Non-elementary Rate Laws

Applicable to both

**Homogeneous reactions**

\[ CO + Cl_2 \rightarrow COCl_2 \]

\[-r_{CO} = k_{CO} C_{CO} C_{Cl_2}^{3/2} \]

n=5/2

**& Heterogeneous reactions**

\[ C_6H_5CH_3 + H_2 \xrightarrow{\text{cat}} C_6H_6 + CH_4 \]

Common practice to write rate law in terms of partial pressure!

\[ P_i = C_i RT \]

**IMPORTANT!!!!**

Reaction orders cannot be deduced from reaction stoichiometry. They must be determined from experiments or literature.
REVERSIBLE REACTIONS

All rate laws for reversible reactions **MUST** reduce to the thermodynamic relationship relating the reacting species concentrations at equilibrium, the rate of reaction is exactly zero (-\( r_A = 0 \)).

\[
aA + bB \xrightleftharpoons[k_{\text{reverse}}]{k_{\text{forward}}} cC + dD
\]

For the general equation the concentrations are related by the thermodynamic relationship for the *concentration equilibrium constant*, \( K_c \). (Appendix C)

**Thermodynamic Relationships Involving the Equilibrium Constant**

e.g. gas-phase reaction

\[
\frac{b}{a} \ A + \frac{b}{a} \ B \xrightleftharpoons[k_{\text{reverse}}]{k_{\text{forward}}} \frac{c}{a} \ C + \frac{d}{a} \ D
\]

How do we describe the equilibrium constant?

\[
RT \ln K = -\Delta G
\]
For ideal gases, $K_C$ and $K_P$ are related by $K_P = K_C (RT)^\delta$

$$\delta = \frac{c}{a} + \frac{d}{a} - \frac{b}{a} - 1$$

Where the true dimensionless $K$, is written in terms of:

$$K = \frac{a_C a_D}{a_A a_B}$$

$f_i =$ fugacity of species $i$

$f^\circ_i =$ fugacity of the standard state

$$\gamma_i = \text{activity coefficient}$$

$$a_i = \frac{f_i}{f_i^\circ} = \gamma_i P_i$$

For ideal gases $K_\gamma = 1.0 \text{ atm}^{-\delta}$
So why is this so important?

All rate laws for reversible reactions **MUST** reduce to the thermodynamic relationship relating the reacting species concentrations at equilibrium, the rate of reaction is exactly zero.

\[-r_A = 0\]

\[aA + bB \xleftrightarrow{\text{forward}} \text{k}_{\text{forward}} \xrightarrow{\text{reverse}} cC + dD\]

1) Write rate law for forward and reverse

\[-r_{A,\text{forward}} = k_{\text{forward}} C_A^a C_B^b\]

\[r_{A,\text{reverse}} = k_{\text{reverse}} C_C^c C_D^d\]

2) Net rate law \( r_{A,\text{NET}} = r_{A,\text{forward}} + r_{A,\text{reverse}} \)

\[-r_{A,\text{NET}} = k_{\text{forward}} C_A^a C_B^b - k_{\text{reverse}} C_C^c C_D^d\]

3) Does it reduce to the equilibrium constant?

\[-r_{A,\text{NET}} = 0 = k_{\text{forward}} C_A^a C_B^b - k_{\text{reverse}} C_C^c C_D^d\]

\[0 = k_{\text{forward}} (C_A^a C_B^b - \frac{k_{\text{reverse}}}{k_{\text{forward}}} C_C^c C_D^d)\]

\[C_A^a C_B^b = \frac{k_{\text{reverse}}}{k_{\text{forward}}} C_C^c C_D^d\]

\[\frac{k_{\text{forward}}}{k_{\text{reverse}}} = C_C^c C_D^d = K_C\]
EXAMPLE- CLASS EXERCISE

How do we write the rate law then?

Elementary reversible reaction \[ A \xrightleftharpoons[k_{rA}]{k_{fA}} 2B \]

1) Write for forward reaction

\[ -r_{Af} = k_{fA} C_A \]

2) Write for the reverse reaction

\[ r_{Ar} = k_{rA} C_B^2 \]

3) Net rate \[ r_{Net} = r_{Af} + r_{Ar} \]

\[ r_{A,NET} = -k_{fA} C_A + k_{rA} C_B^2 \]

4) Does this rate law satisfy our requirement that, at equilibrium, it must reduce to an equation that is thermodynamically consistent with \( K_C \)? Let's see.

Pull out \(-k_{fA}\)

Substitute \( K_C \)

At equilibrium remember

\[ -r_{A,NET} = 0 \]

\[ -r_{A,NET} = k_{fA} \left[ C_A - \frac{C_B^2}{k_{fA}/k_{rA}} \right] \]

Therefore at equil

\[ K_C = C_B^2/C_A \]
THE REACTION RATE CONSTANT, \( k \)

We assume that the variable that affects the reaction rate constant the most strongly is temperature, therefore \( k_A(T) \).

Swedish chemist Arrhenius first suggested the following equation that correlates temperature to the reaction rate constant. **SINGLE MOST IMPORTANT STEP IN CHEMICAL KINETICS!**

\[ k_A(T) = Ae^{-E/RT} \]

**Arrhenius Equation**

- \( A \) = preexponential factor or frequency factor
- \( E \) = activation energy, J/mol or cal/mol
- \( R \) = gas constant = 8.314 J/mol•K = 1.987 cal/mol•K
- \( T \) = absolute temperature, K
Activation Energy, \( E \)
The minimum energy necessary to form an unstable intermediate during the reaction.

Preexponential Factor or Frequency Factor, \( A \)
A constant indicating how many collisions have the correct orientation to lead to products.

Activation Energy can be thought of as a barrier to energy transfer (from kinetic to potential) between reacting molecules that must be overcome.

**WHY?**

1. The molecules need energy to distort or stretch their bonds so that they break and form new bonds.

2. The steric and electron repulsion forces must be overcome as the reacting molecules are brought closer together.
By increasing the temperature we increase the kinetic energy of the reactant molecules which can in turn be transferred to internal energy to increase the stretching and bending of the bonds causing them to be in an activated state, vulnerable to bond breaking and reaction.

\[ A + BC \rightleftharpoons A \cdots B \cdots C \rightarrow AB + C \]
CALCULATING THE ACTIVATION ENERGY

Determined experimentally by carrying out experiments at different temperatures. Reactions with large activation energies are very temperature sensitive.

\[ \ln k_A = \ln A - \frac{E}{R} \left( \frac{1}{T} \right) \]

CLASS EXERCISE

Consider the following elementary reactions:

1. \( A \xrightarrow{k_1} B \)
2. \( A \xrightarrow{k_2} D \)
3. \( A \xrightarrow{k_3} Y \)
4. \( A \xrightarrow{k_4} U \)

1) Which reaction has the highest activation energy?
2) Which reactions have the same activation energy?
3) Which reaction is temperature insensitive?
Most useful form of Arrhenius equation:

\[ k(T_o) = A e^{-E/RT_o} \]
\[ k(T) = A e^{-E/RT} \]

Take ratio:

\[ k(T) = k(T_o) e^{\frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right)} \]

Now, if we know the specific reaction rate, \( k(T_o) \), and we know the activation energy, \( E \), then we can find the specific reaction rate, \( k(T) \), at any other temperature!
For 1 point: EXTRA CREDIT

Estimate the Arrhenius parameters (E, and A) for the decomposition of nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrzocine from the following data:

<table>
<thead>
<tr>
<th>$k$, s$^{-1}$</th>
<th>0.208</th>
<th>0.363</th>
<th>0.843</th>
<th>1.41</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$, K</td>
<td>463.1</td>
<td>465.4</td>
<td>468.7</td>
<td>471.3</td>
</tr>
</tbody>
</table>
For 2 points: EXTRA CREDIT

You are called to an explosive testing facility where your experiments have been being carried out. Unfortunately, there is an uncontrolled fire due one of your colleagues, increasing the temperature of a room. Your experiment is setup inside and contains 50 lbs of nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrzocine. You are upset. At approximately what temperature is your experiment destroyed, the building gone, and your colleague fired when they can’t blame it on you?

\[ E = 149 \pm 1.1 \text{ kJ/mol} \]
\[ A = \exp (29.35 \pm 0.26 \text{ s}^{-1}) \]