichiometric equation
* If needed, convert stream compositions to mass % and determine molecular weights of each component
* Write down component material balance equations filling in known information. Compare # of unknowns and equations to determine if the problem can be solved.
* Solve for unknowns
* Check answers by making sure the total masses in and out are balanced

**How far a reaction has gone**

* Concentration: C, start at C0, end at C
  + Easy to understand
  + Directly measurable
  + No limitation on numerical values
  + Hard to compare reactions and component amounts
* Conversion: X, start at 0, goes up to 1, X = (C0-C)/C0 = 1 - C/C0
  + Easy to understand
  + % of initial component reacted (0 < X < 1)
  + Different value for each component
* Extent of reaction: starts at 0, goes up to infinity (see equation above)
  + Same value for every reactant
  + Greater than 0
  + Depends on stoichiometry
  + No upper limit on numerical value
  + Depends on size of reaction amounts

**Thermodynamics vs. Kinetics**

Thermodynamics

* energy/mass balances
  + Extent of reaction
* Equilibrium
* Dictated extent (how much) of a reaction

Kinetics

* Rate
* Mechanism
* Equipment design
* Determines speed (how fast) of a reaction

**Molecular collision theory**

* 2 or more molecules collide with sufficient energy to overcome repulsive forces and form new covalent bonds
* Depends on orientation of molecules
* Uses frequency of collision of molecules to explain rate of reaction
* Assumes breakdown of intermediates is so fast that it does not influence overall reaction rate

**Transition theory**

* High energy state, unstable
* Quickly decomposes to form products
* Assumes activated transition intermediate is always in equilibrium with reactants
* Overall rate of reaction depends on decomposition of transition complex into products

**Rate of Reaction**

ri = (1/V) \* (dNi/dt)

* ri = reaction rate
* V = volume
* Ni = moles of i
* t = time
* Number of moles of reactant/product that is consumed/produced per unit time and unit volume

aA + bB ⟶ rR + sS

* -rA/a = -rB/b = rR/r = rS/s

**Elementary Reactions**

Rate of reaction corresponds to stoichiometric equation

A + B ⟶ C

* -rA = kCACB
  + k = reaction rate constant
  + CA = molar concentration of A
  + rA = rate of reaction (negative sign denotes depletion)

**Non-Elementary Reactions**

Reaction rates not necessarily related to stoichiometry.

Made up of sets of elementary reactions

**Reaction Order**

-rA = kCAaCBb...CDd

a + b + ... + d = n

* a, b, ..., d not necessarily related to stoichiometric coefficients
* Order of reaction
  + ath order with respect to A
  + Nth order overall
* Dimensions of rate constant k for nth order reaction are (time)-1(concentration)1-n
* Elementary reaction, the stoichiometric coefficients are the order

**First Order Reaction**

-ri = kCi = kCi,0(1-X) = k(Ci,0 + viξ/V)

* (V = volume of reaction)
* Ci = Ci,0e-kt
* X = 1-e-kt

**Irreversible Elementary Reaction**

2A + B ⟶ 3C

-rA = kCA2CB

-rB = 1/2 kCA2CB

rC = 3/2 kCA2CB

**Reversible Elementary Reaction**

A + B ↔ C

rA = -k1CACB + k2CC

rB = -k1CACB + k2CC

rC = -k2CC + k1CACB

**Arrhenius’ Law**

For many reactions, rate expression can be written as a product of a temperature-dependent term and a composition-dependent term

ri = f1(temperature) \* f2(composition) = k \* f2(composition)

k = k0e-E/RT

* K0 is frequency or pre-exponential factor
* E is activation energy
* R = 8.314 J/mol\*K
* T = temperature in K

Plot ln(k) vs 1/T

* Slope = -E/R
* ln(r2/r1) = E/R (1/T1 - 1/T2)

**Ideal Batch Reactor**

Assumptions:

* Composition varies with time
* Uniform composition
* Constant volume
* Isothermal
* Very simple
* Little supporting equipment
* Small-scale experimental studies on reaction kinetics

ri = 1/V dNi/dt = d(Ni/V)/dt = dCi/dt

XA = (NA,0-NA)/NA,0 = 1- CA/CA,0

dXA = -dCA/CA,0

First Order Reaction

* -rA = -dCA/dt = kCA = kCA,0(1-X) = k(CA,0 + viξ/V)
* Integration: -ln CA/CA,0 = kt
* dXA/dt = k(1-XA)
* Integration: -ln(1-XA) = kt

**Irreversible Second Order, Bimolecular Elementary Reaction**

-rA = -dCA/dt = kCA2 = kCA,02(1-XA)2

Integration: 1/CA - 1/CA,0 = 1/CA,0 \* XA/(1-XA) = kt

**Second Order, Bimolecular Elementary Reaction**

-rA = -dCA/dt = -dCB/dt = kCACB = CA,0 dXA/dt = k(CA,0 - CA,0XA)(CB,0 - CA,0XA)

* M = CB,0/CA,0 (only valid if M ≠ 1)
* -rA = kCA,02(1-XA)(M-XA)
* Integrate: ln(1-XB)/(1-XA) = ln(M-XA)/M(1-XA) = ln(CBCA,0/CB,0CA) = ln(CB/MCA) = CA,0(M-1)kt = (CB,0 - CA,0)kt

**A + 2B → Products**

-rA = -dCA/dt = kCACB = kCA,02(1-XA)(M-2XA)

* Integrate: ln(CBCA,0/CB,0CA) = ln(M-2XA/M(1-XA)) = CA,0(M-2)kt (M≠2)
* 1/CA-1/CA,0 = 1/CA,0 \* XA/1-XA = 2kt (M = 2)

**Rate Data Analysis: Integral Method**

1. Set up rate equation based on hypothesized elementary reaction model
2. Integrate model to obtain f(C) = kt (i.e. -ln(CA/CA,0)
3. Examine the plot of f(C) vs. t with the data for linearity, which would indicate a valid reaction model

**Irreversible Trimolecular Third Order Reactions**

A + B + D → products

* -rA = -dCA/dt = kCACBCD
* CA,0dXA/dt = kCA,03(1-XA)(CB,0/CA,0 - XA)(CD,0/CA,0 - XA)
* Integration: ln(1-XB/1-XA) = ln(M-XA)/M(1-XA) = ln(CBCA,0/CB,0CA) = ln(CB/MCA) = CA,0(M-1)kt = (CB,0-CA,0)kt (M≠1)

**Trimolecular Reactions**

A + 2B → R

-rA = -dCA/dt = kCACB2

dXA/dt = kCA,02(1-XA)(M-2XA)2

Integration: (2CA,0-CB,0)(CB,0-CB)/CB,0CB + ln(CA,0CB/CACB,0) = (2CA,0-CB,0)2kt (M≠2) or 1/CA2 - 1/CA,02 = 8kt (M=2)

**Empirical Rate Equations of nth Order**

-rA = -dCA/dt = kCAn

Integration: CA1-n - CA,01-n = (n-1)kt (n≠1)

**Zero-Order Reactions**

-rA = -dCA/dt = k

Integration: CA,0-CA = CA,0XA = kt