## Non-Elementary Reactions

- Most observable reactions are non-elementary; they represent the net result of several reactions, e.g.:

$$2A \underset{}{\overset{K_{R1}}{\rightleftharpoons}} C + D \dashrightarrow D$$

$$C + E \overset{K_{R3}}{\rightleftharpoons} 2G$$

$$A + B \overset{K_{R2}}{\rightleftharpoons} E$$

$$3A + B \overset{K_{overall}}{\rightleftharpoons} D + 2G$$

- Fundamentally, the kinetics of overall reactions can only be understood by characterizing the rates of each constituent reaction
- In practice, many non-elementary reactions can be modeled by simple, overall rate expressions

## Power Law Expressions

*Many rate laws conform closely to expressions of the following form:*

$$r_A = -k_A' a_A^{\alpha} a_B^{\beta} \quad \text{or} \quad r_A = -k_A c_A^{\alpha} c_B^{\beta}$$

*$\alpha$ and $\beta$ are called the 'order of the reaction' with respect to A and B, respectively. $\alpha+\beta$ is the overall order of the reaction*

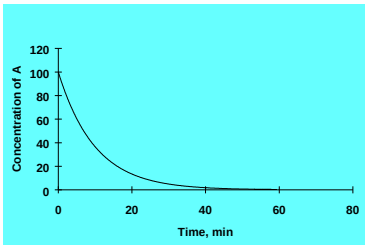
## Evaluating Reaction Rate Expressions

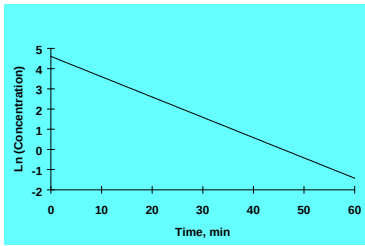
- Integral methods rely on comparison of *c* vs. *t* data with predictions developed by integration of the mass balance
- Differential methods rely on comparison of *dc/dt* data with the differential form of the mass balance

## Integrated Mass Balances for Reactions in Batch Reactors

- 1st Order: $\frac{dc_A}{dt} = r_A = -k_1 c_A$ $\quad \ln\frac{c_A(t)}{c_A(0)} = -k_1 t$
- 2nd Order: $\frac{dc_A}{dt} = r_A = -k_2 c_A^2$ $\quad \frac{1}{c_A(t)} - \frac{1}{c_A(0)} = k_2 t$
- *n*th Order (*n*≠1): $\frac{dc_A}{dt} = r_A = -k_n c_A^n$ $\quad \frac{1}{n-1}\left\{\left[c_A(t)\right]^{1-n} - \left[c_A(0)\right]^{1-n}\right\} = k_n t$

## *c* vs. *t* and ln *c* vs. *t* for a 1st Order Reaction in a Batch Reactor




## Reactions in which Concentrations of Several Reactants Vary

- Stoichiometry can be taken into account explicitly if the initial reactants are present in stoichiometric ratios
- Reactions can often be made pseudo-$n^{th}$ order by providing all reactants but one in great excess of the stoichiometric requirement

## Simplifying a Rate Expression to Make it Pseudo-First or Zero Order

$A + 2B \rightarrow 2P$

*General (hypothesized):* $r_A = -k_n c_A^\alpha c_B^\beta = -k_n c_A^\alpha \left(c_{B,0} - 2\Delta c_A\right)^\beta$

*If $c_{B,0} >> c_{A,0}$:* $r_A \approx -k_n c_A^\alpha \left(c_{B,0}\right)^\beta = -k_n^* c_A^\alpha$

*General (hypothesized):* $r_A = \dfrac{k_1 c_A c_B}{k_2 + c_A}$

*If $c_A >> k_2$:* $r_A \approx k_1 c_B$

*If $c_A << k_2$:* $r_A \approx \dfrac{k_1}{k_2} c_A c_B$

## Differential Methods

- Rely on analysis of *r* (*dc*/*dt* in a batch reactor) vs. *c*
- Especially useful when a product of the reaction affects the reaction rate significantly

$$r_A = -k_n c_A^n$$

$$\ln|r_A| = \ln k_n + n \ \ln c_A$$

## Reversible Reactions and Equilibrium

- Reversible, elementary reactions:

$$a\mathrm{A} + b\mathrm{B} \underset{k_{PA}}{\overset{k_{AP}}{\rightleftarrows}} p\mathrm{P} + r\mathrm{R}$$

$$r_{\mathrm{A}} = -k_{\mathrm{AP}}'(a_{\mathrm{A}})^{a}(a_{\mathrm{B}})^{b} + k_{\mathrm{PA}}'(a_{\mathrm{P}})^{p}(a_{\mathrm{R}})^{r}$$

- *At equilibrium, $r_A$=0, and:*

$$\frac{k_{\mathrm{AP}}'}{k_{\mathrm{PA}}'} = \frac{(a_{\mathrm{P},eq})^{p}(a_{\mathrm{R},eq})^{r}}{(a_{\mathrm{A},eq})^{a}(a_{\mathrm{B},eq})^{b}} = K_{eq}$$

## The Kinetic View of Chemical Equilibrium

$$a\mathrm{A} + b\mathrm{B} \leftrightarrow c\mathrm{C} + d\mathrm{D}$$

For ***elementary*** (single-collision) reactions in a single phase

$$r_{\mathrm{A,net}} = -k_f\{\mathrm{A}\}^{a}\{\mathrm{B}\}^{b} + k_b\{\mathrm{C}\}^{c}\{\mathrm{D}\}^{d}$$

At equilibrium, $r_{\mathrm{A,net}}$=0, so:

$$k_f\left[\{\mathrm{A}\}^{a}\{\mathrm{B}\}^{b}\right]_{equil} = k_b\left[\{\mathrm{C}\}^{c}\{\mathrm{D}\}^{d}\right]_{equil}$$

$$\left[\frac{\{\mathrm{C}\}^{c}\{\mathrm{D}\}^{d}}{\{\mathrm{A}\}^{a}\{\mathrm{B}\}^{b}}\right]_{equil} = \frac{k_f}{k_b} \equiv K_{eq}$$

## Equilibrium Constants and Chemical Activity

- **Equilibrium constants describe relationships that must apply among the species participating in a reaction, if the reaction is at equilibrium. The relationships are among the *activities* of the species.**
- **Since changing the standard state concentration or reference environment changes the numerical value of the activity of a species, it also changes the numerical value of the equilibrium constant, but clearly, it cannot change the underlying tendency of the reaction to occur.**
- **Once the standard state conditions are established, $K_{eq}$ is established, and that value applies in *all* environments (as long as the individual activities are evaluated relative to those standard states).**

## The Kinetic View of Chemical Equilibrium

- Observations about $K_{eq}$
  - $K_{eq}$: a pure, dimensionless number. Can be manipulated any way that any other number can be.
  - $K_{eq}$ describes a relationship that must be satisfied by the constituents of a ***reaction*** at ***equilibrium***. Equilibrium is meaningless for an individual species or group of species in the absence of a defined reaction relating them.
  - The ratio corresponding to $K_{eq}$ can be computed regardless of whether the reaction is at equilibrium. This ratio is called the ***reaction quotient***, ***Q***. If $Q>K_{eq}$, the actual ratio of products to reactants is greater than the equilibrium value, $r_b>r_f$, and products will be converted to reactants, thereby driving the system toward equilibrium.

## The Kinetic View of Chemical Equilibrium

- Additive (Sequential) Reactions

$$H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-} \qquad K_{eq,1} = \frac{\{H^+\}^2\{CO_3^{2-}\}}{\{H_2CO_3\}} = 10^{-16.68}$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3(s) \qquad K_{eq,2} = \frac{\{CaCO_3(s)\}}{\{Ca^{2+}\}\{CO_3^{2-}\}} = 10^{+8.48}$$

$$Ca^{2+} + H_2CO_3 \leftrightarrow 2H^+ + CaCO_3(s) \qquad K_{eq,3} = \frac{\{H^+\}^2\{CaCO_3(s)\}}{\{Ca^{2+}\}\{H_2CO_3\}}$$

## The Kinetic View of Chemical Equilibrium

- Additive (Sequential) Reactions

$$K_{eq,1} = \frac{\{H^+\}^2\{CO_3^{2-}\}}{\{H_2CO_3\}} = 10^{-16.68} \qquad K_{eq,2} = \frac{\{CaCO_3(s)\}}{\{Ca^{2+}\}\{CO_3^{2-}\}} = 10^{+8.48}$$

$$K_{eq,3} = \frac{\{H^+\}^2\{CaCO_3(s)\}}{\{Ca^{2+}\}\{H_2CO_3\}} = K_{eq,1}K_{eq,2} = 10^{-8.20}$$

- $K_{eq}$ of Additive (Sequential) Reactions
  - Equal to the product of the constituent reactions
  - Doubling a reaction yields a reaction with $K_{eq,2}=(K_{eq,1})^2$
  - Not the ratio of a (single) forward to a (single) reverse rate constant

## The Kinetic View of Chemical Equilibrium

- Reversed Reactions

$$H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-} \qquad K_{eq,1} = \frac{\{H^+\}^2\{CO_3^{2-}\}}{\{H_2CO_3\}} = 10^{-16.68}$$

$$2H^+ + CO_3^{2-} \leftrightarrow H_2CO_3 \qquad K_{eq,2} = \frac{\{H_2CO_3\}}{\{H^+\}^2\{CO_3^{2-}\}} = \frac{1}{K_{eq,1}} = 10^{+16.68}$$

- $K_{eq}$ of a reversed reaction is the inverse of $K_{eq}$ of the original reaction

## Some Limiting Cases of Reaction Kinetics

| Approximation | Corresponding Criteria and Effect |
|---|---|
| **Irreversible Reaction** | **Forward rate >> Reverse rate (or vice versa);**<br>**$t_{char}$ >> time available for reaction;**<br>**Reaction far from equilibrium;**<br>***Eliminates one rate term from mass balance*** |
| **Equilibrium Reaction** | **Forward rate = Reverse rate;**<br>**$t_{char}$ << time of interest;**<br>***Eliminates forward and reverse rate terms for a given reaction from mass balance, and substitutes equilibrium constant*** |
| **Stoichiometric or Complete Reaction** | **Equilibrium lies far to product side and $t_{char}$ << time of interest;**<br>***Eliminates forward and reverse rate terms for a given reaction from mass balance, and substitutes stoichiometry*** |

## Temperature Dependence of Reaction Rates

- The effect of temperature on kinetics can often be modeled using the Arrhenius equation:

$$k = k_{\mathrm{Ar}} \exp\left(-\frac{E_{\mathrm{Ar}}}{RT}\right)$$

$$\ln k_{T_2} - \ln k_{T_1} = \ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_{\mathrm{Ar}}}{R} \exp\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

*Since $E_{Ar}$ is always positive, the equation indicates that k always increases with T*

## The Energy-Based View of Chemical Equilibrium

- Reminder: Absolute energy is not measurable; only changes in energy can be measured. Absolute values of energy can be assigned by choosing some baseline at which energy is defined to be zero and measuring energy changes required to shift from that condition to another
- The ***Potential*** associated with a location is the potential energy per unit amount of the "item" that the energy acts on; equivalently, the energy input required to move a unit amount of the item to that location, from the baseline (zero energy) location
  - Gravitational potential acts on objects with mass and is potential energy per unit mass, in a given gravitational environment
  - Electrical potential acts on charged objects is potential energy per unit charge in a given electrical environment
  - ***Chemical potential*** acts on chemical species and is potential energy per mole of that species in a given chemical environment