A Chemist’s View of the Universe

- System – what we care about
- Surroundings – everything else
- Boundary – separates system from surroundings

Some basic definitions

- Work – motion against an opposing (external) force
- Heat – energy change associated with a change in temperature
  - *Exothermic* – releases heat to the surroundings
  - *Endothermic* – absorbs heat from the surroundings

Internal Energy (U or E)

- Total energy of the system (kinetic and potential)
- Internal energy is a state function, which means we can define a change in it as $\Delta U = U_f - U_i$.

Enthalpy (H)

- Total potential energy of the system
- Enthalpy is a state function, which means we can define a change in it as $\Delta H = H_f - H_i$.

1st Law of Thermodynamics

- The internal energy of an isolated system is constant.
- The only ways to change the internal energy of a system are heat and work
  - $\Delta U = Q + W$
- The change in internal energy for a system is equal and opposite to the change in internal energy for the surroundings
  - $\Delta U_{sys} + \Delta U_{surr} = \Delta U_{tot} = 0$

1st Law of Thermodynamics

- “Greedy” convention (Ch and ChE’s)
  - Heat *absorbed* by system → $Q>0$
  - Heat *released* by system → $Q<0$
  - Work *done to* system → $W>0$
  - Work *done by* system → $W<0$

Hess’s Law

- Direct application of the properties of state functions.
- The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided. (whether they are real or not)
- This can be extended to ANY thermodynamic variable

Phase Changes (Transitions)

- Any change of phase will have a corresponding change in enthalpy
- Because enthalpy is a state function, several useful properties emerge.
- Consider a change of phase (or state) from A to B with a change of enthalpy = ΔH. For the reverse process (going from B to A), the change in enthalpy will be $-\Delta H$.
- Consider a change from A to C. We can consider this as happening in two steps: first from A to B and then from B to C. Thus $\Delta H_{A\rightarrow C} = \Delta H_{A\rightarrow B} + \Delta H_{B\rightarrow C}$

Enthalpies of reaction

- A similar type of analysis can be performed for a chemical reaction. We can define the standard reaction enthalpy as the change in enthalpy between the products and the reactants, in the standard state:

$$\Delta H_{rxn}{}^{o} = \sum_{products} \nu_i H_{m,i}{}^{o} - \sum_{reactants} \nu_i H_{m,i}{}^{o}$$

where ν_i refers to the stoichiometric coefficient of species i, and $H_{m,i}$ refers to the molar enthalpy of species i (aka enthalpy of formation). The ^{o} indicates standard state.

The 2^{nd} Law of Thermodynamics

- Used to predict spontaneity (tendency for a process to happen naturally)
- The 1^{st} Law only talks about conservation of energy, it says **nothing** about the *direction* that a process will tend to go in!
  - Why don't balls leave the ground and bounce up?
  - Why doesn't shattered glass reform?
  - Why doesn't green pigment separate into blue and yellow pigments?

The 2^{nd} Law of Thermodynamics

- The 2^{nd} Law describes how spontaneity is related to the *distribution* of energy, **not** to the *total* energy.
- Energy tends to flow in a direction where it will be more “spread out”, or dispersed.

So What’s Entropy?

- This leads to another view of the 2nd law: “The entropy of an isolated system increases in the course of a spontaneous change”
  - $\Delta S_{tot} > 0$
- Related to chaos, randomness, disorder
- Notice that Q is not a state function but S is!

Phase transitions

- Previously we saw that for a phase transition occurring at a constant pressure, $Q=\Delta H_{tr}$
- This means that we can also calculate ΔS_{tr}:

$$\Delta S_{tr}=\frac{\Delta H_{tr}}{T_{tr}}$$

where T_{tr} is the temperature at which the transition occurs

Thus exothermic processes (freezing, condensing) have (-) changes in entropy, while endothermic processes (melting, boiling) have (+) changes in entropy

How is entropy measured?

- In an analogous fashion to enthalpy, we can define the reaction entropy change as:

$$\Delta S_{rxn}{}^{o} = \sum_{products} v_i S_{m,i}{}^{o} - \sum_{reactants} v_i S_{m,i}{}^{o}$$

- Note that unlike $H_m{}^o$, which can = 0 for substances in their standard state, $S_m{}^o$ is $\neq 0$ (unless T=0)

Gibbs free energy

- let’s define the Gibbs free energy as $G=H-TS$.
- For a macroscopic change, $\Delta G = \Delta H - T\Delta S$
- This also leads to the familiar conclusion that for a spontaneous process $\Delta G \leq 0$
- ΔG also represents the *maximum non-PV work* that can be done by a system

How can ΔG be measured?

- As for the other thermodynamic quantities we have encountered, we can define the standard free energy change for a reaction as:

$$\Delta G_{rxn}{}^{o} = \sum_{products} v_i G_{m,i}{}^{o} - \sum_{reactants} v_i G_{m,i}{}^{o}$$

- As with enthalpy of formation, $\Delta G_f{}^o$ for an element (or a naturally occurring diatomic molecule) = 0.
- Experimentally ΔG is often obtained by determining ΔH and ΔS separately.

Gibbs energy and the equilibrium constant

- What does ΔG_{rxn}^{o} represent? It is the difference in the (molar) Gibbs energies of products and reactants, in their standard state.

  $\Delta G_{rxn}{}^{o} = -RT \ln K$ is the crucial link between thermodynamics (energy) and chemical equilibrium
- Notice that if K>1 then the products are favored at equilibrium, while if K<1 then the reactants are favored.
- In general, where Q is the reaction quotient

$$\Delta G_{rxn} = \Delta G_{rxn}{}^{o} + RT \ln Q$$

Calculate $\Delta H°_{298}$ for the process $Sb(s) + 5/2\ Cl_2(g) \longrightarrow SbCl_5(g)$ from the following information:

$Sb(s) + 3/2Cl_2(g) \longrightarrow SbCl_3(g)$

$\Delta H°_{298} = -314$ kJ

$SbCl_3(s) + Cl_2(g) \longrightarrow SbCl_5(g)$

$\Delta H°_{298} = -80$ kJ

Calorimetry – it's da bomb!

- Experiments may be done at constant volume (bomb) or constant pressure (coffee-cup)
- Entire system is *adiabatic* – there is no heat lost between the system (sample) and the surroundings (water bath and metal casing)
- The change in temperature of the calorimeter will be proportional to the heat that it absorbs: $Q \alpha \Delta T$, or $Q=C\Delta T$, where C is the heat capacity of the calorimeter.

Example

- In a preliminary experiment, the heat capacity of a bomb calorimeter assembly is found to be 5.15 kJ/^{o}C. In a second experiment, a 0.480 g sample of graphite (carbon) is placed in the bomb with an excess of oxygen. The water, bomb, and other contents of the calorimeter are in thermal equilibrium at 25.00 ^{o}C. The graphite is ignited and burned, and the water temperature rises to 28.05 ^{o}C. Calculate ΔH for the reaction: $C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)$

Solution

- The key to this problem is to realize that all the heat absorbed by the calorimeter must have come from the combustion reaction.
- First calculate the heat absorbed by the calorimeter using Q = CΔT:

$$Q_{cal} = 5.15\ \frac{kJ}{°C} * (28.05 - 25.00\ °C) = 15.7\ kJ$$

- The heat given up by the reaction must be equal and opposite to this: Q_{rxn} = -15.7 kJ

- We can then equate this to ΔU for the combustion of 1 mol of graphite:

$$\Delta U = \frac{-15.7\ kJ}{0.480\ g\ C} * \left(\frac{12.011\ g\ C}{1\ mol}\right) = -393\ kJ/mol$$

- Finally, recall that ΔH = ΔU + RTΔn for an isothermal process. Since the temperature change is pretty small (3.05 ^{o}C) we can assume that it is isothermal. Δn = (1-1) = 0 so ΔH ≈ ΔU. Thus ΔH = -393 kJ/mol

Calorimetry revisited – that's one fancy coffee cup!

- For isobaric measurements, use a thermally insulated vessel that is open to the atmosphere
- More sophisticated calorimeters can be used
  - Adiabatic flame combustion
  - Differential scanning
  - Isothermal titration
- For solids and liquids, $\Delta H \approx \Delta U$ since their volume is negligible (at least compared to gases)

Example

- A 15.5 g sample of a metal alloy is heated to 98.9 ^{o}C and then dropped into 25.0 g of water in a calorimeter. The temperature of the water rises from 22.5 to 25.7 ^{o}C. Calculate the specific heat of the alloy.

Solution

- The key to solving this problem is to realize that all the heat lost by the hot solid must be gained by the water in the cup.
- First we will find the heat absorbed by the water: Q_{H2O} = mcΔT so

$$Q_{H_2O} = 25.0g * 4.184\ \frac{J}{g\ {}^{\circ}C} * (25.7 - 22.5\ {}^{\circ}\mathrm{C}) = 334\ J$$

- This must be equal and opposite to the heat lost by the alloy (remember the sign convention!) so Q_{alloy} = -334 J
- Finally calculate the specific heat of the alloy:

$$c = \frac{Q}{m\Delta T} = \frac{-334\,J}{15.5g * (25.7 - 98.9\,°C)} = 0.29\ \frac{J}{g\,°C}$$

Example

- A 50.0 mL sample of 0.250M HCl at 19.50 ^{o}C is added to 50.0 mL of 0.250M NaOH, also at 19.50 ^{o}C, in a calorimeter. After mixing, the solution temperature rises to 21.21 ^{o}C. Calculate the heat of this reaction.

Solution

- First recognize the reaction that is taking place: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$
- Now let’s make a few assumptions/simplifications:
  - Take solution volumes to be additive so the total volume of solution is 50.0+50.0 = 100.0 mL
  - Consider the NaCl(aq) solution to be sufficiently dilute that the density and specific heat are the same as those for pure water (1.00 g/mL and 4.184 J/g^oC)
  - The system is perfectly insulated, so no heat escapes from the calorimeter
  - The heat required to warm any part of the calorimeter (other than the NaCl solution) is negligible)

- Find the heat retained in the calorimeter:

$$Q = mc\Delta T = \rho V c\Delta T = 100.0mL * 1.00\frac{g}{mL} * 4.184\frac{J}{g°\mathrm{C}} * (21.21 - 19.50\ °\mathrm{C}) = 715\, J$$

- Finally find the heat of reaction: Q_{rxn} = Q_p = -Q_{cal} = -715 J

Chemical Kinetics

- Study of the rates of chemical reactions
  - How quickly a process can take place
- Understanding of the mechanism of a reaction
  - How (on a molecular level) a process can take place
- Because these measurements are changing with respect to time and are sensitive to many variables, they are notoriously difficult experiments to carry out!

Factors affecting the rate of a chemical reaction

- Concentration
- Pressure (gases only)
- Temperature
- Presence of a catalyst
- Understanding the dependence of a reaction on these factors can aid our optimization of a chemical process

Measuring the rate of a reaction

- We can define the rate in terms of the loss of a reactant or the formation of a product:

$$v = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

  - Notice that this means the rate is related to the slope (tangent line) to the curve
- However this doesn’t take into account the stoichiometry of the reaction (i.e. if the reaction is R→2P the rate of formation of a product will be twice as great as the loss of reactant).
- In terms of a given component i, $v = \frac{1}{\nu_i}\frac{d[i]}{dt}$ where ν_i is the stoichiometric number.

In pictures

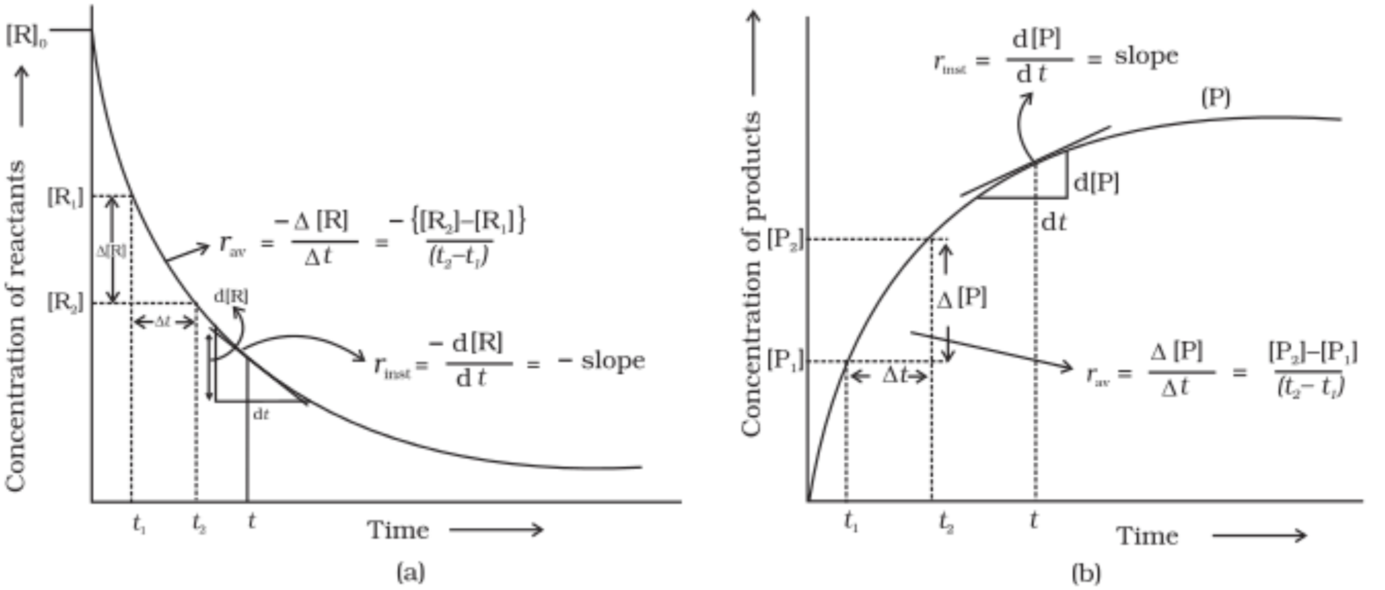


Fig. 4.1: *Instantaneous and average rate of a reaction*

http://textbook.s-anand.net/ncert/class-xii/chemistry/4-chemical-kinetics

Rate laws

- It is found experimentally that the rate of a reaction is usually proportional to the concentration of each reactant, raised to a certain power: $v = k[A]^x[B]^y$

  where x and y are the orders of the reaction with respect to A and B, respectively. The orders may be any real number (including 0 and fractions). The overall order is given by x+y.
- In general the orders must be determined experimentally and are NOT necessarily the stoichiometric coefficients of the reaction (unless the reaction is elementary).

Determination of the rate law for a reaction

- Isolation method – systematically vary the concentrations of the reactants so that all are in a large excess except for one. This allows the determination of the order of that one species.
- For example, if the general rate law is $v = k[A]^x[B]^y$ and B is present in a large excess, then its concentration can be assumed to be constant as the reaction proceeds, which means that d[B]/dt→0. Thus we can write the rate law as $v = k'[A]^x$ where $k' = k[B]^y$ and we can find the values of k' and x by curve-fitting.

Determination of the rate law for a reaction

- Typically the *initial* rates are measured. For example if B is in excess then the initial rate can be written as

$$v_o = k'[A]_o^{\,x}$$

- Thus we can plot v_o vs. $[A]_o$ and get k' and x by fitting the data nonlinearly (power law), or we can linearize the equation by taking the log of both sides:

$$\log v_o = \log k' + x \log[A]_o$$

- We can repeat this process where A is held in excess, and determine a new pseudo-rate constant k'' ($k'' = k[A]^x$) and y, and therefore also get the original rate constant k.

Example

- The recombination of iodine atoms in the gas phase in the presence of argon was investigated and the order of the reaction was determined by the method of initial rates. The initial rates of the reaction $2I(g)+Ar(g) \rightarrow I_2(g)+Ar(g)$ were as follows:

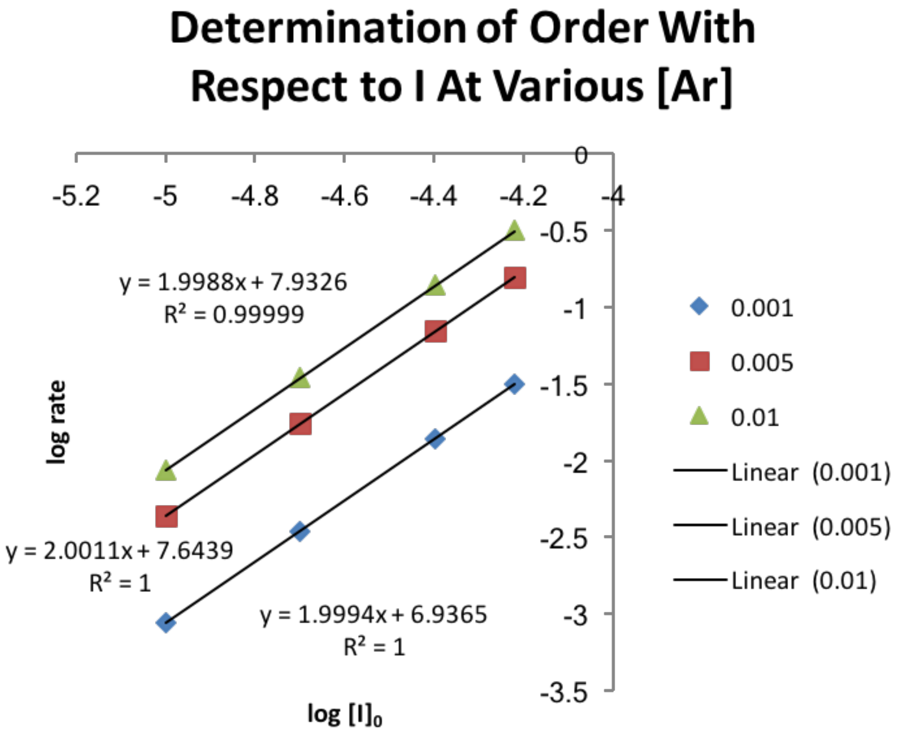
$[I]_o$ (10^{-5} mol/L)	**1.0**	**2.0**	**4.0**	**6.0**
v_o (mol/L*s)	a) $8.70 X 10^{-4}$	$3.48 X 10^{-3}$	$1.39 X 10^{-2}$	$3.13 X 10^{-2}$
	b) $4.35 X 10^{-3}$	$1.74 X 10^{-2}$	$6.96 X 10^{-2}$	$1.57 X 10^{-1}$
	c) $8.69 X 10^{-3}$	$3.47 X 10^{-2}$	$1.38 X 10^{-1}$	$3.13 X 10^{-1}$

Example

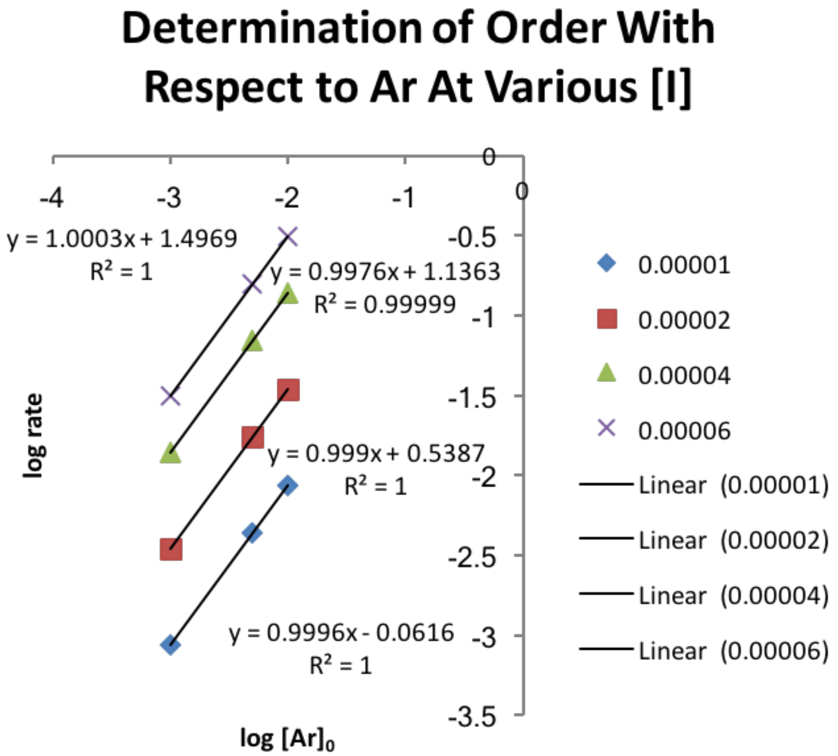
- The Ar concentrations are a)1.0 mmol/L, b) 5.0 mmol/L and c) 10.0 mmol/L. Determine the orders of reaction with respect to the I and Ar atom concentrations and the rate constant.

Solution

- Since the rate law will be of the form $v_o = k[I]_o{}^x[Ar]_o{}^y$, we need to plot the dependence of the rate on both $[I]_o$ and $[Ar]_o$. A log-log plot will be helpful as the slope will give us the order with respect to that substance.



Determination of Order With Respect to I At Various [Ar]



Determination of Order With Respect to Ar At Various [I]

Solution

- From the first graph, the slope is 2 which means that the reaction is 2nd order with respect to I. From the second graph, the slope is 1 which means that the reaction is 1st order with respect to Ar. Thus the rate law is

$$v_o = k[I]_o{}^2[Ar]_o$$

- Notice that this is the rate law only for the *initial rate* – it is possible that the reaction has a different rate law as the reaction proceeds.

Solution

- We can get the rate constant from the intercepts of either set of lines. In the first experiment, $k' = k[Ar]_0$. In the second experiment, $k''=k[I]_0^2$. In either case, $k \approx 8.6*10^9$ L^2/mol^2s.

log k'	k'	$[Ar]_0$	k
6.9365	8639727	0.001	8639726607
7.6439	44045343	0.005	8809068674
7.9326	85624885	0.01	8562488476

log k’’	k’’	$[I]_0$	k
-0.0616	0.867761	0.00001	8677607450
0.5387	3.457005	0.00002	8642512347
1.1363	13.68674	0.00004	8554212160
1.4969	31.39786	0.00006	8721626801

How will each of the following affect the rate of the reaction: $CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$ if the rate law for the reaction is rate = $k\,[NO_2]\,[CO]$?

(a) Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm

(b) Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

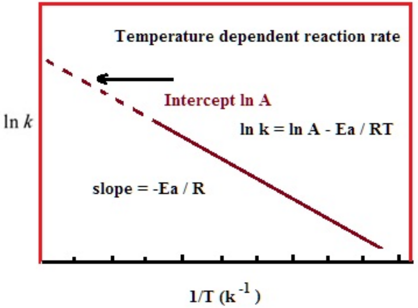
The Arrhenius equation

- A plot of ln k vs 1/T should give a straight line, with a slope of E_a/R and an intercept of ln A:

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

- As T→∞, k→k_o (or A), which is called the *frequency factor*. It is also called the pre-exponential factor since the above equation can be written as

$$k = Ae^{-E_a/RT}$$



http://chemistry.tutorvista.com/inorganic-chemistry/arrhenius-equation.html

More on the Arrhenius equation

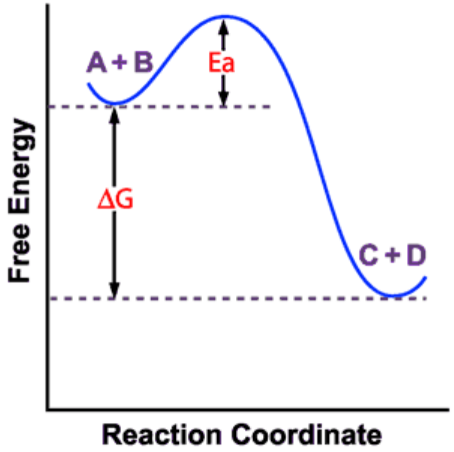
- The pre-exponential factor A represents the fastest possible rate for a reaction, which would only be limited by diffusion. This can be interpreted as being related to the rate of successful collisions between reactant molecules to yield product molecules.
- Notice that the fraction of molecules with an energy greater than E_a is given by an exponential decay, known as a Boltzmann distribution. Only those molecules with an energy that exceeds the activation energy will be able to react to form products.
- The higher the activation energy, the more the rate constant will depend on T.

Temperature dependence of the reaction rate

Arrhenius equation

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

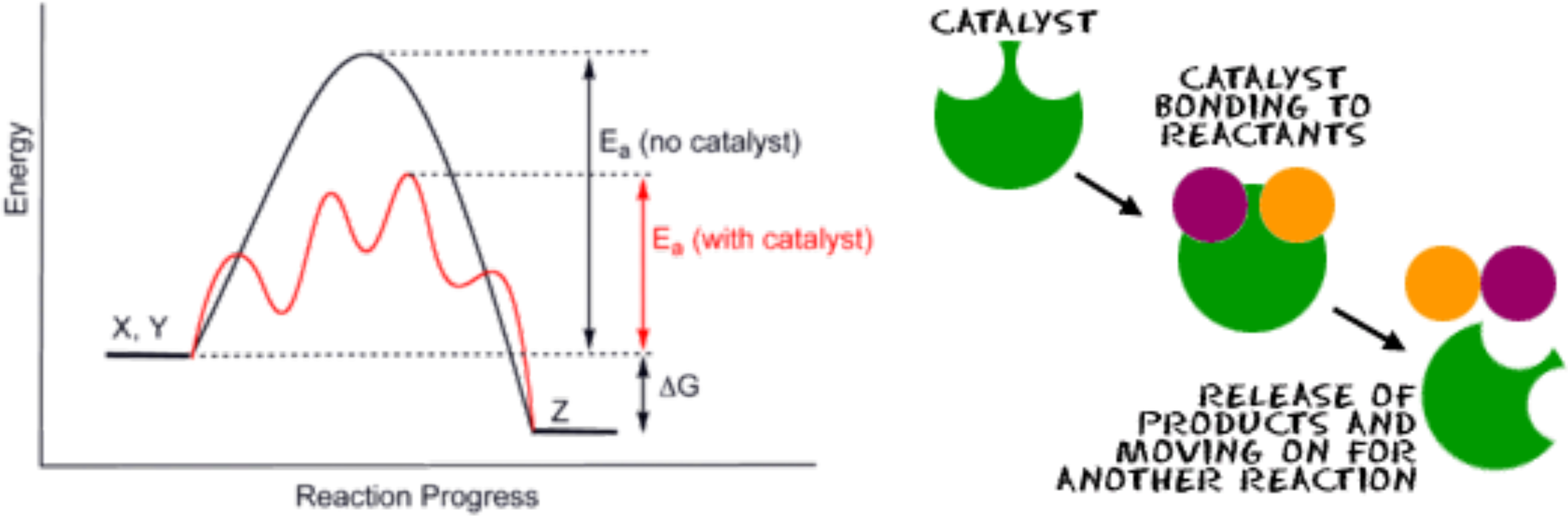
E_a is the activation energy of the reaction.



http://www.wiley.com/college/boyer/0470003790/reviews/kinetics/kinetics_stability.htm

Role of a catalyst

- Accelerate the rate of a reaction
  - Lower activation energy
  - Provide alternate path
- Does not change the thermodynamics or equilibrium of a reaction
  - ΔG, ΔH, ΔS and K are all the same as for the uncatalyzed reaction


Energy
X, Y
E_a (no catalyst)
E_a (with catalyst)
ΔG
Z
Reaction Progress
CATALYST
CATALYST BONDING TO REACTANTS
RELEASE OF PRODUCTS AND MOVING ON FOR ANOTHER REACTION

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Theoretical description of the rate laws

- Although the parameters for a rate law are experimentally determined, it is sometimes possible to calculate (or predict) them from first principles. This requires a knowledge of the way in which the reaction takes place, also known as the mechanism.
- Most reactions are thought to occur in a series of (relatively) well understood steps, each of which is known as an elementary reaction.
- In an elementary reaction, typically a small number (1-3) atoms, molecules or ions collide with each other and form a product.

Theoretical description of the rate laws

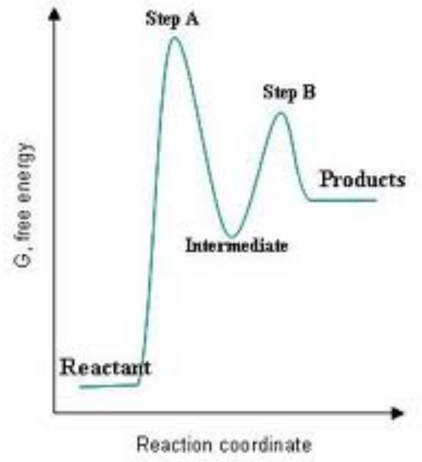
- Molecularity – the number of molecules (or atoms or ions) that come together in an elementary reaction
  - *Unimolecular*- one particle breaks apart or rearranges, i.e. dissociation or isomerization
  - *Bimolecular*- two particles collide with each other
  - *Termolecular* (rare)-three particles *simultaneously* collide with each other

Theoretical description of the rate laws

- Because elementary reactions are of a known molecularity, we can write down the rate laws for them simply by looking at how many species are present:
  - $A \rightarrow P$ $v=k[A]$
  - $A+B \rightarrow P$ $v=k[A][B]$
- A <u>mechanism</u> is a combination of elementary reactions that tries to explain the sequence of events (steps) of a chemical reaction

Rate-determining step

- The rate-determining step is the slowest "relevant" step in a chemical reaction, and determines the overall rate of the reaction. It also dictates how much product can be formed.
- Typically the slowest step in a chemical reaction has the highest activation energy since $k = Ae^{-E_a/RT}$
- In the diagram on the right, the local minima correspond to *intermediates* – this means that they can be (theoretically) isolated.
- The maxima correspond to *transition states* – they are very unstable and not isolable



http://chemwiki.ucdavis.edu/Wikitexts/UC_Davis/UCD_Chem_2C%3A_Larsen/Chem_2C%3A_Homework/Team_1/Chapter_24%3A_Kinetics