Chemical Kinetics

Chemical kinetics is the study of *time dependence of the change in the concentration* of reactants and products.

"The field of chemical kinetics has not yet matured to a point where a set of unifying principles has been identified…There are many different theoretical models for describing how chemical reactions occur." (M&S, 1137)

Generally, we want to understand the rate of reaction:

Recall from Slide CEq-2…

$$\nu_A A(g) + \nu_B B(g) \rightarrow \nu_Y Y(g) + \nu_Z Z(g)$$

Reactants

$$n_A(t) = n_A(0) - \nu_A \xi(t)$$

$$n_B(t) = n_B(0) - \nu_B \xi(t)$$

Products

$$n_Y(t) = n_Y(0) + \nu_Y \xi(t)$$

$$n_Z(t) = n_Z(0) + \nu_Z \xi(t)$$

For each constituent…

$$\frac{dn_A(t)}{dt} = -\nu_A \frac{d\xi(t)}{dt}$$

$$\frac{1}{V}\frac{dn_A}{dt} = \frac{d[A]}{dt} = -\frac{\nu_A}{V}\frac{d\xi(t)}{dt}$$

Rate of reaction, $v(t)$

$v(t)$, the rate of reaction, is defined as the rate of change in $\xi(t)$ with time per unit volume

$$v(t) = \frac{1}{V}\frac{d\xi(t)}{dt} = -\frac{1}{v_A}\frac{d[A]}{dt} = -\frac{1}{v_B}\frac{d[B]}{dt} = \frac{1}{v_Y}\frac{d[Y]}{dt} = \frac{1}{v_Z}\frac{d[Z]}{dt}$$

Note all quantities are positive. What are units of $v(t)$?

Examples:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$v(t) = \frac{1}{V}\frac{d\xi(t)}{dt} =$$

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

$$v(t) = \frac{1}{V}\frac{d\xi(t)}{dt} =$$

The integrated rate law

The rate can be expressed as a function of the reactant concentrations. Most common function is of form:

$$v(t) = \frac{1}{V}\frac{d\xi}{dt} = k[A]^m[B]^n$$

Rate laws must be determined *experimentally* and, generally, cannot be deduced from the balanced reaction!!

General

$$v_A A(g) + v_B B(g) \rightarrow v_Y Y(g) + v_Z Z(g)$$

$$v(t) = k[A]^m[B]^n$$

Example

$$2\mathrm{NO(g)} + \mathrm{O_2\,(g)} \rightarrow 2\mathrm{NO_2\,(g)}$$

$$v(t) = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

The Order:

Units of k, rate constant

$$v(t) = \frac{1}{V}\frac{d\xi}{dt} = k[A]^m[B]^n$$

$\frac{\text{concentration}}{\text{time}}$

$(\text{concentration})^m$

$(\text{concentration})^n$

Rate Law	Order	Units of k
$v = k$	0	
$v = k[A]$	1	
$v = k[A]^2$	2	
$v = [A][B]$	1 in [A], [B] 2 overall	
$v = k[A]^{1/2}$	1/2	

Rate laws can be complicated

$H_2(g) + I_2(g) \rightarrow 2HI(g)$ $\qquad v(t) = k[H_2][I_2]$

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ $\qquad v(t) = \dfrac{2k'[H_2][Br_2]^{1/2}}{1 + k''[HBr][Br_2]^{-1}}$

These rate laws suggest that these two reactions occur via different mechanisms (sets of individual steps).

The first may be a elementary reaction (one step) whereas the latter is certainly a multistep process.

We will soon explore how to obtain complicated rate laws from suggested mechanisms.

Elementary Rxns vs. Complex Reactions

Complex Reactions

Reactants → Intermediates → Products

Elementary Reactions

Reactants → Products

Molecularity of Elementary Reactions:

Unimolecular $A \rightarrow \text{products}$

Bimolecular $A + B \rightarrow \text{products}$

Termolecular $A + B + C \rightarrow \text{products}$

Finding rate laws experimentally

There are two common methods for determining rate laws:

Method of isolation

Set up reaction so one reactant is in excess. Any change in rate will be due to changes in other reactant. Repeat for other reactant.

$$v = k'[B]^n \quad \text{where} \quad k' = k[A]^m$$

Method of initial rates

Measure concentration change as a function of time, ~$v(t)$, for a series of experimental conditions. (Conditions must include sets where the reactant A has the same initial concentration but B changes and vice versa).

First order reactions

The reaction: $A + B \rightarrow \text{products}$ has rate law: $v(t) = -\frac{d[A]}{dt} = k[A]$

Let's integrate…

$$\frac{d[A]}{[A]} = -kdt \longrightarrow \int_{[A]_0}^{[A]_t} \frac{1}{[A]} d[A] = -\int_0^t kdt$$

Solution:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln[A]_t = \ln[A]_0 - kt$$

$$[A]_t = [A]_0 e^{-kt}$$

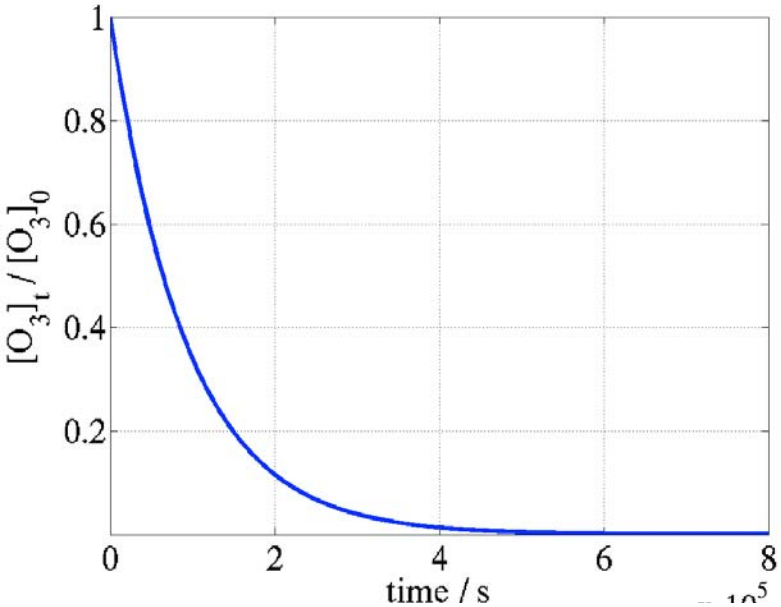
First order reactions decay exponentially.

Ozone decays via first order kinetics

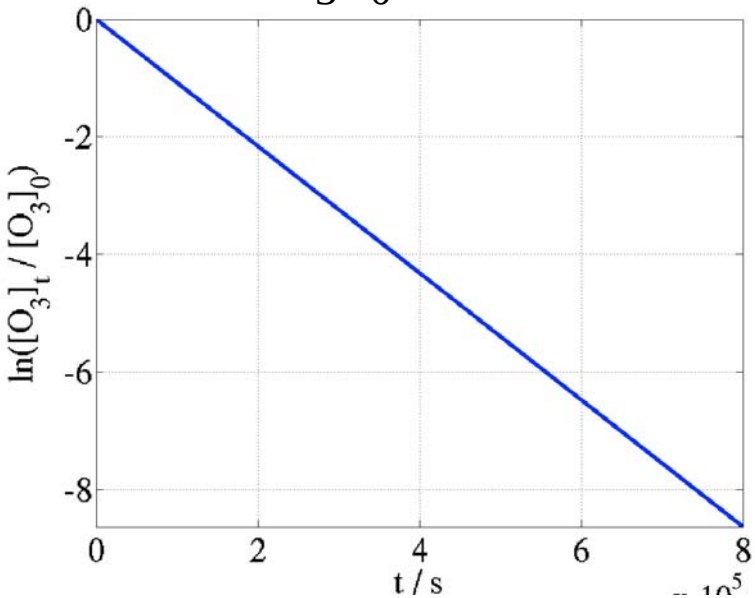
$$O_3(g) \rightarrow O_2(g) + O(g)$$

$k = 1.078 \times 10^{-5}\ s^{-1}$ at 300 K

$$[O_3]_t = [O_3]_0 e^{-kt}$$



$$\ln \frac{[O_3]_t}{[O_3]_0} = -kt$$

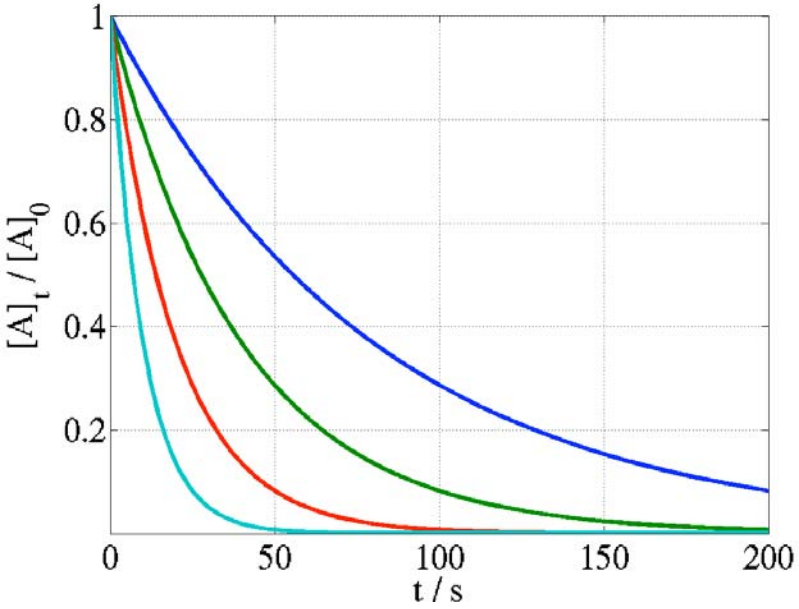


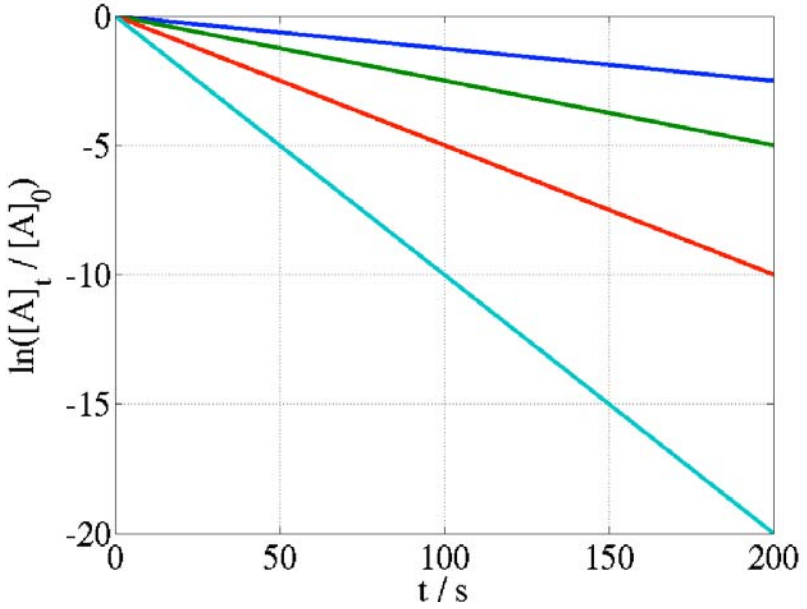
What is slope?

What happens as *k* increases?

$$[A]_t = [A]_0 e^{-kt}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$





k = 0.0125 s^{-1}

k = 0.0250 s^{-1}

k = 0.0500 s^{-1}

k = 0.1000 s^{-1}

Half-life of a first order reaction

The *half-life, $t_{1/2}$,* is the time it takes to fall to ½ of the starting concentration:

At $t = t_{1/2}$, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$

$$\frac{[A]_{1/2}}{[A]_0} = \frac{1}{2} = e^{-kt_{1/2}}$$

$$\downarrow$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

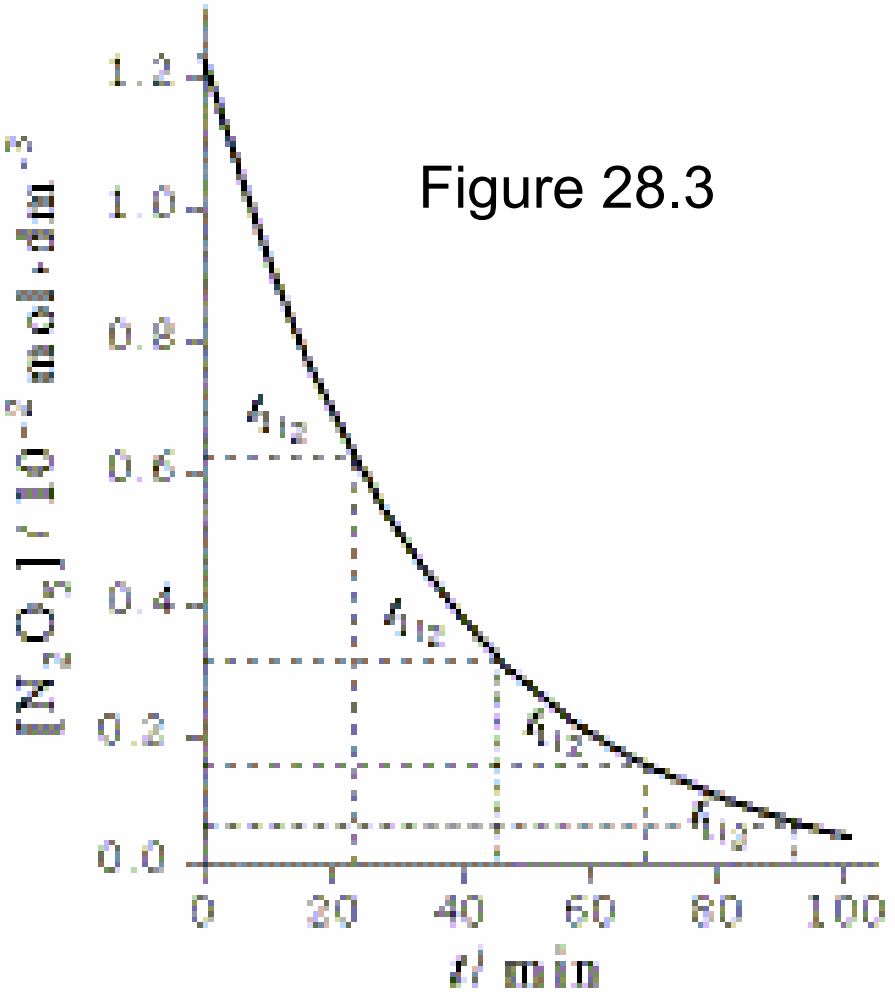


Figure 28.3

Other order reactions…

Second order reaction:	$2A \rightarrow \text{products}$	$A + B \rightarrow \text{products}$
Second order rate:	$v(t) = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^2$	$v(t) = -\frac{d[A]}{dt} = k[A][B]$
Integrated rate law:	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$	$\frac{1}{([A]_0 - [B]_0)} \ln\left(\frac{[B]_0[A]_t}{[A]_0[B]_t}\right) = kt$

Zero order reaction: $A \rightarrow \text{products}$

Zero order rate: $v(t) = -\frac{d[A]}{dt} = k$

Integrated rate law: $[A]_t = [A]_0 - kt$

Pseudo-first order reactions

You can “overload” the other reactants to determine the order with respect to one individual reactant (method of isolation).

For $A + B \rightarrow$ products , what happens if [B] >> [A]?

$$v(t) = -\frac{d[A]}{dt} = k[B][A]$$

Reversible reactions (small $\Delta_r G$)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

Assume first order, elementary rxn in both directions

Rate: $$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

Conservation of Mass:

$$[A]_0 + [B]_0 = [A] + [B]$$

$$[B] = [A]_0 + [B]_0 - [A]$$

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}\left([A]_0 + [B]_0 - [A]\right)$$

Integrate:

$$\ln\left(\frac{k_1[A]_t - k_{-1}\left([A]_0 + [B]_0 - [A]_t\right)}{k_1[A]_0 - k_{-1}[B]_0}\right) = -(k_1 + k_{-1})t$$

At equilibrium

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad -\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

At equilibrium… $-\frac{d[A]}{dt} = 0 \longrightarrow k_1[A]_{eq} = k_{-1}[B]_{eq}$

The forward rate equals the reverse at equilibrium.

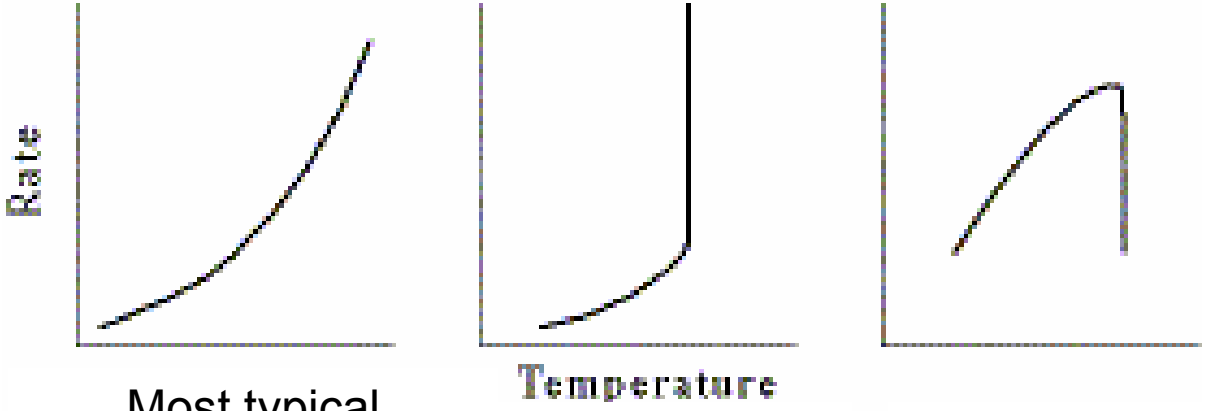
What is the equilibrium constant for this reaction?

In terms of rate constants?

Temperature Dependence of k

Svante Arrhenius
Winner of the 3rd Nobel Prize in Chemistry

The rate constant can vary in different ways with T.



Most typical follows Arrhenius Eq

Exploisive Rxn

Enzyme Kinetics

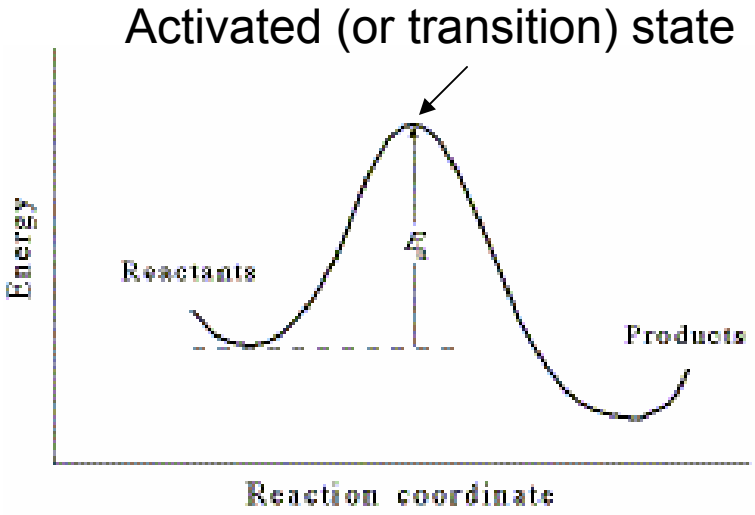
Differential form of the Arrhenius Equation:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

Arrhenius Parameters

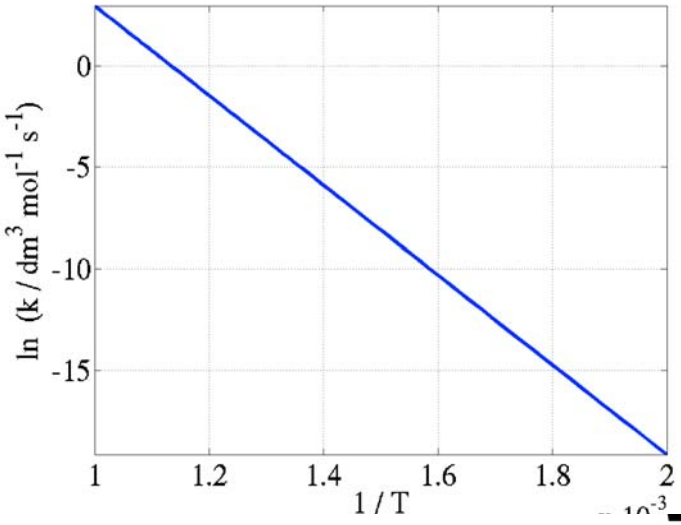
Integrated forms of Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad k = Ae^{-E_a/RT}$$



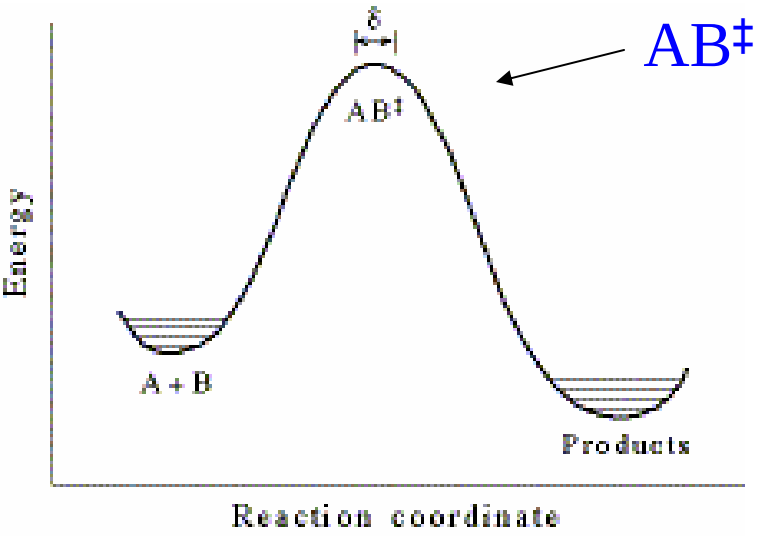
E_a is the activation energy. This is the energy required to get over a barrier (at the activated or transition state) between the reactants and products. E_a has units of energy and is T independent.

A is the pre-exponential or Arrhenius factor and is also T independent. A is a measure of rate at which collisions occur (and takes lots of things into acct such as orientation, molecular size, number of molecules per volume, molecular velocity, etc).



$2HI(g) \rightarrow I_2(g) + H_2(g)$

Transition-State Theory



$AB^{\ddagger}$ is the transition state (or activated complex.)

Transition state theory assumes that the transition state and reactants are in equilibrium with each other, and uses concepts from chemical equilibrium and statistical mechanics to find kinetic info such as rate constants!

Eyring Equation (key to transition-state theory)

$$k = \frac{k_B T}{h} K_C^{\ddagger}$$

From CEq: $K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$

So…

Relating E_a to thermodynamics!

Necessary Pieces…

Arrhenius Equation: $\ln k = \ln A - \frac{E_a}{RT}$

Differentiate wrt T: $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$ or $E_a = RT^2 \frac{d \ln k}{dT}$

From Eyring Equation: $\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_C^{\ddagger}}{dT}$

van't Hoff Equation (for K_c): $\frac{d \ln K_C}{dT} = \frac{\Delta U}{RT^2}$

Putting it all together…

What about A, the pre-exponential?

$$E_a = RT + \Delta U^{\ddagger} \quad \text{and} \quad \Delta U^{\ddagger} = \Delta H^{\ddagger} - RT\Delta^{\ddagger} n_g$$

so $$\boxed{E_a = RT + \Delta H^{\ddagger} - RT\Delta^{\ddagger} n}$$

Unimolecular Gas Phase Reaction

$A \rightarrow A^{\ddagger} \rightarrow \text{Products}$ so

Bimolecular Gas Phase Reaction

$A + B \rightarrow AB^{\ddagger} \rightarrow \text{Products}$ so

Transition State Theory and NMR Lab

In the NMR/N,N-DMA Paper, Gasparro et al. found an activation energy of 70.3 kJ/mol and a pre-factor of 1.87×10^{10} s^{-1}. Using these values find…

$$\Delta H^{\ddagger} \qquad \Delta S^{\ddagger} \qquad \Delta G^{\ddagger}$$

Why is TST important?