Soil Physical Chemistry

Lac.1

1- Activity and Standard state:

- Activity is a measure of the effective concentration of a reactant or product in a chemical reaction. The concentration of a substance does not always accurately describe its reactivity in a chemical reaction. The activity or effective concentration differ from the actual concentration because of inter-ionic attraction and repulsion.

- The different between activity and concentration becomes substantially large when the concentration of the reactants is large.
- At high concentrations, the individual particles of the reactants may exert a mutual attraction to each other, or exhibit interactions with the solvent in which the reaction takes place .

- On the other hand, in very dilute condition, interactions are less, if not negligible. To correct for the difference between actual and effective concentration, the ***activity coefficient*** (ϒ) is introduced.
- The activity coefficient expresses the ratio of activity to concentration:
- $(aA)/(cA) = \Upsilon$ or $aA = \Upsilon cA$

ϒ= activity coefficint

aA = activity of species A

cA = concentration of species A

The activity coefficient is not a fixed quantity, but varies in value depending on the condition. In very dilute (infinite dilution) conditions, the activity coefficient approaches unity. The value of ϒ ~ 1.0 and, hence, activity equals concentration:

$$aA = cA$$

- Activity coefficient apply to cations as well as to anions:
- Cation: $ϒ+ = (a+) / (m+)$
- Anion: $ϒ- = (a-) / (m-)$
- Where :
- m+ = concentration of cations
- m- = concentration of anions

- The mean activity coefficient is then:

- $\Upsilon \pm = \{[(a+)/(m+)][(a-)/(m-)\}]^{1/2}$

- Or $\Upsilon \pm =[(\Upsilon+)(\Upsilon-)]^{1/2}$

- The mean ionic activity formulated above is valid only for monoprotic (1-1) electrolytes, such as HCl and NaCl. For polyprotic electrolytes, the formula for the mean activity coefficient of the ions change into:
- Or $\Upsilon \pm =[(\Upsilon+)(\Upsilon-)^{2}]^{1/3}$
- For compounds such as $CaCl_2$
- Or $\Upsilon \pm =[(\Upsilon+)^{2}(\Upsilon-)]^{1/3}$
- For compounds such as H_2SO_4

- Consequently, the mean activity coefficient of the ions in (1-3) and (3-1) electrolytes, e.g., $AlCl_3$, is then
- $\Upsilon \pm = [(\Upsilon +)(\Upsilon -)^{3}]^{1/4}$ for compounds as $AlCl_3$
- Or $\Upsilon \pm = [(\Upsilon +)^{3}(\Upsilon -)]^{1/4}$ for compounds as H_3PO_4
-

- Activity coefficient in the standard state is indicated by $ϒ^{\circ}$. A standard state is defined for each substance in terms of a set of reference conditions. Each pure substance in its standard state is assigned an activity of unity.

- The standard state of solid and liquids is usually chosen as the pure substances under standard conditions of 1 atm pressure and a specified temperature. Since 298.15K,eqivalent to 25°C,is commonly used temperature, it is called the ***reference temperature***. The standard state of gas is a perfect gas, obeying
- $PV = nRT$ at 1 atm pressure and specified temperature.

- Debye-Huecke Theory and Activity Coefficients:
- The individual ion activity coefficient can be calculated using the Debye-Hueckle equation:
- $-\log \Upsilon i = (A z_i^{2} \Gamma I) / (1 + d_i B \Gamma I)$
- ***Where:***
- ***A,B =constant of the solvents at a specified temperature and pressure.***
- ***Z= valence i= ion species I = ionic strength***
- ***di = effective diameter of the ion***

Ionic Strength:

The concept of ionic strength was introduced by Lewis and Randall (1921) to assess the combined effect of the activities of several electrolytes in solution on a give electrolytes. It is a useful relation in comparing solutions of diverse composition, as in soil water, river water, lake water, and ocean water.

- The ionic strength is defined as:

- $I = \frac{1}{2} \Sigma mi \, z_i^2$

- Where:

- m = moles of ions L-1

- zi = charge of the ions.

- I = ionic strength

- The summation is taken over all ions, positive and negative. For example the ionic strength of a 1 M $CaCl_2$ solution is:
- $\mathbf{I = \frac{1}{2} \Sigma[(m_{Ca} \times 2^2) + (m_{Cl} \times 1^2) + (m_{Cl} \times 1^2)]}$
- $\mathbf{I = \frac{1}{2} \Sigma [(1 \times 4) + 2(1 \times 1)] = 3}$

- That of a ½ M NaCl solution is:

- $\mathbf{I=½\ \Sigma[(m_{Na}\ x\ 1^2)+(m_{Cl}\ x\ 1^2)]}$

- $\mathbf{I=½\ \Sigma\ [(1/2\ x\ 1)+(1/2\ x\ 1)]=1/2}$

Example:

- Try to calculate the Ionic strength of the following soil solution, for which chemical analysis revealed ion concentration as listed:

Ions	ppm(mg/L)	mol/L	$m_i z_i^2$
Na^+	**2300**	**(2300/23*1000) = 0.100**	**$0.100*1^2 = 0.100$**
Ca^{2+}	**80**	**(80/40*1000) = 0.002**	**$0.002*2^2 = 0.008$**
Mg^{2+}	**48**	**(48/24*1000) = 0.002**	**$0.002*2^2 = 0.008$**
SO_4^{2-}	**288**	**(288/96*1000) = 0.003**	**$0.003*2^2 = 0.012$**
Cl^-	**1750**	**(1750/35*1000) = 0.050**	**$0.050*1^2 = 0.050$**
CO_3^{2-}	**60**	**(60/60*1000) =0.001**	**$0.001*2^2 = 0.004$**
HCO_3^-	**2745**	**(2745/61*1000) = 0.045**	**$0.045*1^2 = 0.045$**

- $I=1/2(0.100+0.008+0.008+0.012+0.050+0.004+0.045) = 0.114$
- The average ionic strength for water in rocks is about 0.100, whereas streams and lakes have ionic strength of about 0.010. The ionic strength of ocean water is approximately 1.0. The higher the ionic strength, the lower will be the ion activity (lower ϒ).

Solubility Product Principle

Dealing with the equilibrium of sparsely soluble solids

Lac.2

How do we deal with solids?

- The solids are only slightly soluble (very little dissolves in water).
- What does dissolve behaves as a strong electrolyte (100% dissociation).
- Solutions become saturated and solid may remain at bottom of container.
- Can solubility be manipulated?

AgCl (s) ⑦ Ag^+ + Cl^-

s s s

- What is the equilibrium constant?

$$K_{sp} = (Ag^+)(Cl^-) \qquad = s^2$$

- Now what about the value of the K_{sp}?

$$K_{sp} = 1.6 \times 10^{-10}$$

- Can we calculate the solubility, s?

$$s = (K_{sp})^{1/2} = 1.3 \times 10^{-5}\ M$$

Write the dissociation of the solids and the K_{sp} expressions

- AgBr (s) ⑦ Ag^{+} + Br^{-} $K_{sp} = (Ag^{+})(Br^{-})$

- CaF_2 (s) ⑦ Ca^{++} + $2F^{-}$ $K_{sp} = (Ca^{++})(F^{-})^2$

- $Fe(OH)_3$ (s) ⑦ Fe^{+3} + $3OH^{-}$

$K_{sp} = (Fe^{+3})(OH^{-})^3$

What is the pH of a bottle of Milk of Magnesia, a common antacid?

Milk of Magnesia is $Mg(OH)_2$ with $K_{sp} = 8.9 \times 10^{-12}$

$$Mg(OH)_2\,(s) \;⑦\; Mg^{++} + 2OH^-$$

$$s \qquad\qquad s \qquad\qquad 2s$$

$$K_{sp} = (Mg^{++})(OH^-)^2 = s(2s)^2 = 4s^3$$

$$s = (K_{sp}/4)^{1/3} = 1.3 \times 10^{-4}\ M$$

$(OH^-) = 2s = 2.6\ 10^{-4}$ M pOH = 3.58 pH = 10.42

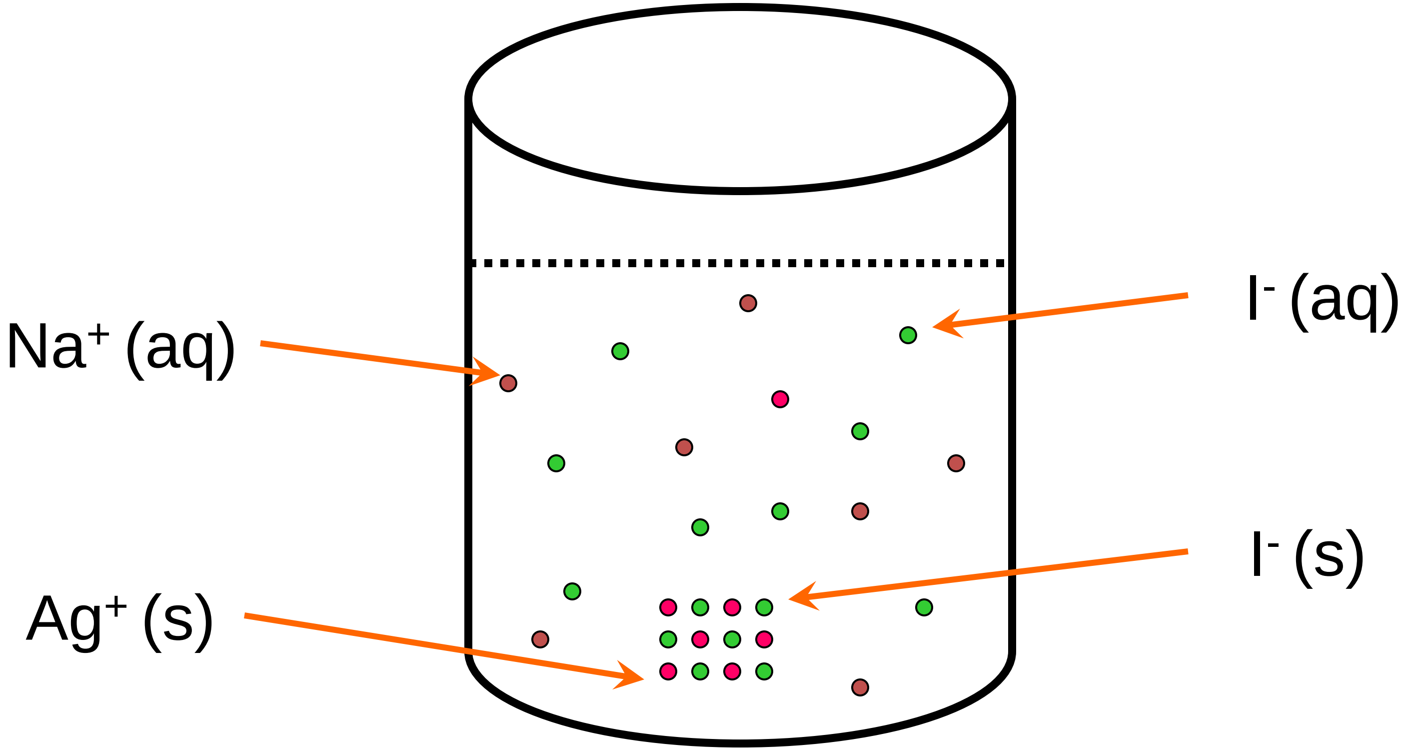
Would the solubility of AgI be the same or different in a solution of NaI? If different, how?

To address this you need to write a reaction and consider Le Chatelier’s principle-

AgI(s) ⑦ Ag^+ + I^-

The addition of the NaI causes the reaction to shift to the left. Hence the solubility decreases!

A beaker with NaI, where the aqueous I^- is radioactive, and a crystal of AgI is placed in the beaker, where the I^- in the solid is non-radioactive.



Na^+ (aq)

I^- (aq)

I^- (s)

Ag^+ (s)

The beaker is allowed to sit for a period of time.

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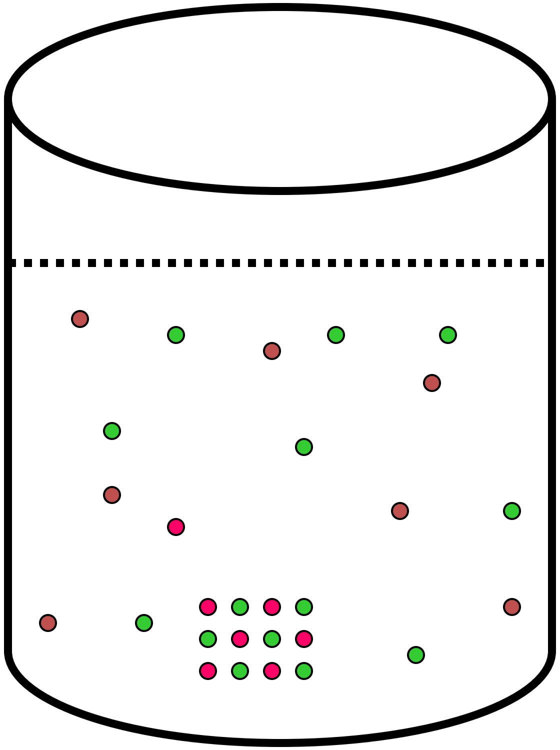
After a period of time, what do you notice about the distribution of the radioactive I^-?



Explain the observation.

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What happened in the beaker?

$AgI (s)$ ⑦ $Ag^+ + I^-$

dissolves to saturate the aqueous NaI solution with AgI

However, after time passes, the radioactive I^- is found in the solid AgI.

The process is dynamic, as AgI is constantly dissolving and crystallizing.

What influences the solubility?

- What would happen if we added HCl to the AgCl solution? Decreases solubility

- What would happen if we added NH_3 to the AgCl solution?

The addition of ammonia adds a new twist! As the Ag^+ reacts to form a <u>complex ion</u> as shown below:

$Ag^+ + 2NH_3$ ⑦ $Ag(NH_3)_2^+$ K = ?

Free silver ion

Complexed silver ion

The formation of complex ions

Ammonia will react with silver (I) ion:

Reactant or product favored?

$Ag^+ + NH_3$ ⑦ $\cancel{Ag(NH_3)^+}$ $K_1 = 2.1 \times 10^3$

$\cancel{Ag(NH_3)^+} + NH_3$ ⑦ $Ag(NH_3)_2^+$ $K_2 = 8.2 \times 10^3$

$Ag^+ + 2NH_3$ ⑦ $Ag(NH_3)_2^+$ $K_f = K_1K_2 = 1.7 \times 10^7$

Thiosulfate, used in photography, is an even stronger complexing agent. Why?

$Ag^+ + 2S_2O_3^{-2}$ ⑦ $Ag(S_2O_3)_2^{-3}$ $K_f = 2.9 \times 10^{13}$

Formation constant

Let’s examine some reactions:

$AgCl\ (s)$ ⑦ $\cancel{Ag^+} + Cl^-$ K_{sp}

Add these two reactions

$\cancel{Ag^+} + 2NH_3$ ⑦ $Ag(NH_3)_2^+$ K_f

$AgCl\ (s) + 2NH_3$ ⑦ $Ag(NH_3)_2^+ + Cl^-$ $K_{sp}K_f$

How is the solubility of AgCl (s) influenced?

According to Le Chatelier’s principle- the solubility of AgCl (s) increases as the (NH_3) is increased.

(Lac3)

Solubility Product:

- The solubility product is the product of ion concentration in saturated solution of a difficulty soluble salt. Consider the dissociation of BA occurring as follows:

- $BA \longleftrightarrow B^{+} + A^{-}$

- Such as $CaSO_4$:
- $CaSO_4 \longleftrightarrow Ca^{2+} + SO_4^{2-}$

- Since the activity of pure solids is unity at equilibrium, application of the mass action Law gives:
- $\mathbf{K_{eq} = K_{sp} = (B^+)(A^-)}$

- In this type of reaction K_{eq} is called the ***solubility product constant*** and the symbol K_{sp} is used.
- The negative Log of K_{sp} is $\mathbf{pK_{sp}}$
- $\mathbf{pK_{sp} = - Log\ K_{sp}}$

- The smaller the(**pK_{sp}**), the more soluble substance. However, if two solutions, each containing one of the ions of a difficulty soluble salt, are mixed, no precipitation will tack place unless the product of the ion concentration in the mixture is greater than the solubility product.

- In saturated solution the concentration of B^+ ion is equal to that of A^- ion. Since the salt is completely ionized, the solubility (S) of the salt can be represented by the individual ion concentration.
- $S = (B^+) = (A^-)$
- By substituting these in equation of pK_{sp}, the K_{sp} can be written as:
- $K_{sp} = (A^-)(A^-) = (A^-)^2$
- Or
- $K_{sp} = (B^+)(B^+) = (B^+)^2$
-

- Therefore:
- $(B+) =(A-) = \Gamma\ K_{sp}$ or $S = \Gamma\ K_{sp}$
- If the system is not at equilibrium, the expression is called activity product (AP) or the ion activity product (IAP) instead of K_{eq}
- Unless the system is exactly in equilibrium, the AP will not be equal to K_{eq}.
- If AP/ $K_{eq} > 1$, the reaction tend to go to the ***Left .***
- If AP/ $K_{eq} < 1$, the reaction tend to go to the ***Right .***(dissolution) or the formation of (A^-) and (B^+).

- Log AP/ K_{eq} will be zero at equilibrium.
- The most common use of these expression is in describing the extent to which a particular solution is super saturated or under saturated with respect to a particular solid phase.
- The term ***saturation index*** is often used for Log (IAP/$K_{\mathbf{eq}}$) for dissolution reaction. The saturation index (SI) for gypsum, for example, would be
- **SI = Log (a Ca^{2+} * a SO_4^{2-}) solution**
- **K_{sp} (gypsum)**

- A useful modification to all expression for state of saturation is to normalize for the number of ions (***v***) in the expression for the ion activity product. This give the saturation ratio (***SR***):

- $SR= (IAP/K_{eq})^{1/v}$

- Example: The composition of well-water in sulamani is:

Ions	*mg/L*	*mmol/L*	*mol/L*	
Ca^{2+}	109	(109/40) =2.72	(2.72/1000)	= 0.002
Mg^{2+}	24	(24/24) =0.99	(0.99/1000)	= 0.002
Na^+	117	(117/23 =5.09	(5.09/1000)	= 0.005
K^+	7	(7/39 =0.18	(0.18/1000)	= 0.00018
HCO_3^-	183	(183/ 61)=3.00	(3.00/1000)	= 0.003
$SO4^{2-}$	238	(238/96)=2.48	(2.48/1000)	= 0.0024
Cl^-	171	(171/35) = 4.82	(4.82/1000)	= 0.0049
H_4SIO_4	48			
Temp	25°C			

- a) What is the ionic strength of the solution?
- b) What are the activity coefficient for Ca^{2+} and SO^{2-}_4, based on the extend Debye-Hukel equation?
- c) By how much is the water under saturated or Super saturated with respect to gypsum ($CaSO_4$)?

- Solution:
- $I = ½ \Sigma C_i Z_i^2$
- $I = 1/2[2.72+0.99+2.48)*4+5.09+0.18+3.2+4.82]*10^{-3}$
- $= 18.9*10^{-3}$ Mol/L
- **=** 0.0189 Mol/L
- H_4SiO_4 does not appear in the ionic strength because it is ***uncharged.***

- b) The activity coefficients are given by:
- $\log \Upsilon ca^{2+} = -(Az_{ca^{2+}}{}^{2}\Gamma\text{ɪ})/(1+a_i B \Gamma\text{ɪ})$
- $= \quad \dfrac{-0.508 * 4 * (0.0189)^{0.5}}{1+0.328*5*(0.0189)^{0.5}}$
- $= -0.228$
- $\Upsilon Ca^{2+} = 0.591$ for Ca^{2+} and SO_4^{2-}
- c) The ion activity product (IAP) is given by IAP = a Ca^{2+} * aSO_4 = m Ca^{2+} * ΥCa^{2+} *
- m SO_4^{2-} * ΥSO_4^{2-}
- $= (2.72*10^{-3})*0.591 * (2.48*10^{-3}) *0.591$
- $=2.36*10^{-6} = 10^{-5.63}$ under saturated

- The ratio IAP/Ksp = $10^{-5.63}$ / $10^{-4.60}$
- = $10^{-1.03}$
- The number is less than 1, indicating under saturation .
- SR $(10^{-1.03})^{½}$ = $10^{-0.52}$ = 0.31
- SI = Log (IAP/Ksp) =-1.03

- ***Soil as thermodynamic system:***
- From the point of view of thermodynamic, a soil is an assembly of solid, liquid and gaseous matter, as well as are pository of electromagnetic and gravitational fields. These characteristics, together with a surface that enclose the macroscopic region of space field by the soil, define the thermodynamic soil system.

- Thus thermodynamic soil system contain both matter and physical fields and is bounded by a surface of arbitrary shape. This boundary surface is called the thermodynamic wall surrounding the soil system.
- The properties of a soil whether fundamental or not, whose numerical values depend on the quantity of matter in the soil (e.g volume and entropy) are called extensive.

- The properties whose values are not depends
- On the quantity of matter in the soil (e.g, pressure, bulk density, and temperature) are called ***intensive.***
- The ***intensive*** properties of a soil are mathematical field variable (i.e, their values are associated with point in space that are located in the soil).
- If the values of its ***intensive*** properties are same a very where in a soil, the is said to be homogeneous.

- If any one of its intensive properties varies (on the macroscopic scale) from point to point, the soil is said to be hertogenous. Natural soils are invariably heterogeneous because their intensive properties vary spatially on a macroscopic scale, both from the effects of pedochemical properties and from the direct effect of the gravitational field of the earth.

- The thermodynamic wall surrounding a soil is very important part of the system. If the wall permits the free transfer of both matter and thermal energy either in or out, the soil is called an open system and wall is said to be ***diathermal and permeable***. If only certain types of matter may be transfer through the wall, it is said to be ***semipermeable***.

- If the wall permits only the transfer of thermal energy, it is said to be diathermal and the soil is called ***closed system***.
- Finally, if the wall dose not permit the transfer of either matter or thermal energy, it is said to be insulating and the soil is called an a ***diabetic system.***
-

- ***equilibrium constant from thermodynamic data:***
- The derivation of the laws governing equilibrium constant comes from thermodynamics. Chemical thermodynamics is the science of energy relationships within chemical system. In any chemical reaction, energy changes are occurring. A system, which is not in equilibrium, will spontaneously undergo change by releasing energy.

- At equilibrium the energy changes of the reactants must equal the energy changes of the products, and the following relationship is valid:
- ***ΔGr=Σ free energy products - Σ free energy reactants…………………………(1)***
- The standard-state free energy of reaction can be calculated from the standard-state free energy of formation as well. It is the sum of the free energies of formation of the products minus the sum of the free energies of formation of the reactants:
- ***ΔG°r=Σ ΔG°f products - Σ ΔG°f reactants***

- Since the absolute Gibbs free energy (G) of a substance is not measurable, reference states are selected for each substance and change in free energy (ΔG) are then measured.
- ***Equation (1) expressed the first law in thermodynamics.***

- ΔGr is the free energy change of reaction.
- The ΔGr for a reaction is the maximum energy change for that reaction as useful work, measured at constant temperature and pressure.
- or Gibbs free energy(G): The energy associated with a chemical reaction that can be used to do work. The free energy of a system is the sum of its enthalpy (H) minus the product of temperature (Kelvin) and the entropy (S) of the system:
- $G = H - TS$

- ***Gibbs free energy of reaction(Δ Gr):***
- The change in the enthalpy (ΔH) of the system minus the product of temperature (Kelvin) and the change in the entropy (ΔS) of the system:
- $\Delta G = \Delta H - T\Delta S$

- ***Standard-state free energy of reaction(ΔG°):***
- The free energy of reaction at standard state conditions:
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- Standard-State conditions:
- The partial pressures of any gases involved in the reaction is 0.1MPa.
- the conditions of all agues solutions are 1M

- ***Standard-State Free Energy of Formation ($\Delta G_f°$):***
- The change in free energy that occurs when a compound is formed from its elements in their most thermodynamically stable states at standard-state conditions. In other words, it is the difference between the free energy of a substance and the free energies of its elements in their most thermodynamically stable states at standard-state conditions.

- Recall from the enthalpy notes that reactions can be classified according to the change in enthalpy (heat):
- Endothermic – absorbed heat, $\Delta H^\circ > 0$
- Exothermic – releases heat, $\Delta H^\circ < 0$
- Reactions can also be classified according to the change in the free energy of the reaction:
- Endergonic – non spontaneous, $\Delta G^\circ > 0$
- Exergonic –spontaneous, $\Delta G^\circ < 0$
-

- If a reaction is favorable for only one of either entropy or enthalpy, the standard-state free energy equation must be used to determine whether the reaction is spontaneous or not.
- Next we will show how ΔG° is related to the equilibrium constant (K_{eq}) for a reaction. Consider the general reaction:
- $aA + bB \longleftrightarrow cC + dD$
- (When a, b, c and c are number of moles)
-

- The Gibbs free energy of a mole of A at some pressure and temperature is G_A. This is also the definition of the chemical potential of A or $G_A=\mu_A$
- $\mu =(\partial G/\partial n_i)_{T,P}$
- G_A or $\mu_A= \Delta G^\circ_A+RT \text{ Ln } (A)$
- T is degree Kelvin, ΔG°_A is the standard mole Gibbs free energy of A. ΔG°_A is the Gibbs free energy of A at unit activity of A (when [A]=1). The activity can be roughly thought of as the fraction of its total concentration that participates in reactions. For ions the activity is usually less than its concentration.

- For a moles of A:
- A GA = $a\Delta G^{\circ}_{A} + RT \ Ln \ [A]^{a}$
- Now ΔG_{r} for the general reaction equals the difference in the sum of values for the products minus that for the reactants.
- $\Delta G_{r} = (cG_{C} + dG_{D})-(aG_{A} + bG_{B})$
- $\Delta G_{r}= cG_{C} + dG_{D} – aG_{A} – bG_{B}$
- Introducing expressions for the other reacting substances similar to that for A, we obtain:
- $\Delta G_{r} =[c\Delta G^{\circ}_{C} + d\Delta G^{\circ}_{D} – a\Delta G^{\circ}_{A} – b\Delta G^{\circ}_{B}] +RT \ Ln[C]^{c} + RT \ Ln[D]^{d} - RT \ Ln[A]^{a} - RT \ Ln[B]^{b}$

- Collecting and combining terms:
- $\Delta G_{r} = \Delta G_r{}^{\circ} + RT \, Ln \dfrac{[C]^c \, [D]^d}{[A]^a \, [B]^b}$
- At equilibrium $\Delta G_r = 0$
- $\Delta G_r{}^{\circ} = - RT \, Ln \dfrac{[C]^c \, [D]^d}{[A]^a \, [B]^b}$
- or simply $\Delta G_r{}^{\circ} = - RT \, Ln \, Keq.$
- $Ln \, Keq = - \Delta G_r{}^{\circ} / RT$
- Or $Log \, Keq = - \Delta G_r{}^{\circ} / 2.303 \, RT$
-

- Log Keq = - $\Delta G_r°$ / 5.708 at 25°C where $\Delta G_r°$ is in Kj / mol.
- Log Keq = - $\Delta G_r°$ / 1.364 at 25°C where $\Delta G_r°$ is in Kcal / mol.
- ***Example calculation:***
- The reaction of Hematite and Magnetite plus Oxygen as an example:
- $6Fe_2O_3 \longleftrightarrow 4Fe_3O_4 + O_2$
- ***Hematite*** ***Magnetite***
- From standard (in Table)

	ΔG_f° (Kj/mol)	ΔH_f° (Kj/mol)	S° (Kj/mol.K)
Hematite	-742.8	-824.7	$87.7*10^{-3}$
Magnetite	-1012.9	-1116.1	$205.0*10^{-3}$
Oxygen	0	0	$60.4*10^{-3}$

- $\Delta G_r^\circ = 4*(-1012.9) + 0 - 6*(-742.8) = +202.6$ Kj/mol
- $\Delta H_r^\circ = 4*(-1116.1) + 0 - 6*(-824.7) = +241.9$ Kj/mol
- $\Delta S_r^\circ = 4*(205.0*10^{-3}) + 60.4*10^{-3} - 6(87.7*10^{-3}) = +131.6*10^{-3}$ Kj/mol. K
- Note that $\boldsymbol{\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ}$ where T=298.15K (25°C)
- $\boldsymbol{\Delta G_r^\circ} = 241.9 - 298.15(+131.6*10^{-3}) = -202.6$
- $\mathrm{Log}K = -\Delta G_r^\circ / 5.708 = -202.6/5.708$
- $K = -35.49$

- Spontaneous, ΔG° is negative ($\Delta G^\circ < 0$, **K**eq>1)
- Non-Spontaneous, ΔG° is positive ($\Delta G^\circ > 0$, **K**eq<1).
- Equilibrium: $\Delta G^\circ = 0$, **K**eq=1
- If a reaction is favorable for both enthalpy ($\Delta H^\circ < 0$) and entropy ($\Delta S^\circ > 0$) changes, then the reaction will be spontaneous ($\Delta G^\circ < 0$) at any temperature.
- If a reaction is unfavorable for both enthalpy ($\Delta H^\circ > 0$) and entropy ($\Delta S^\circ < 0$) changes, then the reaction will be non-spontaneous ($\Delta G^\circ > 0$) at any temperature.

- Sample free energy calculation (standard-state conditions):

$$NH_4NO_{3\,(s)} \xrightarrow{H_2O} NH_4^{+}{}_{(aq)} + NO_3^{-}{}_{(aq)}$$

Compounds	$\Delta H_f°$	$\Delta S°$
$NH_4NO_{3\,(s)}$	-365.56	151.08
$NH_4^{+}{}_{(aq)}$	-132.51	113.4
$NO_3^{-}{}_{(aq)}$	-205.0	146.4

- Calculate ΔH°,ΔS° and ΔG° for the above reaction to determine whether the reaction is spontaneous or not?

- First let’s calculate ΔH_f°. Note in the above reaction, one mole of $NH_4\ NO_3$ dissociates in water to give one mole each of NH_4^+ and NO_3^-:
- $\Delta H^\circ = \Sigma n H^\circ_{f\ \text{products}} - \Sigma n H^\circ_{f\ \text{reactants}}$
- $\Delta H^\circ =[(1\ \cancel{\text{mol}}\ NH_4^+ *-132.51\text{kJ}/\cancel{\text{mol}})(1\cancel{\text{mol}}\ NO_3^- *-205.0\text{kJ}/\cancel{\text{mol}})]-(1\cancel{\text{mol}}\ NH_4\ NO_3 *-365.56\text{kJ}/\cancel{\text{mol}})$
- $\Delta H^\circ = -337.51+365.56$
- $\Delta H^\circ = 28.05\ \text{kJ}$

- Next, let’s calculate $\Delta S°$:
- $\Delta S° = \Sigma nS°_{\text{products}} - \Sigma nS°_{\text{reactanrs}}$
- $\Delta S° = [(1\ \cancel{\text{mol}}\ NH_4^+ * 113.4\text{J/mo}\cancel{\text{l-K}}) + (1\text{mol}\ \cancel{\text{NO}}_3^- * 146.4\text{J/}\cancel{\text{mol}}\text{-K})] - (1\cancel{\text{mol}}\ NH_4\ NO_3 * 151.08\text{J/mol-}\cancel{\text{K}})$.
- $\Delta S° = 259.8 - 151.08$
- $\Delta S° = 108.7\text{J/K}$
- Now we can plug in these values we’ve calculated into the free energy equation.

- Note: The units of ΔH°_f is kJ and the units of ΔS° is J/K. Since ΔG° is generally reported in kJ, we can divide ΔS° by 1000 to converted it to units of kJ/K.
- Note: The temperature in the free energy equation must be in Kelvin, so we must convert the given temperature in Celsius to Kelvin by adding 273.15.
- $T_k = 25^\circ C + 273.15 = 298.15 K$
- $\Delta S^\circ = 108.7 J/K * 1kJ/1000 J = 0.1087kJ/K$
- $\Delta H^\circ = 28.05kJ$

- $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$ plug in ΔH°, ΔS°, and T
- $\Delta G^\circ = 28.05\text{kJ} - (298.15\text{ K})(0.1087\text{ kJ/K})$
- $\Delta G^\circ = 28.05\text{kJ} - 32.41\text{kJ}$
- $\Delta G^\circ = -4.4\text{kJ}$

- Temperature and Free Energy
- If a reaction is favorable for enthalpy ($\Delta H° < 0$), but unfavorable for entropy ($\Delta S° < 0$), then the reaction becomes ***Less Spontaneous*** as temperature increase.
- The standard-state free energy equation states that:
- $\Delta G° = \Delta H° - T\Delta S°$
- If entropy ($\Delta S°$) is unfavorable, the $\Delta S°$ is negative. Subtracting a negative number is the same as adding the respective positive number.

- As the temperature increases, the TΔS° factor (which is added to the enthalpy if the entropy is unfavorable) increases as well. Eventually, the TΔS° factor becomes larger than ΔH° and ΔG° becomes positive, i.e. the reaction is no longer spontaneous.
-

- Sample Calculations (Standard-state conditions):

$$N_{2\,(g)} + 3H_{2\,(g)} \longleftrightarrow 2\,NH_{3\,(g)}$$

Compound	***$\Delta H_f°$***	***$\Delta S°$***
$N_{2\,(g)}$	0	191.61
$H_{2\,(g)}$	0	130.68
$NH_{3\,(g)}$	-46.11	192.45

- 1) Calculate ΔH° and ΔS° for the above reaction. Explain what each of the signs mean.
- $\Delta H^\circ = \Sigma nH^\circ_{f\ \text{products}} - \Sigma nH^\circ_{f\ \text{reactants}}$
- $\Delta H^\circ = [(1\cancel{\text{mol}}\ N_2 * 0\text{kJ}/\cancel{\text{mol}}) + (3\cancel{\text{mol}}\ H_2 * 0\text{kJ}/\cancel{\text{mol}})] - (2\cancel{\text{mol}}\ NH_3 * -46.11\text{kJ}/\cancel{\text{mol}})$
- $\Delta H^\circ = -92.22$ kJ
- ΔH° is negative which is favorable.
- $\Delta S^\circ = \Sigma\ nS^\circ_{\text{products}} - \Sigma nS^\circ_{\text{reactants}}$
- $\Delta S^\circ = (2 \text{ mol } NH_3 * 192.45\text{J/mol-K}) – [(1 \text{ mol } N_2 * 191.61\text{J/mol - K}) + (3 \text{ mol } H_2 * 130.68\text{/mol-K})]$
- $\Delta S^\circ = 384.9 - 583.65 \qquad \Delta S^\circ = -198.75$ J/K

- $\Delta S°$ is negative which is favorable.
- 2) Predict the above reaction is spontaneous at 25°C.
- $T_K = 25°C + 273.15 = 298.15K$
- $\Delta S° = -198.75 J/K * 1kJ/1000J = -0.19875 kJ/K$
- $\Delta H° = -92.22 kJ$
- $\Delta G° = \Delta H° - T\Delta S°$ plug in $\Delta H°$,$\Delta S°$,and T
- $\Delta G° = -92.22 kJ – (298.15K)(-0.19875 kJ/K)$
- $\Delta G° = -92.22 kJ + 59.25 kJ$
- $\Delta G° = -32.96 kJ$
- $\Delta G°$ is negative, so the reaction is ***Spontaneous.***

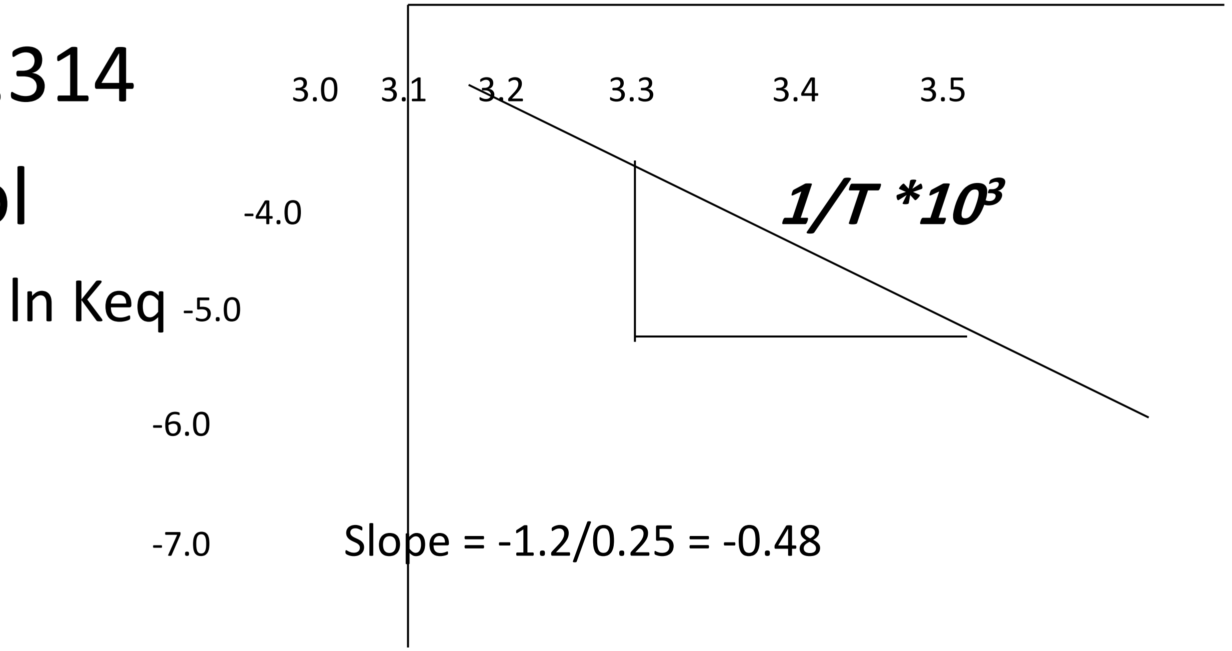
- ***Example:*** The thermodynamic equilibrium constant of enzymatic reaction in the soil determined with the following results:

Temperatures (°C).	***Keq of association/dm³ mol⁻¹***
22	$1.83 * 10^3$
30	$5.78 * 10^3$
38	$8.10 * 10^3$

Calculate the value of ΔG° for this reaction?

Temperatures (°C)	***Temperatures (K)***
22	***22+ 273.15 = 295.15***
30	***30 + 273.15 = 303.15***
38	***38+ 273.15 = 311.15***

- ***$1/T * 10^3$*** ***$\ln K_{eq}$*** $\ln K_{eq} = -\Delta G_r^\circ / RT$
- 3.389 -6.303
- 3.300 -5.153
- 3.215 -4.816
- Slope = $-\Delta G^\circ / R$ ***($R = 8.314$ J/mol-K)***
- $-0.48 = -\Delta G^\circ / 8.314$
- $\Delta G^\circ = 3.99$ J/mol
-



Slope = -1.2/0.25 = -0.48

Free energy and Cell potentials:

- Cell potential a measure of the driving force behind an electrochemical reaction, reported in volts. The potential of an electrochemical cell measures how far an oxidation-reduction reaction is from equilibrium.

- The Nernst equation relates the standard-state cell potential with the cell potential of the cell at any moment in time:
- $Cu \xrightarrow{\qquad} Cu^{2+} + 2e^-$ -0.34V
- $2\ (Ag^+ + e^- \xrightarrow{\qquad} Ag)$ +0.80V

$Cu + 2\ Ag^+ + \cancel{2e^-} \xrightarrow{\qquad} Cu^{2+} + \cancel{2e^-} + 2Ag$ +0.46V

$Cu_{(S)} + 2\ Ag^+_{(aq)} \xrightarrow{\qquad} Cu^{2+}_{(aq)} + 2Ag_{(S)}$

If we rearrange the equation, we get:

$E = E° - RT/\ nF\ lnQ$ multiply the entire equation by nF.

- $nFE = nFE^\circ - RTLnQ$
- This equation is very similar to the equation that relates the standard-state free energy of reaction with the free energy of reaction at any moment in time during a reaction:
- $nFE = nFE^\circ - RT \ Ln \ Q$
- $\Delta G = \Delta G^\circ + RT \ Ln \ Q$
- We can convert these equations to get the following: **$\Delta G = nFE$ and $\Delta G^\circ = nFE^\circ$**
- This shows that free energy of a oxidation-reduction reaction is directly proportional to the cell potential of the reaction.
-

- ***Example:***
- $H_2O \qquad H^+ + OH^-$
- $\Delta G^\circ = \Sigma\ \Delta G^\circ$ products - $\Sigma\ \Delta G^\circ$ reactants
- $= \Sigma(\Delta G^\circ_{H+} + \Delta G^\circ_{OH-}) - (\Delta G^\circ_{H2O})$
- $= [0 + (-37.6) - (-56.7)]$
- $= -37.6 + 56.7 = -19.1$
- $\text{Log } K = - \Delta G^\circ / 1.364$
- $\text{Log } K = -19.1/1.364 = -14.002932$
- $\text{Log } K = -14.002932 \quad \therefore K = 10^{-14}$
- $K = (H^+)(OH^-) / (H_2O)$ activity $H_2O = 0$
- $K = (H^+)(OH^-) = 10^{-14}$

Chemical Kinetics

- ***Study of the rates of chemical reactions and the factors that influence the rates.***
- ***Thermodynamics – does a reaction take place?***
- ***Kinetics – how fast does a reaction proceed?***

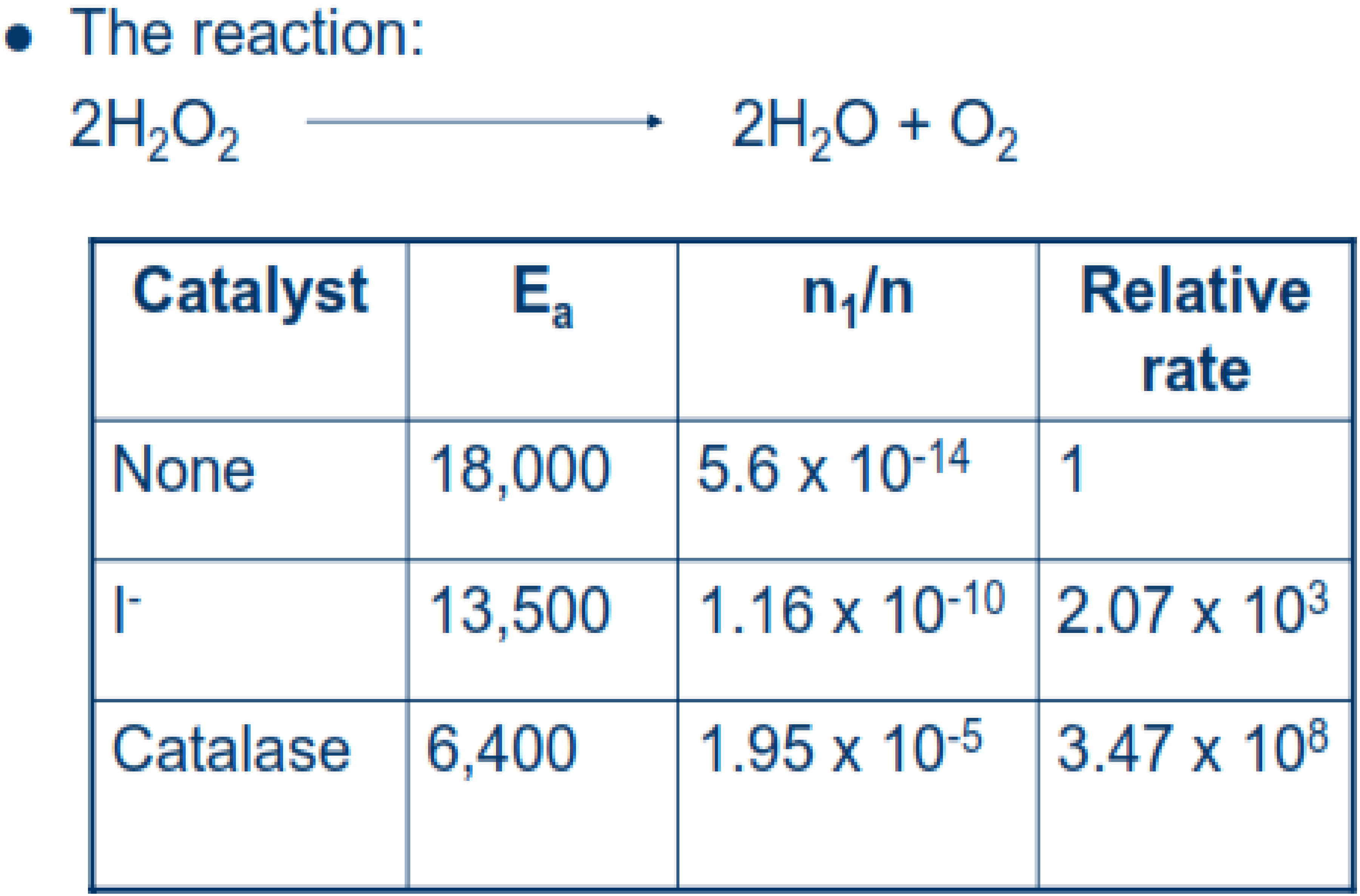
▣ *Collision Theory:*

– Collisions between reacting molecules are necessary before a reaction can occur.

– Only those collisions having sufficient energy are effective in bringing about a reaction activation.

– Colliding molecules must be properly oriented with respect to one another for the reaction to take place.

- ***Example:***

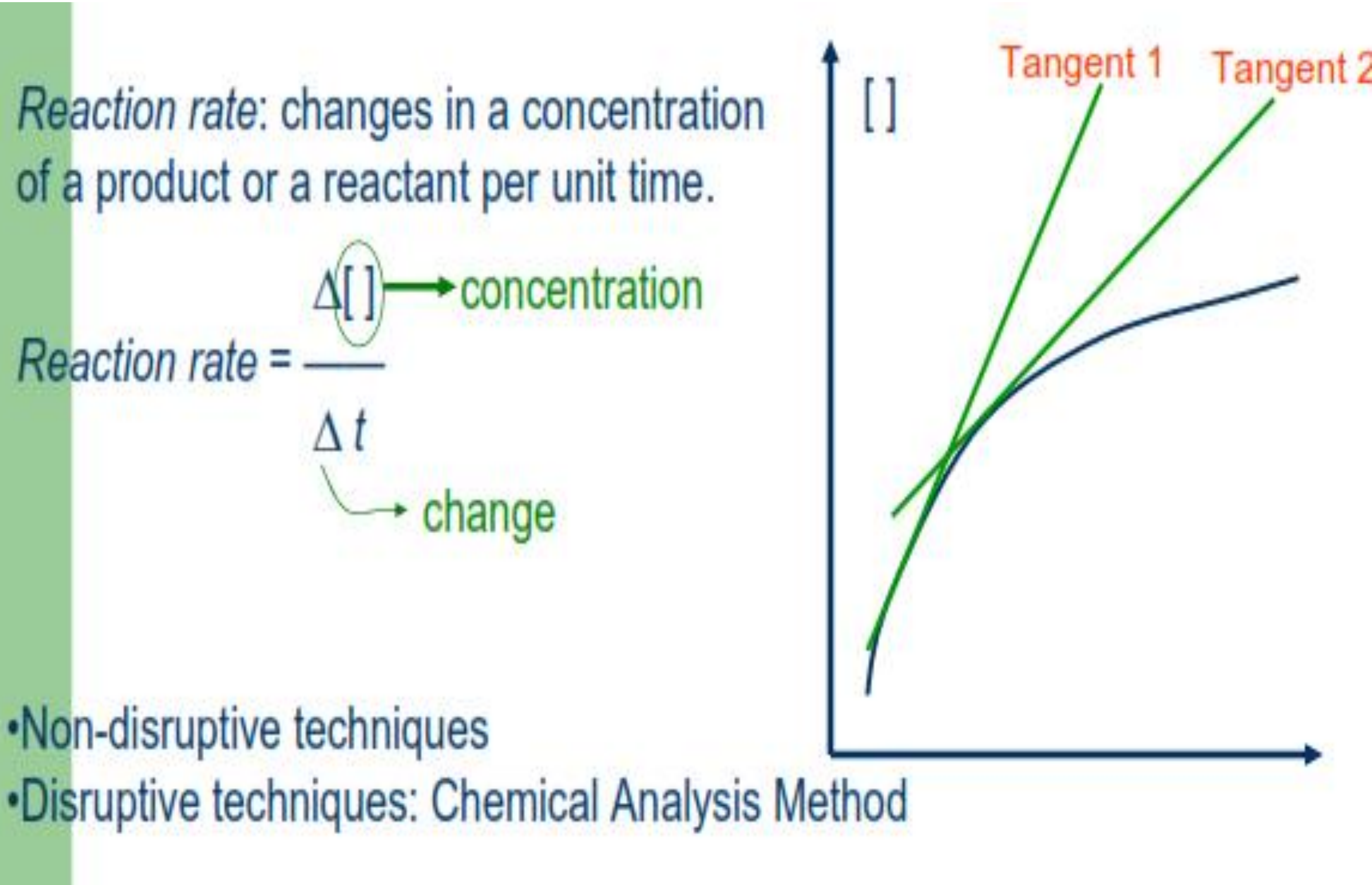


- The reaction:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Catalyst	**E_a**	**n_1/n**	**Relative rate**
None	18,000	5.6×10^{-14}	1
I^-	13,500	1.16×10^{-10}	2.07×10^{3}
Catalase	6,400	1.95×10^{-5}	3.47×10^{8}

- ***Reaction Rate Defined:***



Reaction rate: changes in a concentration of a product or a reactant per unit time.

$$\text{Reaction rate} = \frac{\Delta[\,] \longrightarrow \text{concentration}}{\Delta t}$$

change

- Non-disruptive techniques
- Disruptive techniques: Chemical Analysis Method

Reaction rate is the change in the concentration of a reactant or a product with time (*M*/s).

$$A \longrightarrow B$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

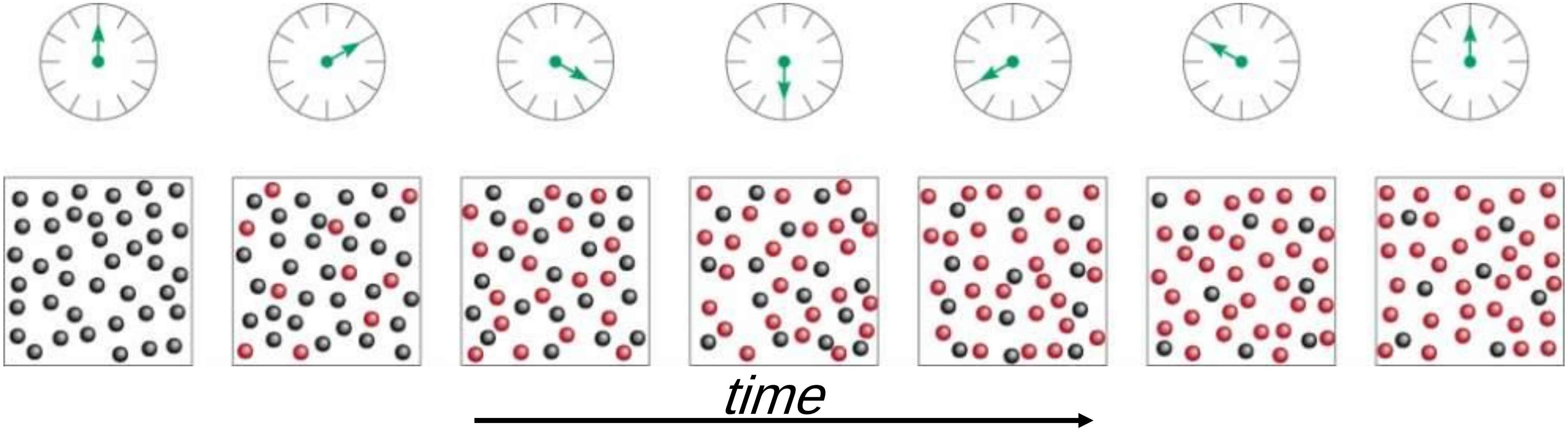
$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

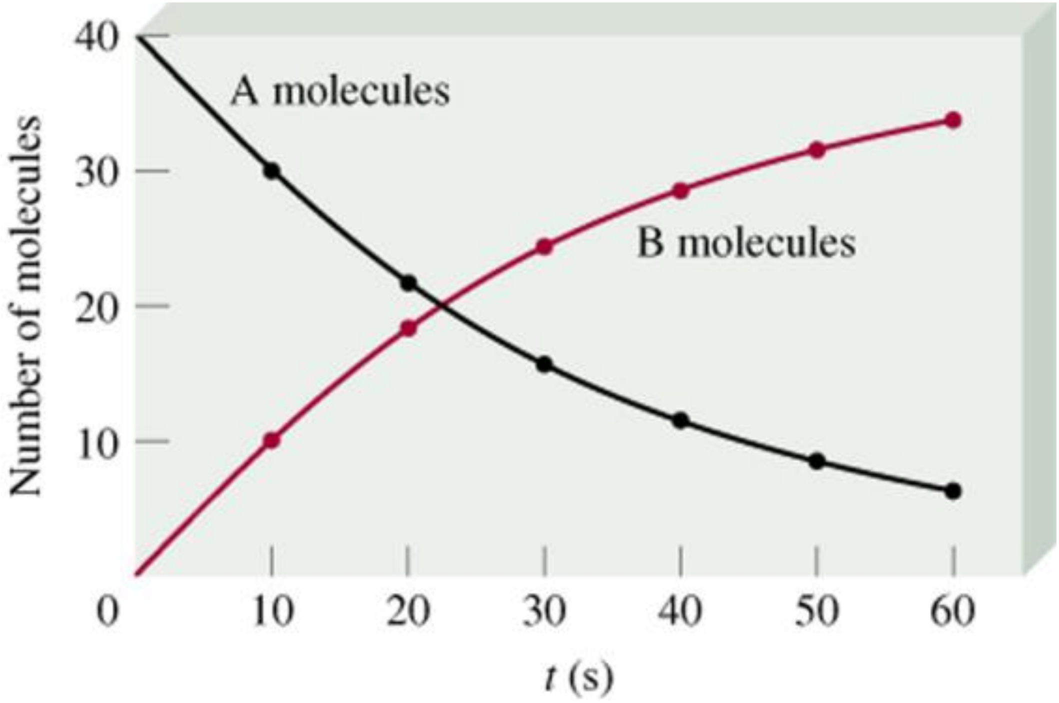
Because [A] decreases with time, $\Delta[A]$ is negative.

$A \longrightarrow B$

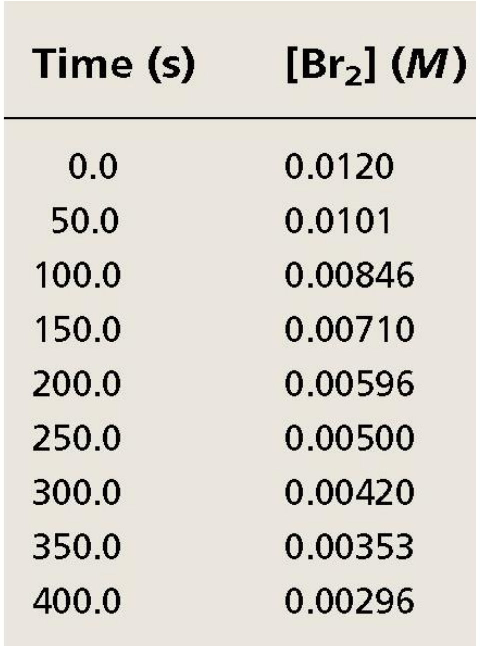


$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

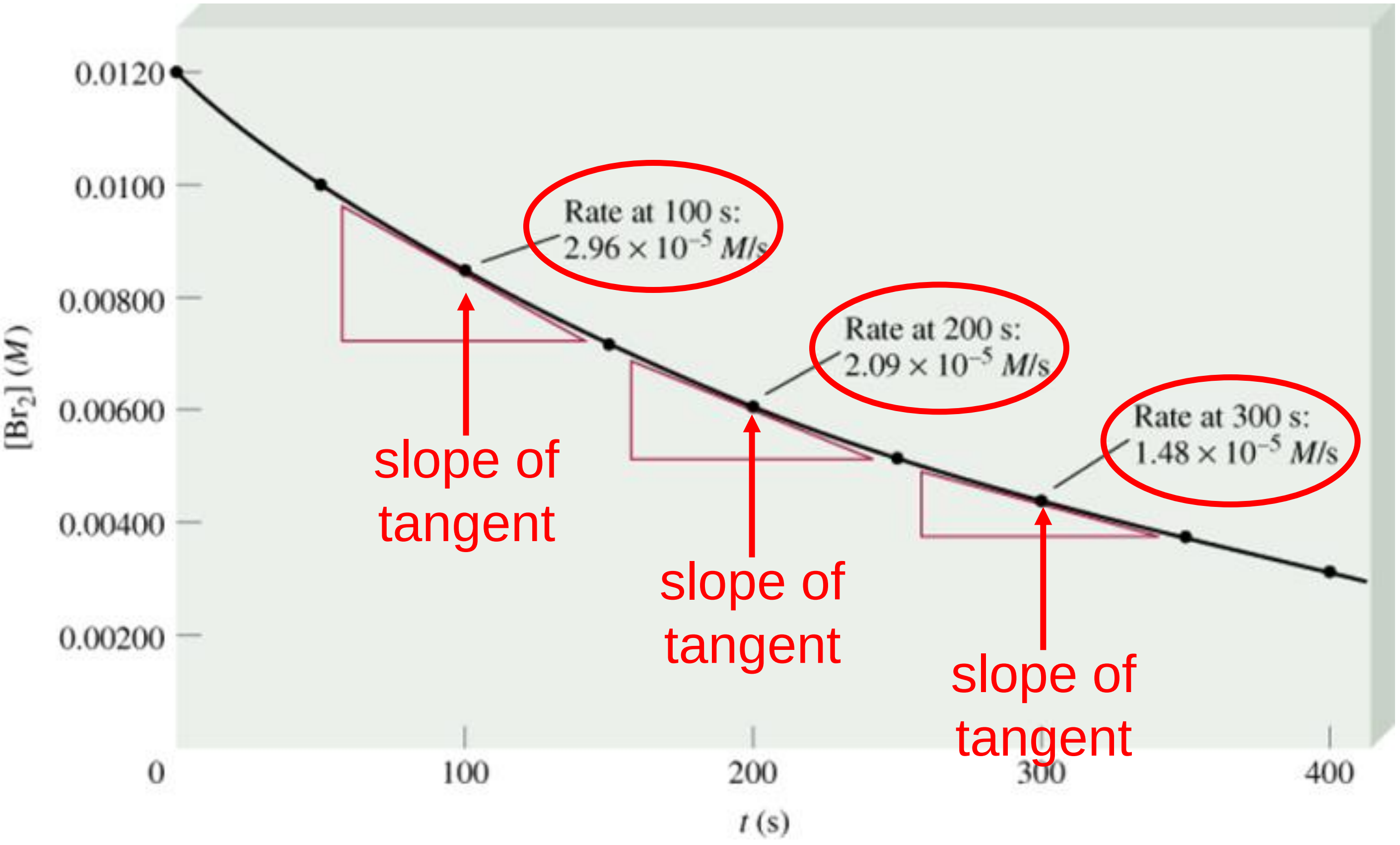
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



$$Br_2\,(aq) + HCOOH\,(aq) \longrightarrow 2Br^-\,(aq) + 2H^+\,(aq) + CO_2\,(g)$$



Time (s)	$[Br_2]$ (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



slope of tangent

slope of tangent

slope of tangent

$$\textbf{\textit{average rate}} = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

instantaneous rate = rate for specific instance in time

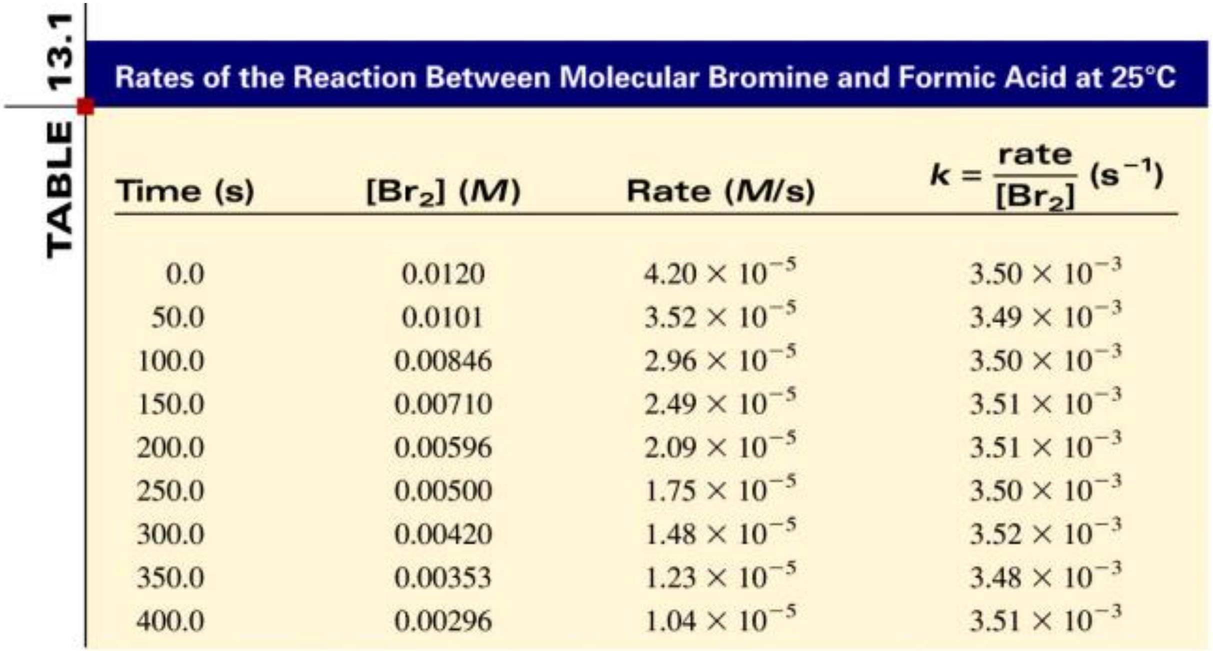


TABLE 13.1

Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

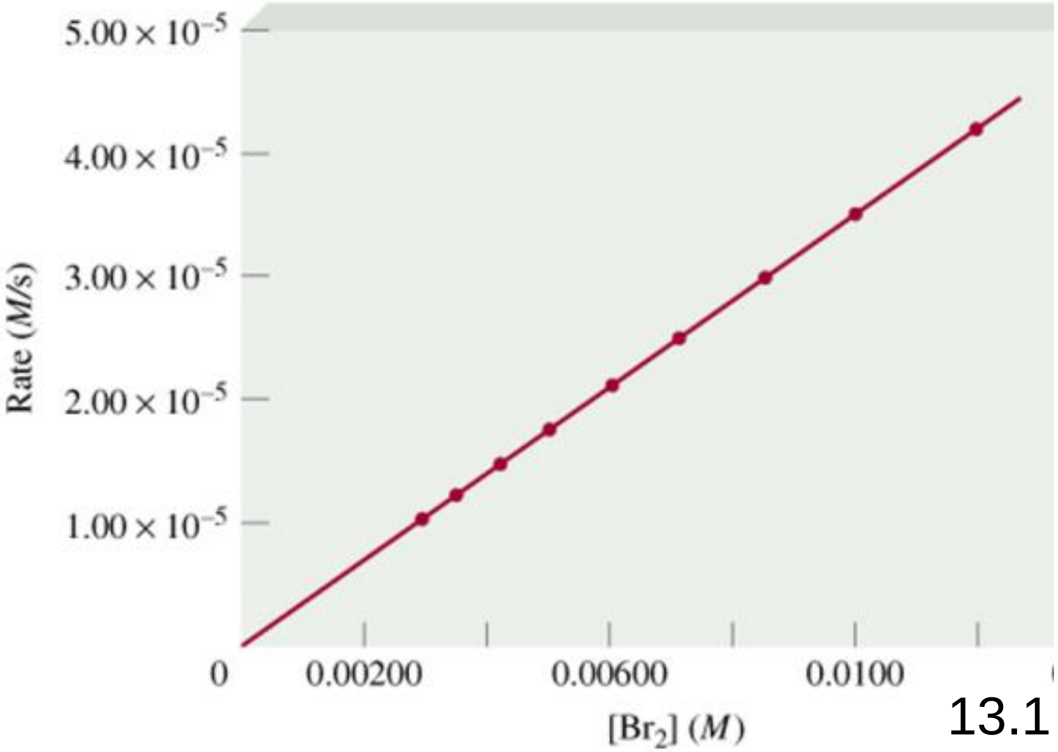
Time (s)	$[Br_2]$ (*M*)	Rate (*M*/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

rate α $[Br_2]$

rate = $k\,[Br_2]$

$$k = \frac{\text{rate}}{[Br_2]} = \textit{\textbf{rate constant}}$$

$= 3.50 \times 10^{-3}\ s^{-1}$



Factors that Affect Reaction Rate

1. **Temperature:**

   Collision Theory: When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.

   Kinetic Theory: Increasing temperature means the molecules move faster.

2. **Concentrations of reactants:**

   More reactants mean more collisions if enough energy is present

3. Catalysts

- Speed up reactions by lowering activation energy.

4. Surface area of a solid reactant

- Bread and Butter theory: more area for reactants to be in contact.

5. Pressure of gaseous reactants or products Increased number of collisions.

The Rate Law

The ***rate law*** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = k\,[A]^{\enclose{circle}{x}}[B]^{\enclose{circle}{y}}$$

reaction is ***x*th order** in A

reaction is ***y*th order** in B

reaction is **(x +y)th order overall**

$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$\text{rate} = k\,[F_2]^x[ClO_2]^y$

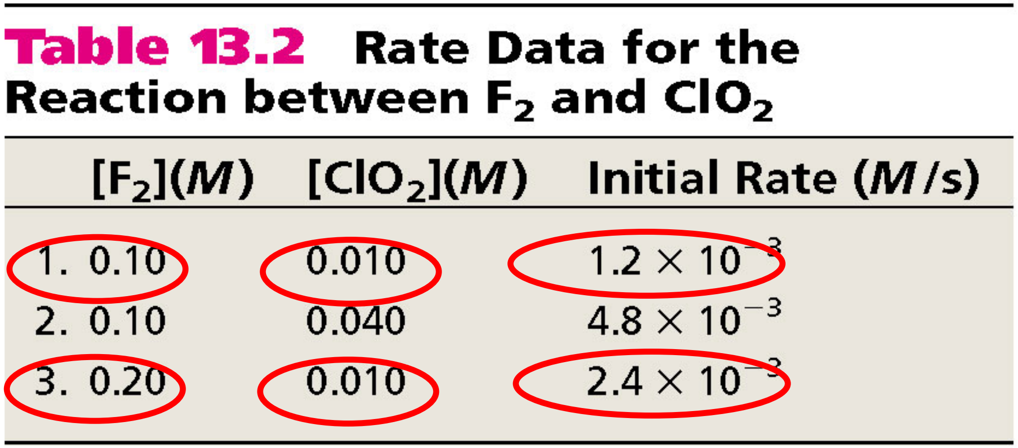


Table 13.2 **Rate Data for the Reaction between F_2 and ClO_2**

	$[F_2]$ (M)	$[ClO_2]$ (M)	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

Double $[F_2]$ with $[ClO_2]$ constant

Rate doubles

$x = 1$

Quadruple $[ClO_2]$ with $[F_2]$ constant

Rate quadruples

$y = 1$

$\text{rate} = k\,[F_2][ClO_2]$

Run #	Initial [A] ($[A]_0$)	Initial [B] ($[B]_0$)	Initial Rate (v_0)
1	1.00 M	1.00 M	1.25×10^{-2} M/s
2	1.00 M	2.00 M	2.5×10^{-2} M/s
3	2.00 M	2.00 M	2.5×10^{-2} M/s

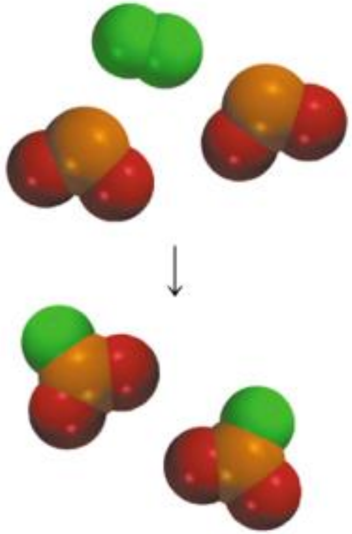
What is the order with respect to A?	0
What is the order with respect to B?	1
What is the overall order of the reaction?	1

$[NO_{(g)}]$ (mol dm^{-3})	$[Cl_{2(g)}]$ (mol dm^{-3})	Initial Rate (mol dm^{-3} s^{-1})
0.250	0.250	1.43×10^{-6}
0.250	0.500	2.86×10^{-6}
0.500	0.500	1.14×10^{-5}

What is the order with respect to Cl_2?	1
What is the order with respect to NO?	2
What is the overall order of the reaction?	3

Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{rate} = k\,[F_2][ClO_2]^1$$

Example: Determine the rate law and calculate the rate constant for the following reaction from the following data:

$S_2O_8^{2-}\ (aq) + 3I^-\ (aq) \rightarrow 2SO_4^{2-}\ (aq) + I_3^-\ (aq)$

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

rate = $k[S_2O_8^{2-}]^x[I^-]^y$

$y = 1$

$x = 1$

rate = $k[S_2O_8^{2-}][I^-]$

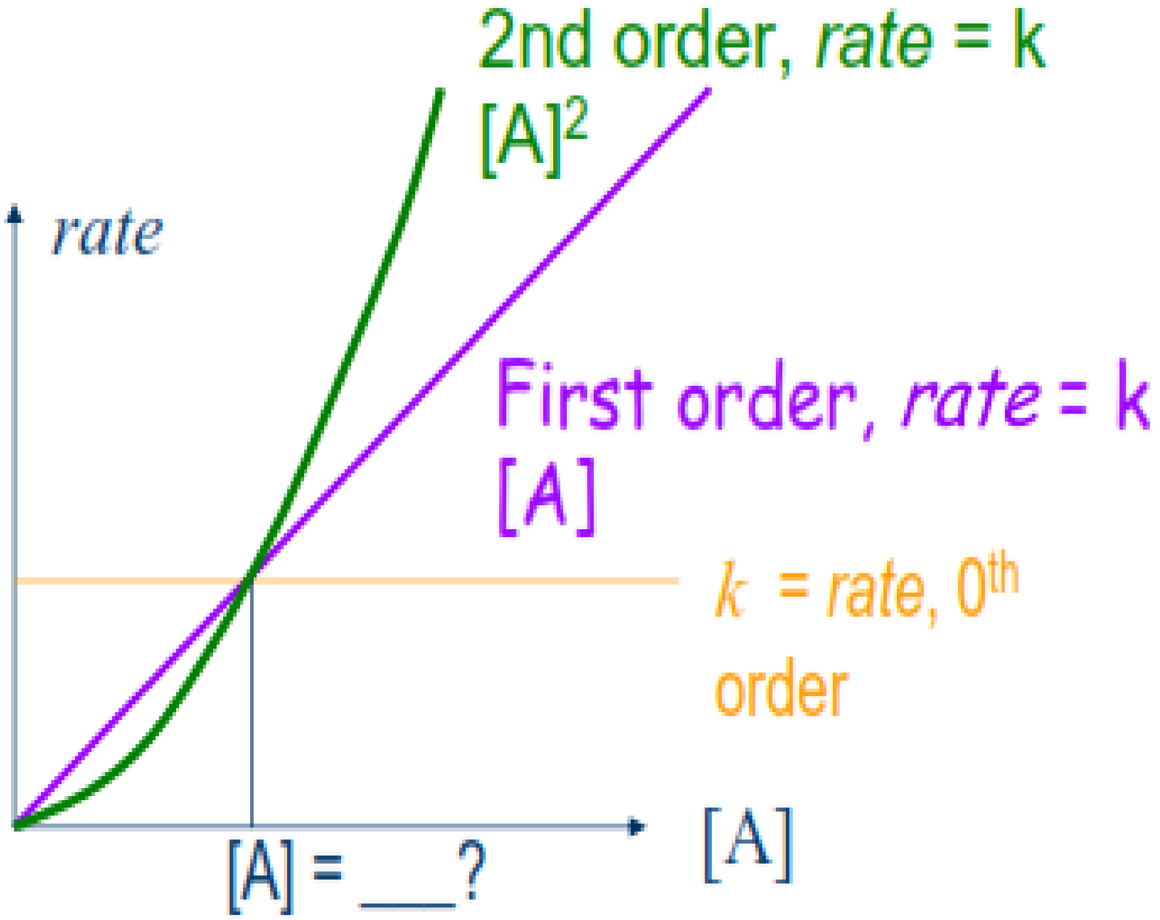
Double $[I^-]$, rate doubles (experiment 1 & 2)

Double $[S_2O_8^{2-}]$, rate doubles (experiment 2 & 3)

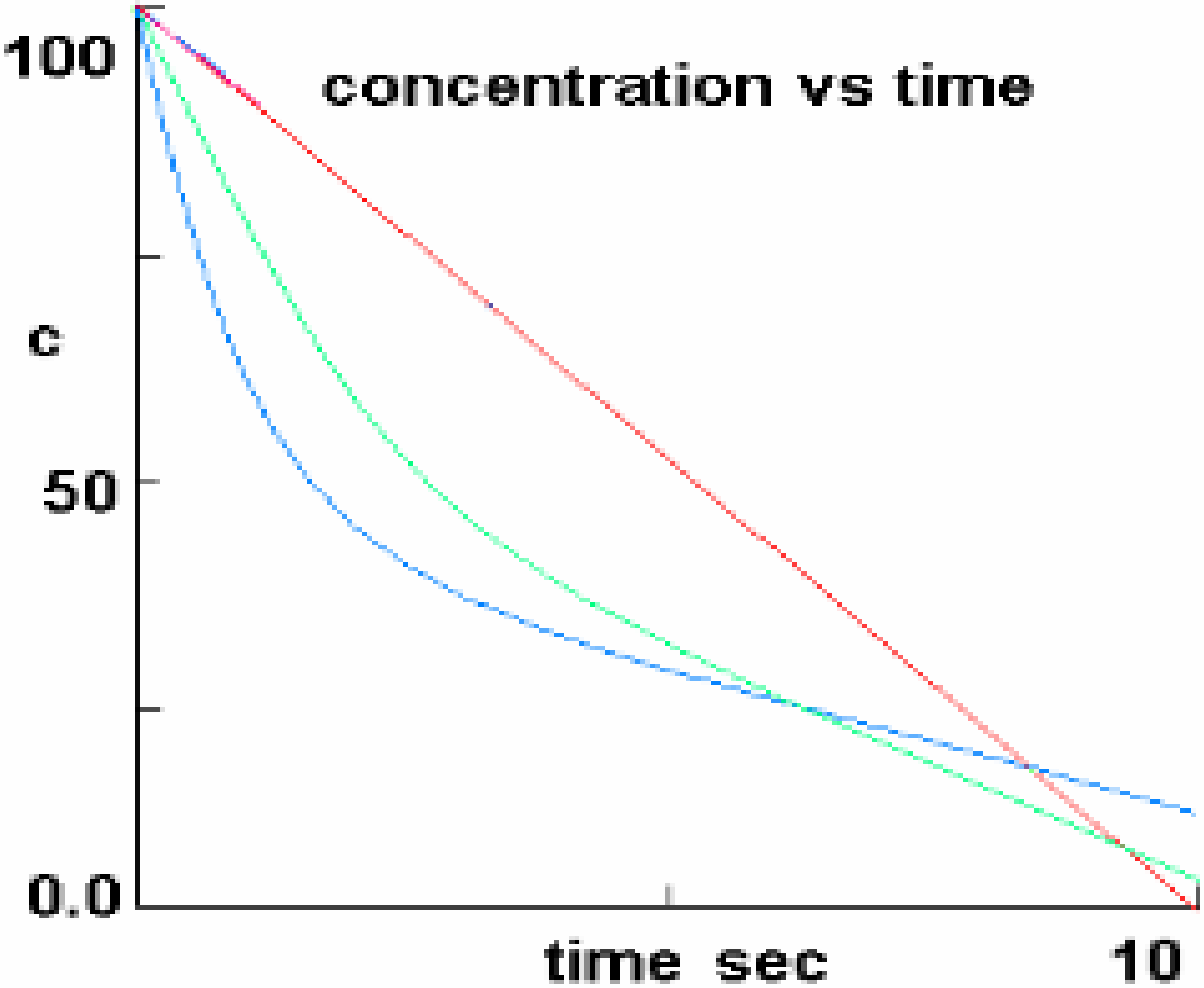
$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}\ M/\text{s}}{(0.08\ M)(0.034\ M)} = 0.08/M\bullet\text{s}$$

- Reaction Order:

$$-\frac{dA}{dt} = k_A[A]^n$$



- **Reaction Plots:**



First-Order Reactions

$\text{rate} = -\dfrac{\Delta[A]}{\Delta t}$

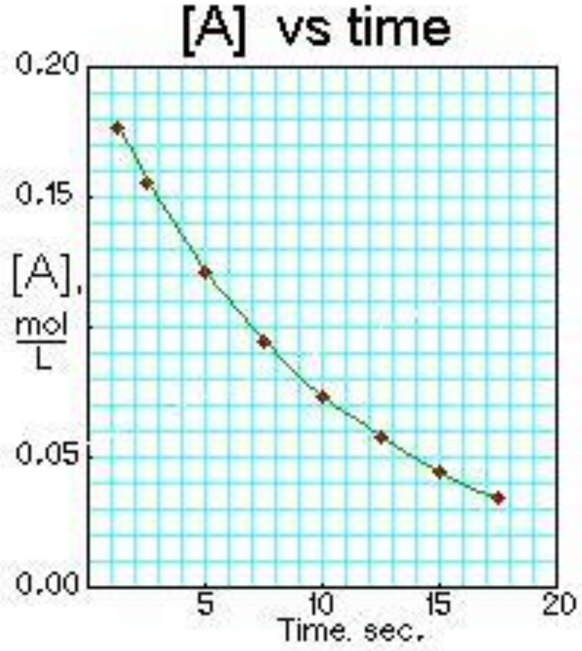
$\text{rate} = k\,[A]$

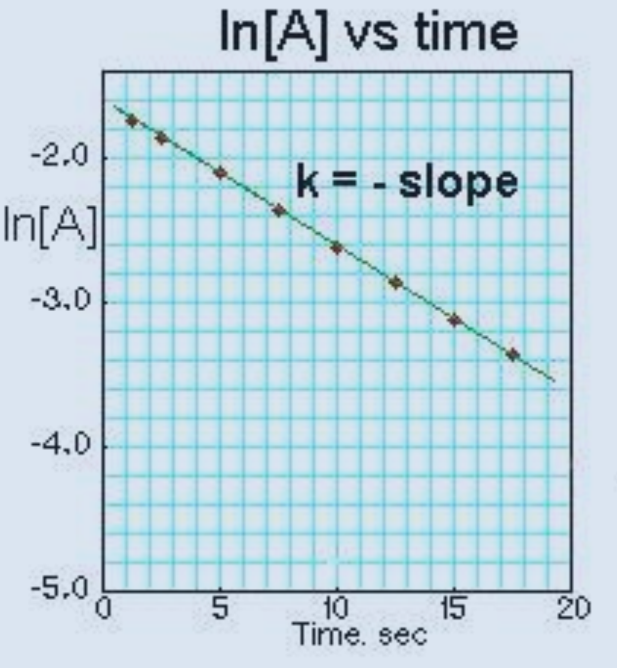
$[A] = [A]_0 e^{-kt}$

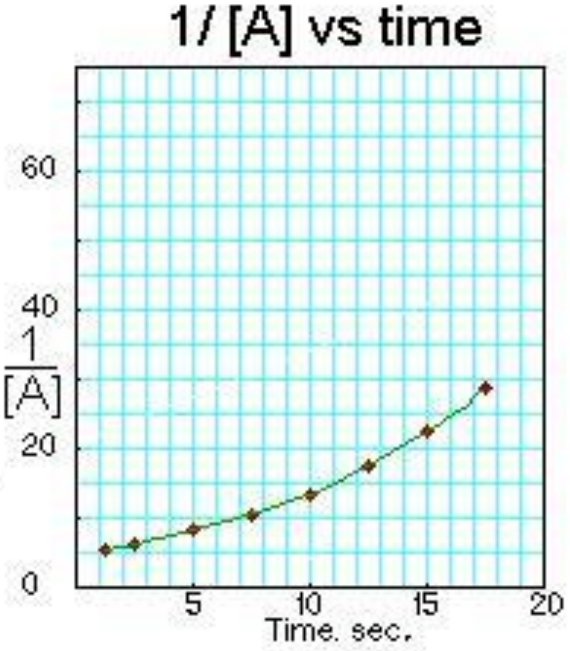
$\boxed{\ln[A] - \ln[A]_0 = -kt}$

$[A]$ is the concentration of A at any time t

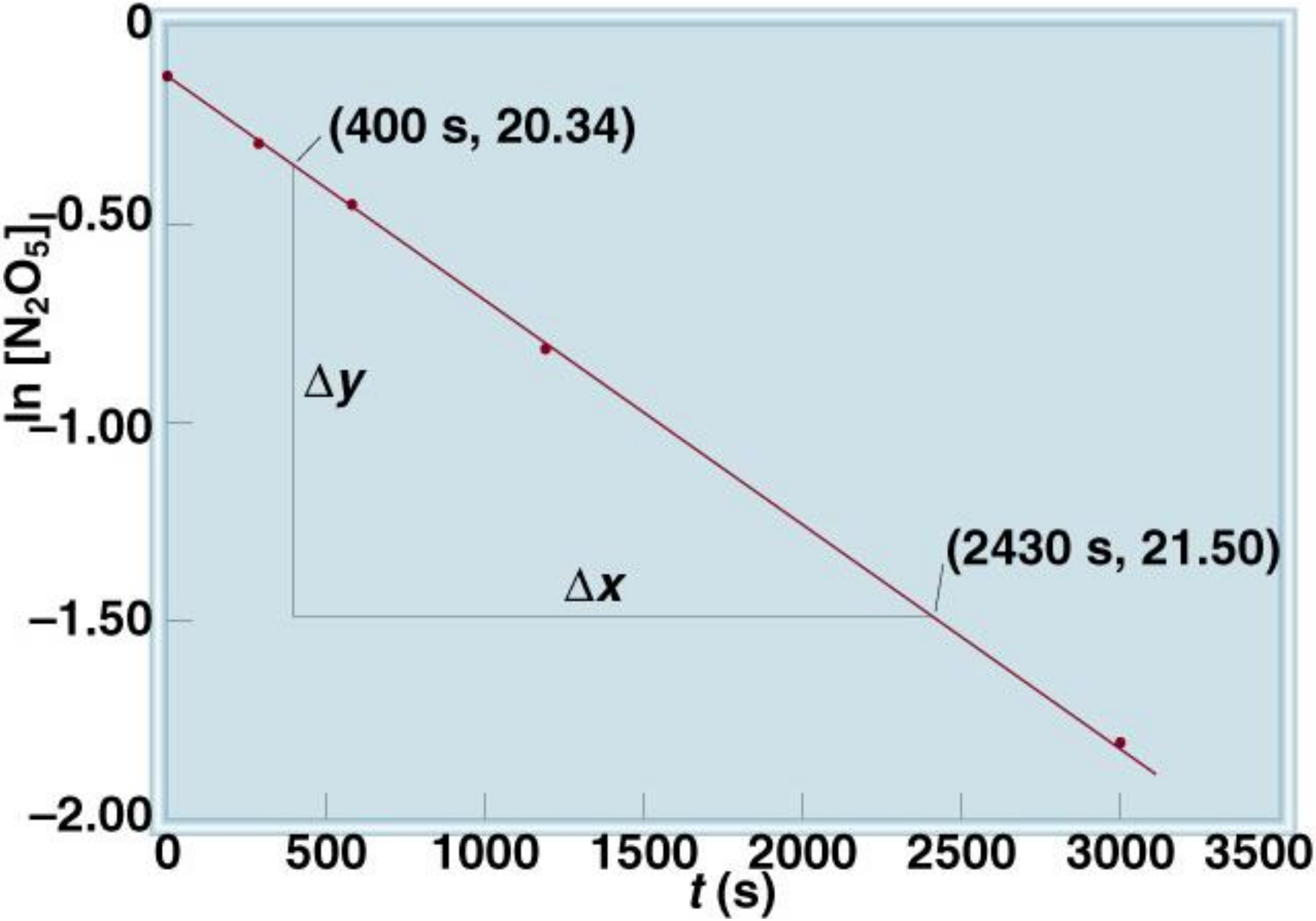
$[A]_0$ is the concentration of A at time $t=0$







Decomposition of N_2O_5



The reaction $2A \longrightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2}\ s^{-1}$ at 80^0C. How long will it take for A to decrease from 0.88 *M* to 0.14 *M* ?

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

$$[A]_0 = 0.88\ M$$

$$[A] = 0.14\ M$$

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

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

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \dfrac{[A]_0}{[A]}}{k} = \frac{\ln \dfrac{0.88\ \cancel{M}}{0.14\ \cancel{M}}}{2.8 \times 10^{-2}\ s^{-1}} = 66\ \text{s}$$

Half life & k of First Order **Decomposition:**

The ***half-life***, ***$t_{1/2}$***, is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

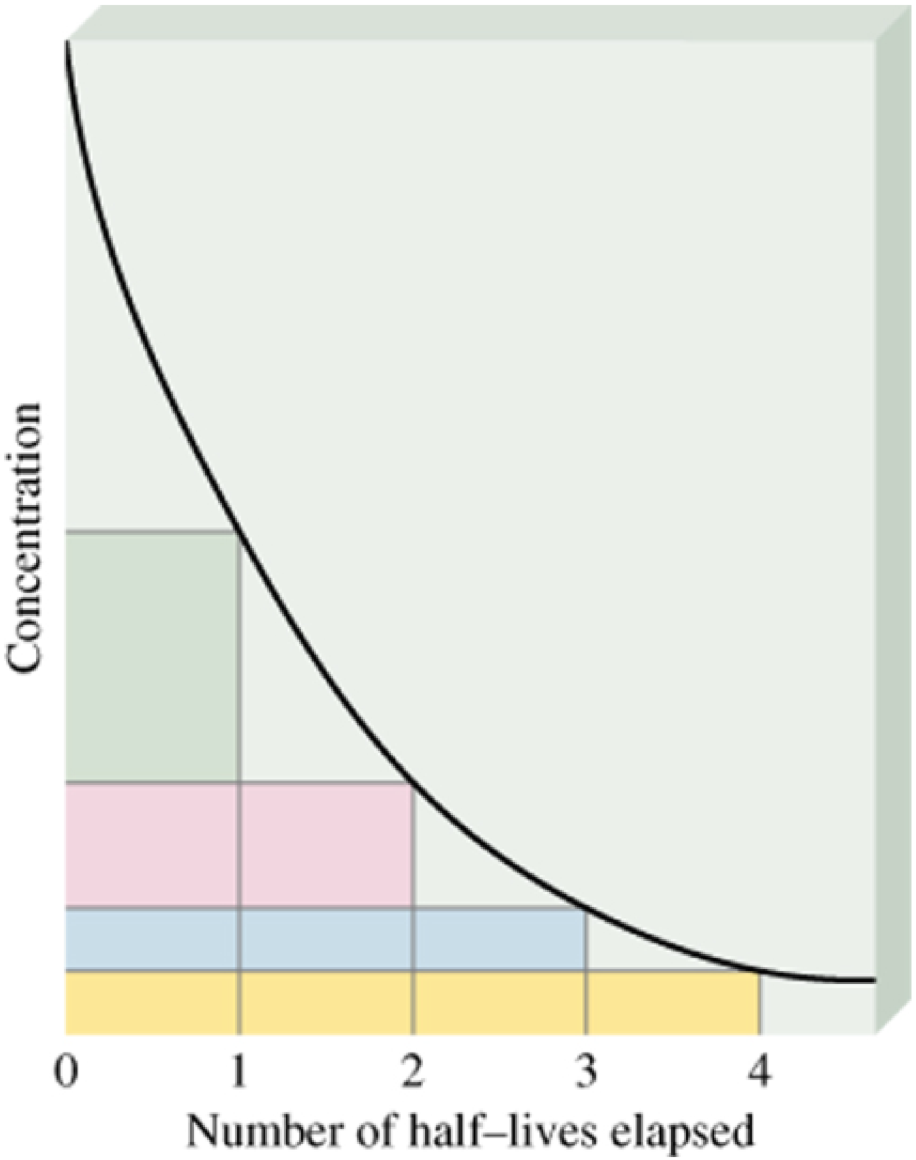
$$t_{1/2} = \frac{\ln \dfrac{\cancel{[A]}_0}{\cancel{[A]}_0/2}}{k} = \frac{\text{Ln } 2}{k} = \boxed{\frac{0.693}{k}}$$

What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4}\ s^{-1}$?

$$t_{1/2} = \frac{\text{Ln } 2}{k} = \frac{0.693}{5.7 \times 10^{-4}\ s^{-1}} = 1200\ s = 20 \text{ minutes}$$

How do you know decomposition is first order?

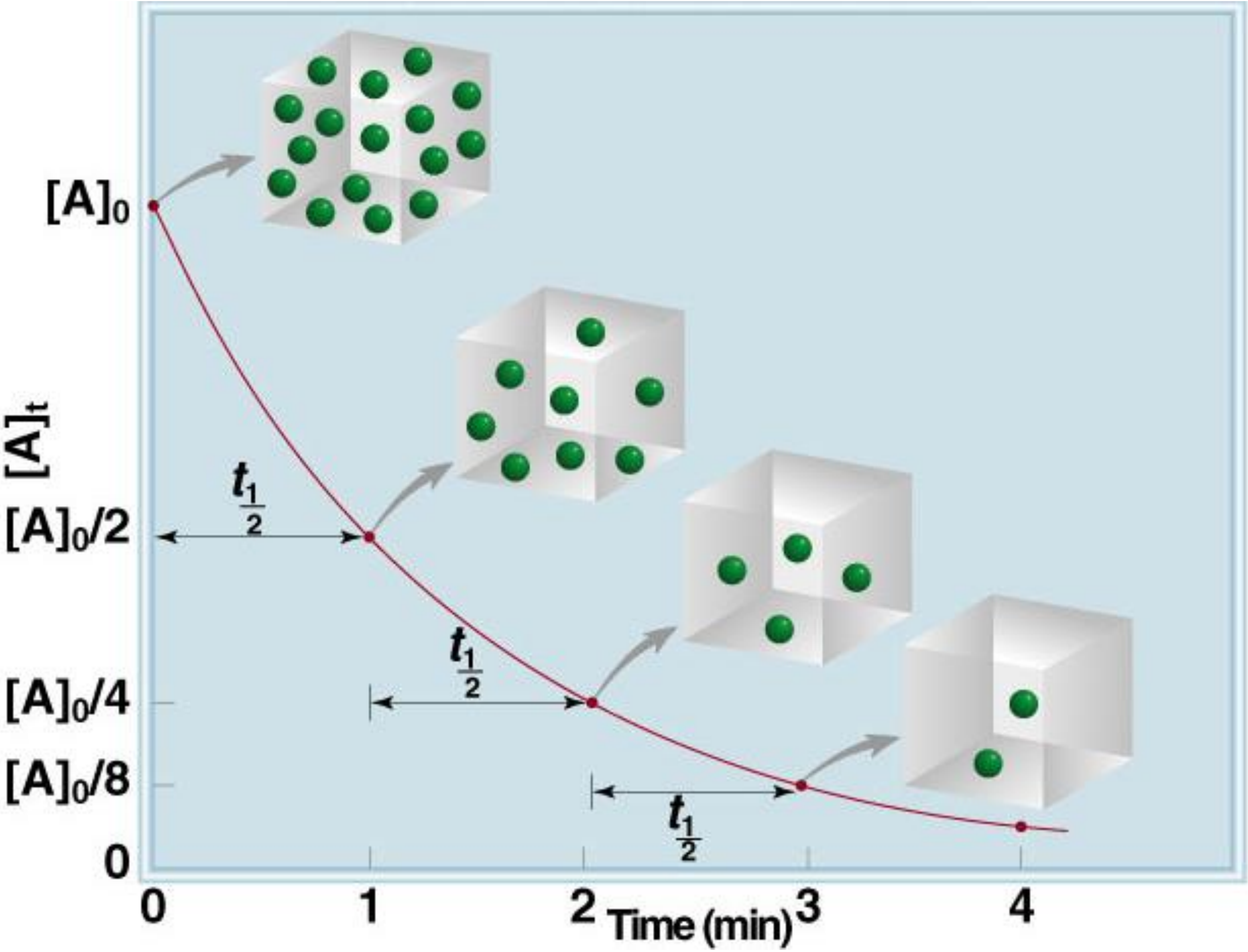
units of k (s^{-1})



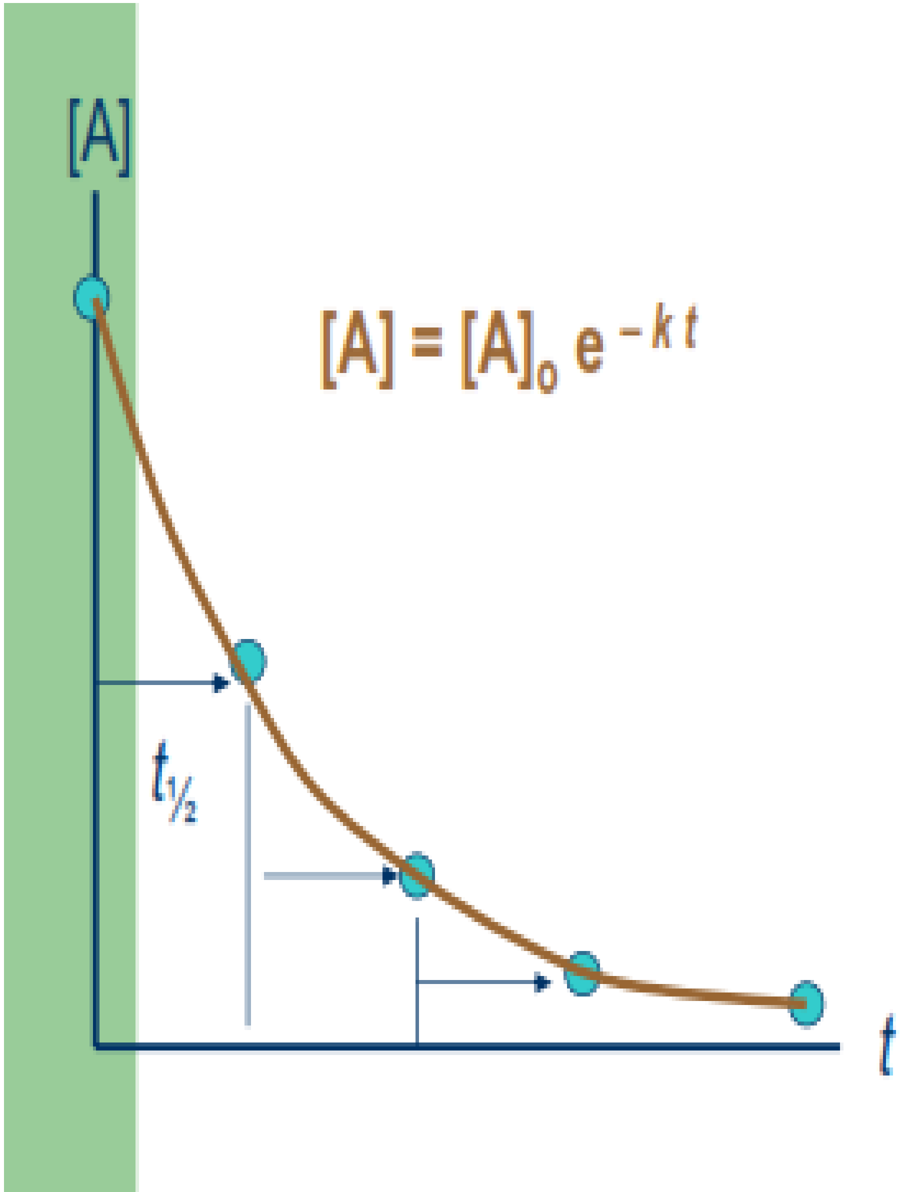
First-order reaction

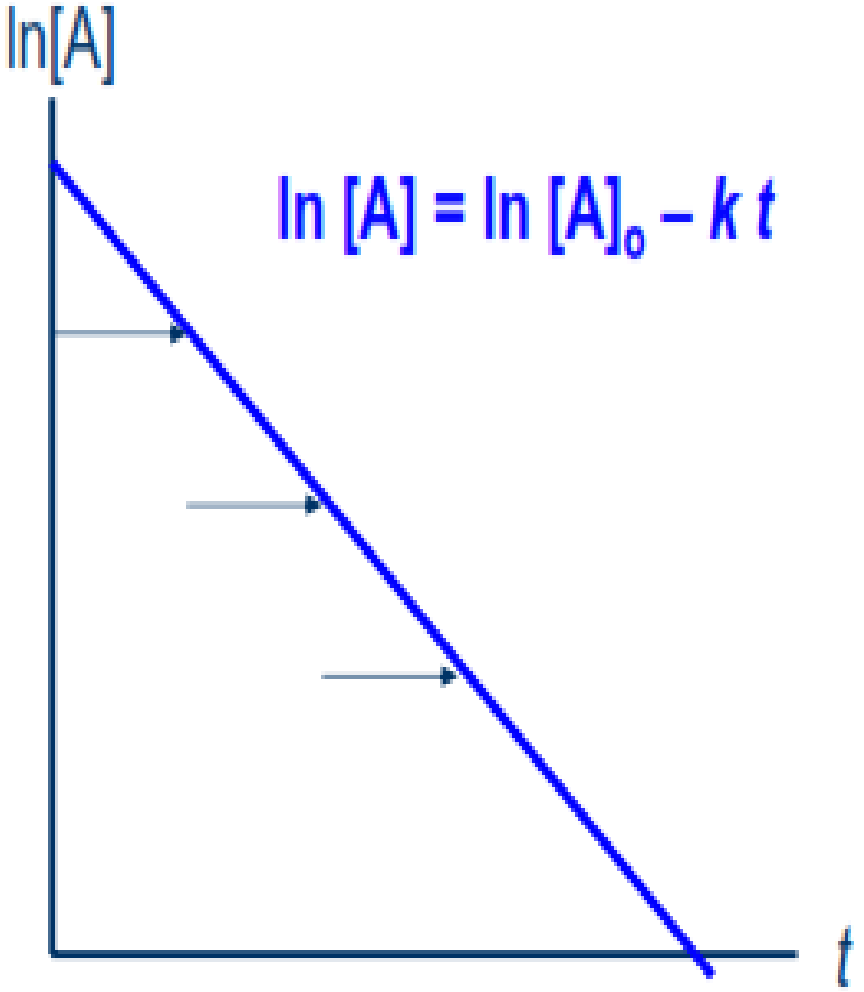
$\mathrm{A} \longrightarrow \text{product}$

# of half-lives	$[\mathrm{A}] = [\mathrm{A}]_0/n$
1	2
2	4
3	8
4	16


$[A]_0$
$[A]_t$
$[A]_0/2$
$[A]_0/4$
$[A]_0/8$
0
$t_{\frac{1}{2}}$
$t_{\frac{1}{2}}$
$t_{\frac{1}{2}}$
0
1
2
3
4
Time (min)

- **Concentration and time of 1st order reaction**





Second-Order Reactions

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \qquad \text{rate} = k\,[A]^2$$

$[A]$ is the concentration of A at any time t

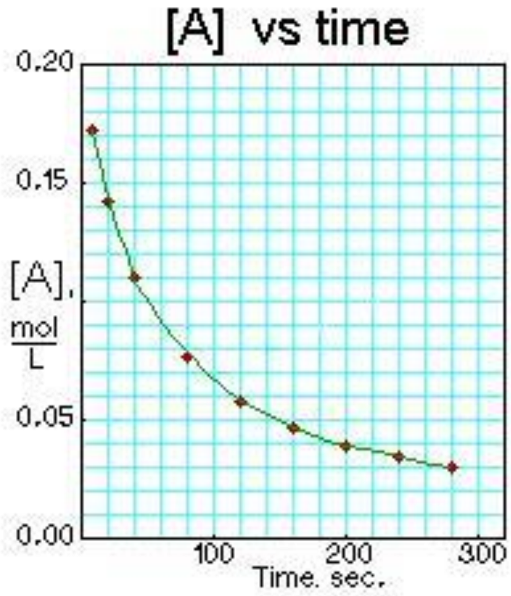
$[A]_0$ is the concentration of A at time $t=0$

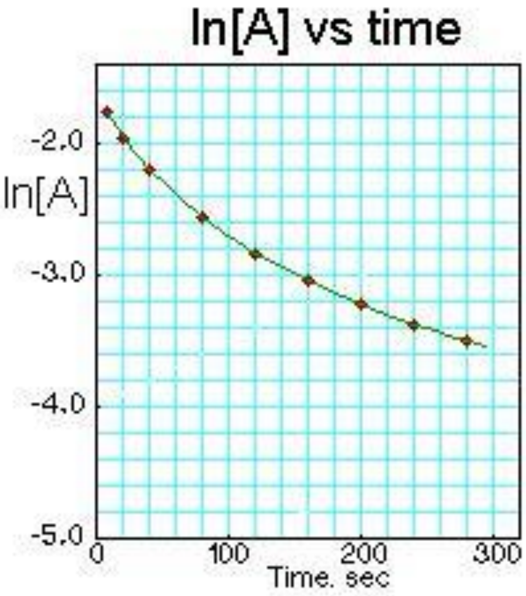
$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

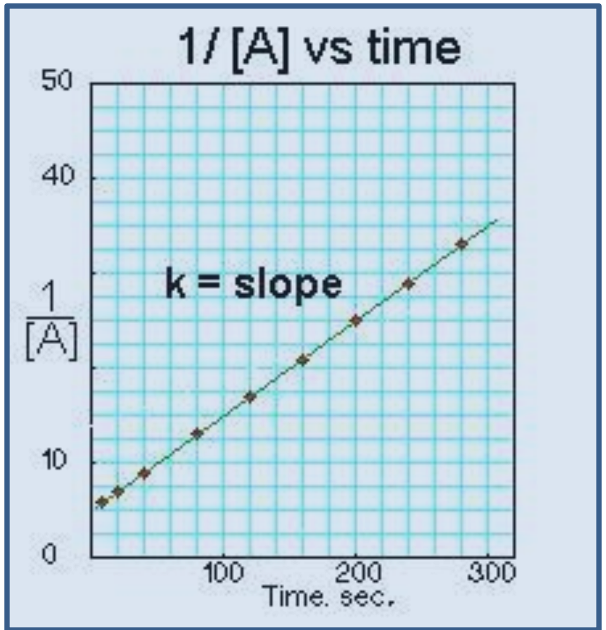
Half life for second order

$$t_{½} = t \text{ when } [A] = [A]_0/2$$

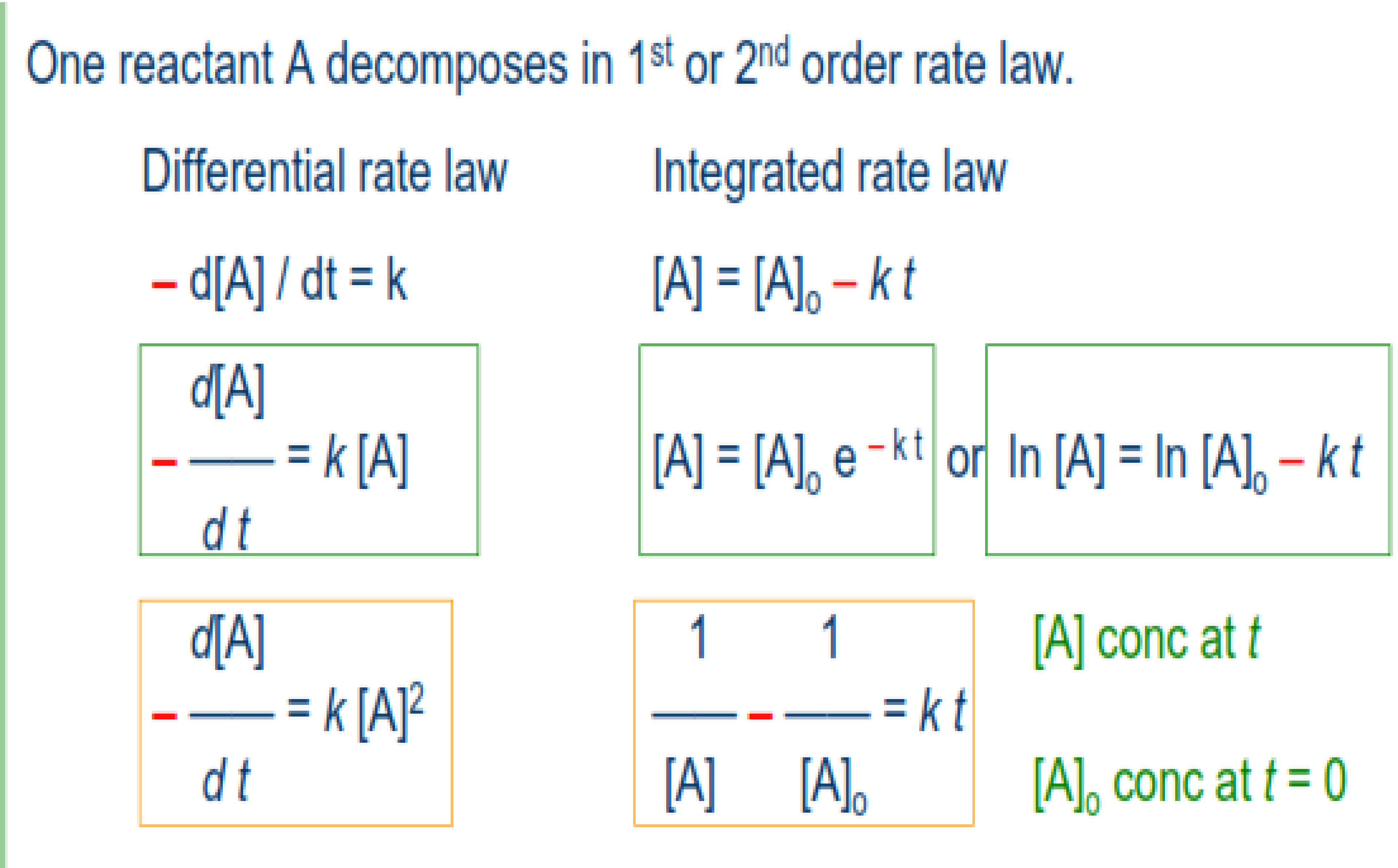
$$t_{½} = \frac{1}{k[A]_0}$$







- **Integrated Rate Laws:**
- **Concentrations as functions of time:**



One reactant A decomposes in 1st or 2nd order rate law.

Differential rate law	Integrated rate law
$-d[A]/dt = k$	$[A] = [A]_0 - k\,t$
$\boxed{-\dfrac{d[A]}{d\,t} = k\,[A]}$	$\boxed{[A] = [A]_0\, e^{-k\,t}}$ or $\boxed{\ln\,[A] = \ln\,[A]_0 - k\,t}$
$\boxed{-\dfrac{d[A]}{d\,t} = k\,[A]^2}$	$\boxed{\dfrac{1}{[A]} - \dfrac{1}{[A]_0} = k\,t}$

$[A]$ conc at t

$[A]_0$ conc at $t = 0$

Zero-Order Reactions

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = k\,[A]^0 = k$$

$$\boxed{[A] - [A]_0 = kt}$$

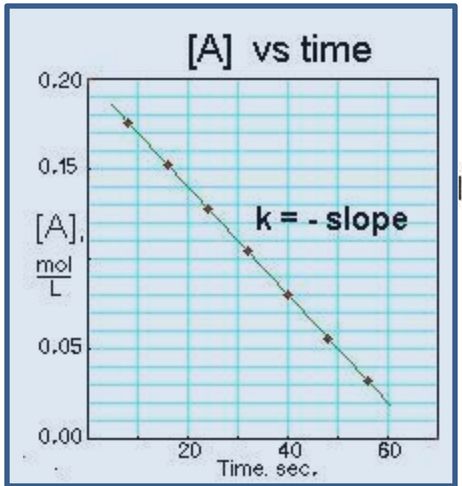
$[A]$ is the concentration of A at any time t

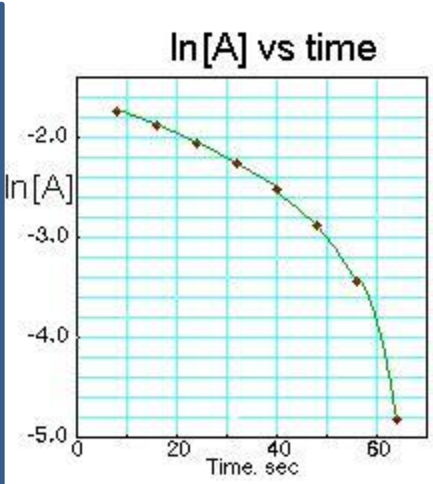
$[A]_0$ is the concentration of A at time t=0

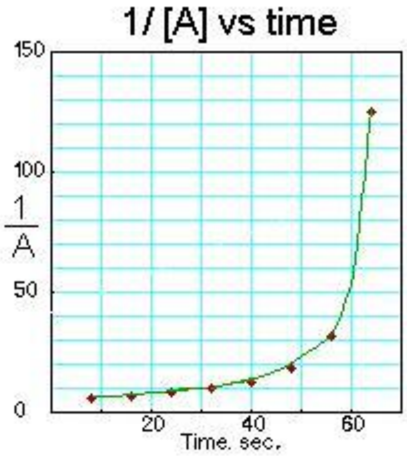
Half life for zero order

$t_{½} = t$ when $[A] = [A]_0/2$

$$t_{½} = \frac{[A]_0}{2k}$$







Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] - [A]_0 = - kt$	$t_{½} = \frac{[A]_0}{2k}$
1	rate = $k\,[A]$	$\ln[A] - \ln[A]_0 = - kt$	$t_{½} = \frac{\text{Ln } 2}{k}$
2	rate = $k\,[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$t_{½} = \frac{1}{k[A]_0}$

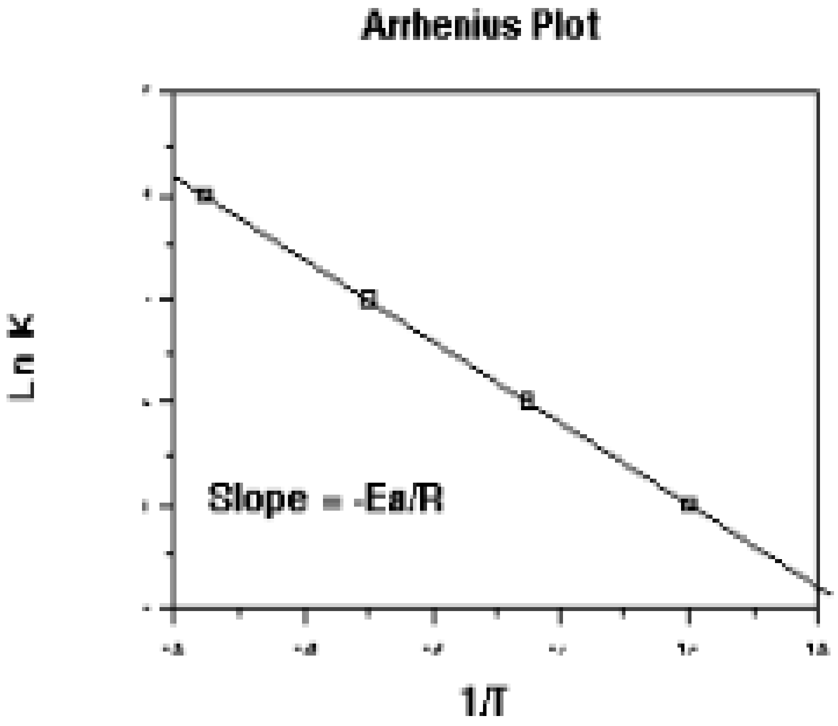
- **Arrhenius Equation:**
- The temperature dependence of the rate constant *k is best* described by the Arrhenius equation:

$$k = A\,e^{-Ea/RT}$$

or $\ln k = \ln A - E_a/RT$

If k_1 and k_2 are the rate constants at T_1 and T_2 respectively, then

$$\ln\frac{k_1}{k_2} = -\frac{E_a}{R}\quad\frac{1}{T_1} - \frac{1}{T_2}$$



- $aA+bB \rightarrow \text{Products}$

Trial	[A]	[B]	Rate M/S
1	0.100	0.100	$2.00*10^{-3}$
2	0.200	0.100	$4.00*10^{-3}$
3	0.200	0.200	$16.00*10^{-3}$

- $aA+bB \rightarrow \text{Products}$
- $M/S \rightarrow \text{Rate} = K[A]^m[B]^n$
- To fined order of reaction:
- For [A]:
- $(0.100/0.200)^m = 2.00*10^{-3}/4.00*10^{-3}$

- $(1/2)^m = 1/2$ mol $=1$

- For [B]:
- $(0.100/0.200)^n = 4.00*10^{-3}/16.00*10^{-3}$
- $(1/2)^n = ¼$
- n =2
- The overall order of reaction:
- 1+2=3rd order
- How to fined K
- Rate = K $[A]^1[B]^2$
- $2*10^{-3} = K(0.1)^1(0.1)^2$
- K =2