General Chemistry
Winter Term 2023/24

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- Website (Slides, Excercises):
- http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/

Login Data for slides:
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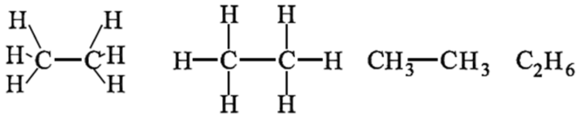
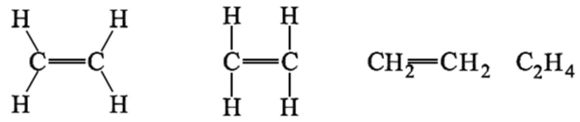
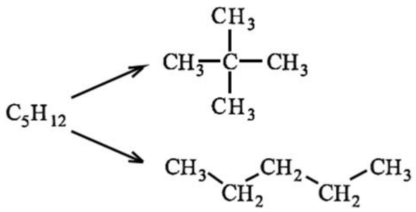
Structural and total formulas

Ethan 

Ethen 

structural formula total formula

Structural and total formulas

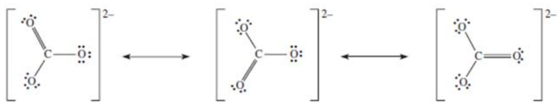


2.2-Dimethyl-propan
(Tetramethyl-methan, Neopentan)

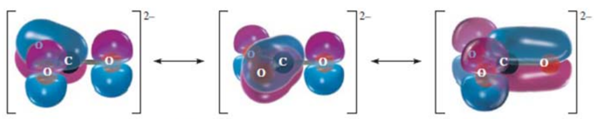
n-Pentan

total formula structural formula

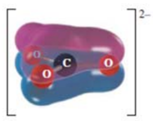
Delocalized bonds: mesomerism



(a) Lewis formulas for valence bond resonance structures



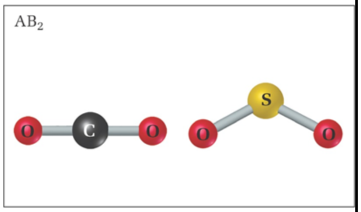
(b) *p*-Orbital overlap in valence bond resonance

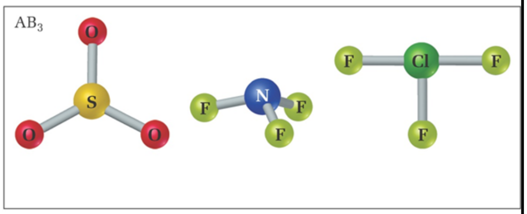


(c) Delocalized MO representation

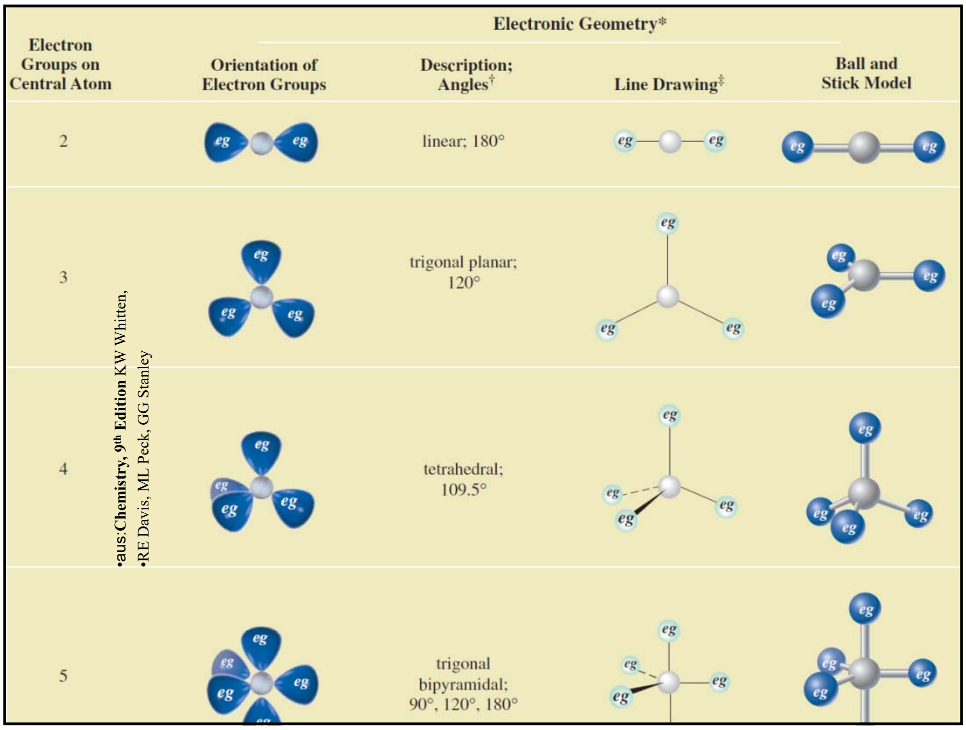
Bonding form and molecular geometry

- Diatomic molecules: always linear
- Three-atom molecules: linear or angled
- More atoms: more complicated shapes



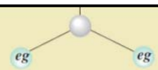
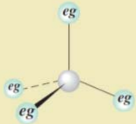
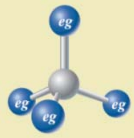
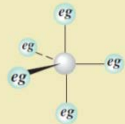
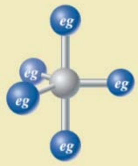
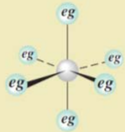
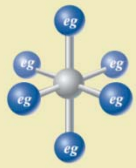


VSEPR-Model



Electron Groups on Central Atom	Electronic Geometry*			
	Orientation of Electron Groups	Description; Angles†	Line Drawing‡	Ball and Stick Model
2		linear; 180°		
3		trigonal planar; 120°		
4		tetrahedral; 109.5°		
5		trigonal bipyramidal; 90°, 120°, 180°		

•aus: Chemistry, 9th Edition KW Whitten,
•RE Davis, ML Peck, GG Stanley

3		120°		
4		tetrahedral; 109.5°		
5		trigonal bipyramidal; 90°, 120°, 180°		
6		octahedral; 90°, 180°		

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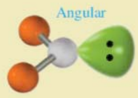
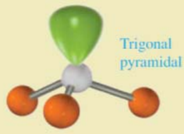
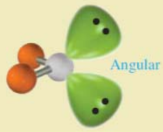
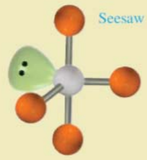
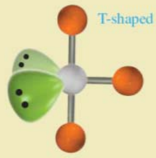
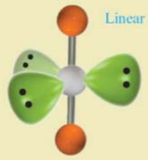
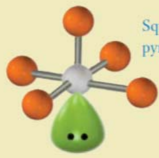
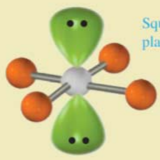
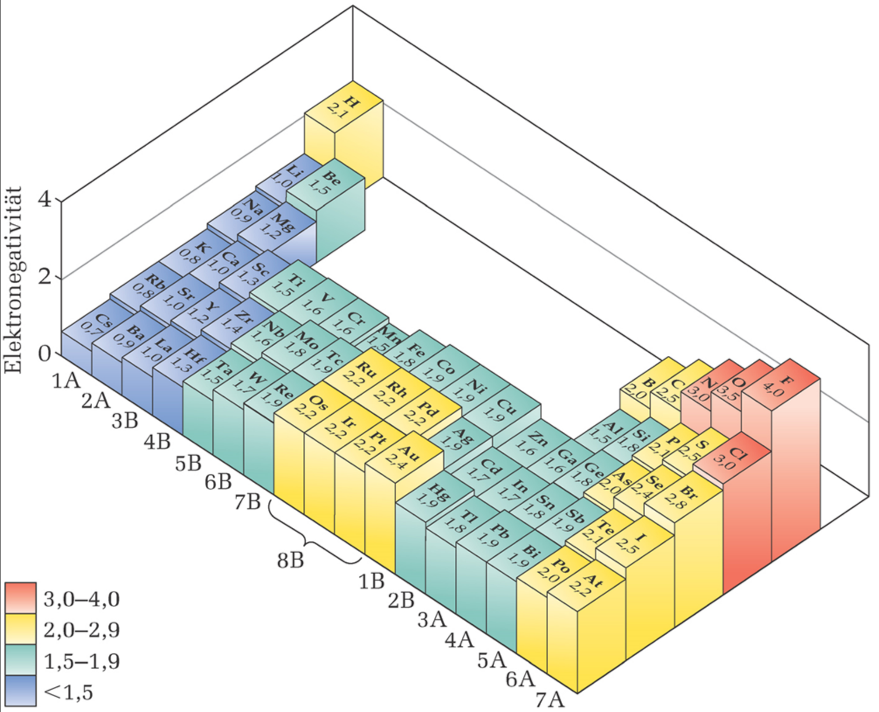
•RE Davis, ML Peck, GG Stanley

General Formula	Electron Groups[a]	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB_2U	3	trigonal planar	sp^2	1		O_3, NO_2^-, SO_2
AB_3U	4	tetrahedral	sp^3	1		NH_3, SO_3^{2-}
AB_2U_2	4	tetrahedral	sp^3	2		H_2O, NH_2^-

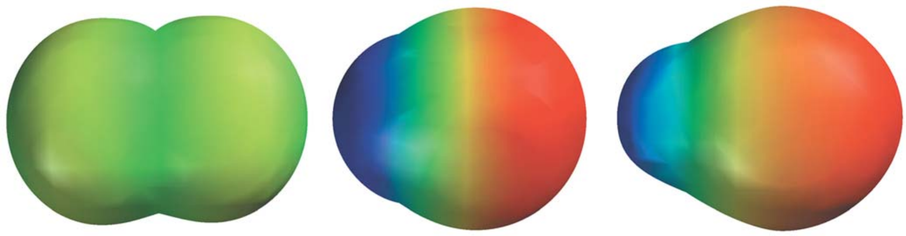
General Formula	Electron Groups[a]	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB_4U	5	trigonal bipyramidal	sp^3d	1		SF_4
AB_3U_2	5	trigonal bipyramidal	sp^3d	2		ICl_3, ClF_3
AB_2U_3	5	trigonal bipyramidal	sp^3d	3		XeF_2, I_3^-

General Formula	Electron Groups[a]	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB_5U	6	octahedral	sp^3d^2	1		IF_5, BrF_5
AB_4U_2	6	octahedral	sp^3d^2	2		XeF_4, IF_4^-



Abbildungen aus: Brown-LeMay, Chemie
siehe www.pearson-studium.de

Distribution of electronic density:
Dipol moments



F_2 HF LiF

- Low electronic density: blue
- high electronic density: red
- average electronic density: green

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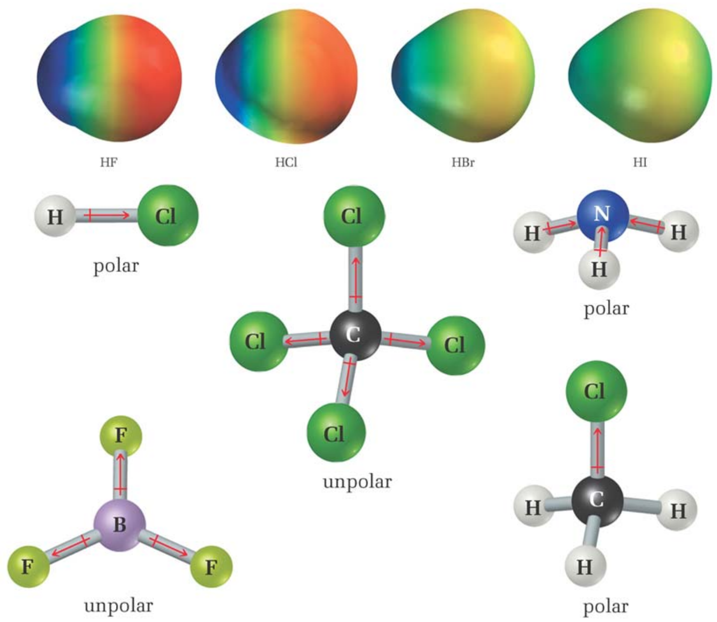
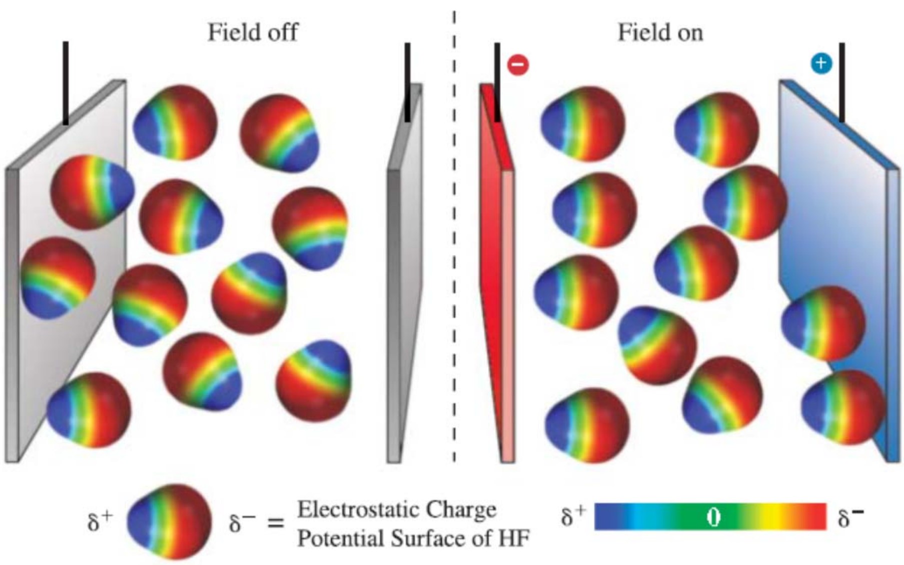


Orientation of dipoles in electrical fields



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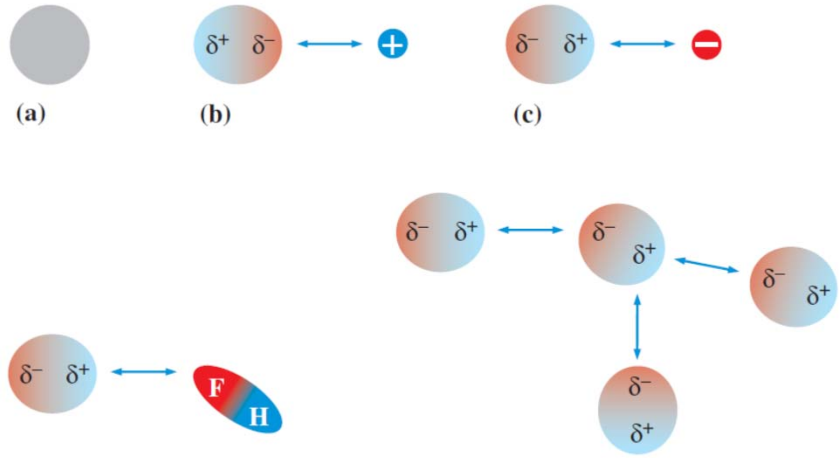
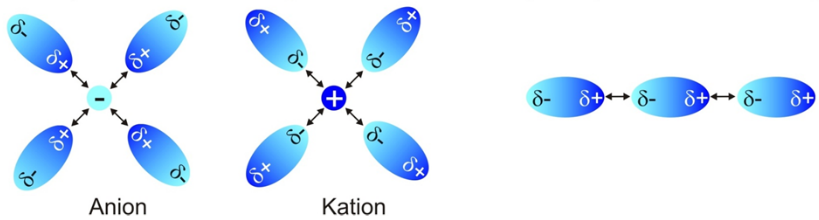
Induced dipol moments



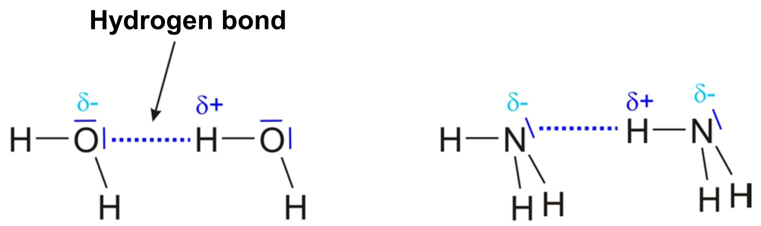
Intermolecular forces

Ion-Dipol

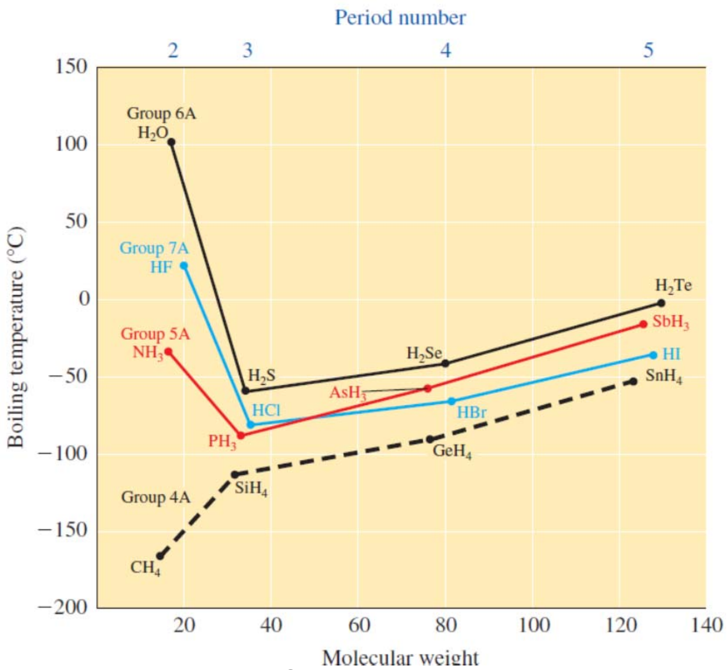
Dipol-Dipol



Hydrogen bonds



Possible partners: N,O,F,Cl



Reaktion kinetics

- Basics, describing quantities
- Definition of reaction rates
- Order of a reaction
- influence of temperature

Some quantities

- molar amount *n*: number of particles, [mol]

$$1\,\text{Mol} = 6{,}022 \cdot 10^{23} \text{ particles}$$

  - Def.: 1 Mol contains as many particles as 12 g of 
- molar mass *M*: Mass of 1 Mol of particles [g/mol]
- molar concentration *c*: particles per volume, [mol/L] (molarity)
  - another: molality, [mol/kg]
    - does not change with temperature

More quantities

- molar fraction *x*: $x_a = \frac{n_a}{n_{total}}$ $\left(= \frac{n_a}{\sum_{i=1}^{j} n_i} \right)$

- partial pressure *p*: $p_a = x_a \cdot p$

- mass fraction *w:* $w_a = \frac{m_a}{m_{gesamt}}$ $\left(= \frac{m_a}{\sum_{i=1}^{j} m_i} \right)$

reaction rate v

$$\mathrm{AB} + \mathrm{C} \longrightarrow \mathrm{A{+}BC}$$

- The higher the educt concentration, the faster the product is formed

  $v_f \propto c(\mathrm{AB})$ and: $v_f \propto c(\mathrm{C})$

  $v_f \propto c(\mathrm{AB}) \cdot c(\mathrm{C})$

- Reactions can proceed in both directions

  $v_r \propto c(\mathrm{A})$ and: $v_r \propto c(\mathrm{BC})$

  $v_r \propto c(\mathrm{A}) \cdot c(\mathrm{BC})$

reaction rate v

•Proportionality is not enough for accurate calculations, so a constant is introduced:

$$v_f = k_f \cdot c(\mathrm{AB}) \cdot c(\mathrm{C})$$

• for $2\mathrm{A} \rightarrow \mathrm{B}$

$$v_f = k_f \cdot c(\mathrm{A}) \cdot c(\mathrm{A}) = k_f \cdot c(\mathrm{A})^2$$

• Stoichiometric coefficients appear as exponents in the rate expression

reaction rate v

Definition of v, example reaction: $\mathrm{H_2} + \mathrm{I_2} \rightarrow 2\mathrm{HI}$

$$\left.\begin{aligned} v &= -\frac{dp(\mathrm{H_2})}{dt} \\ v &= -\frac{dp(\mathrm{I_2})}{dt} \\ v &= \frac{1}{2}\frac{dp(\mathrm{HI})}{dt} \end{aligned}\right\} \quad v = \frac{1}{\nu_A}\frac{dp_A}{dt}$$

Definition of the order of a reaction

- The reaction order is the sum of the exponents of the concentrations in the rate law
- $v = k \cdot c(\mathrm{A}) \cdot c(B)$ — 2nd Order

  $v = k \cdot c(\mathrm{A}) \cdot c(\mathrm{A}) = k \cdot c^2(\mathrm{A})$ — 2nd Order
- $v = -\dfrac{dc(\mathrm{A})}{dt} = k \cdot c(\mathrm{A})$ — 1st Order
- $v = -\dfrac{dc(\mathrm{A})}{dt} = k$ — 0th Order

Reaction 1st Order: A → Product(s)

- rate law:

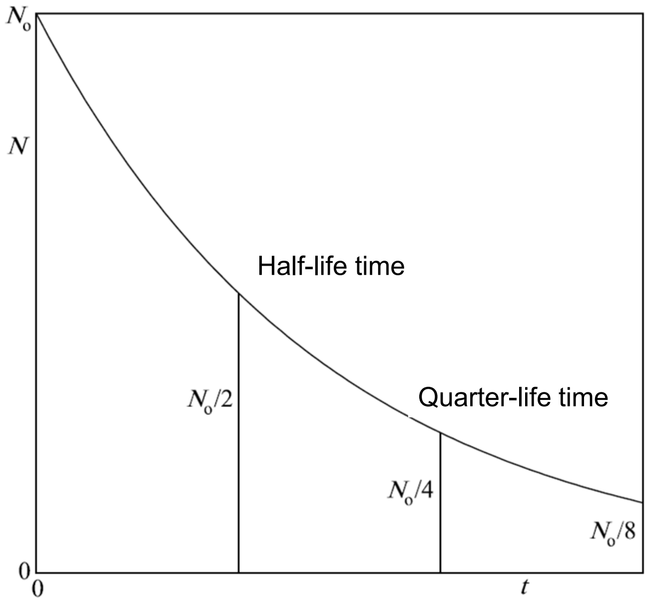
Integration by separation of the variables

Determination of the integration constant C from initial conditions

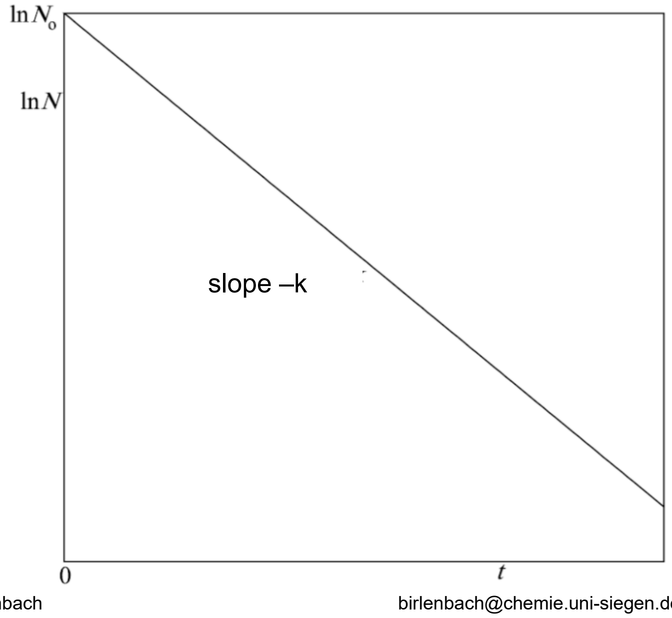
initial condition:

$$\ln c(\mathrm{A}) = -kt + \ln c_0(\mathrm{A})$$

Reaction of first order



Reaction of first order



Reaction of second order: A + B → Products

- rate law: $v = -\frac{dc(\mathrm{A})}{dt} = -\frac{dc(\mathrm{B})}{dt} = k \cdot c(\mathrm{A}) \cdot c(\mathrm{B})$

$$-\frac{dc(\mathrm{A})}{dt} = k \cdot c(\mathrm{A}) \cdot c(\mathrm{B})$$ one more variable! simplify!

$$c(\mathrm{A}) = c_0(\mathrm{A}) - x$$
$$c(\mathrm{B}) = c_0(\mathrm{B}) - x$$
$$c_0(\mathrm{A}) = c_0(\mathrm{B})$$

$$c(\mathrm{A}) \cdot c(\mathrm{B}) = \left(c_0(\mathrm{B}) - x\right) \cdot \left(c_0(\mathrm{A}) - x\right)$$

$$c(\mathrm{A}) \cdot c(\mathrm{B}) = \left(c_0(\mathrm{A}) - x\right)^2 \qquad \frac{dx}{dt} = -k(c_0(\mathrm{A}) - x)^2$$

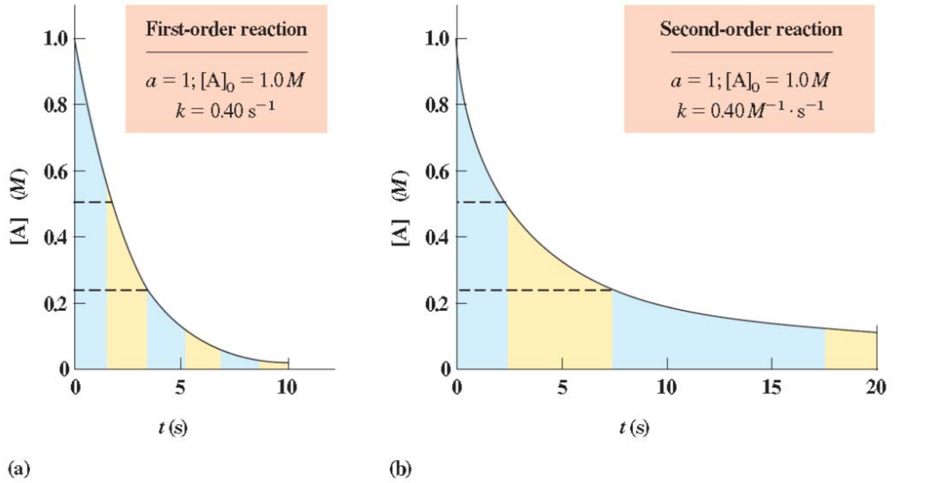
Reaction of second order: A + B → products

$$\frac{dx}{dt} = -k(c_0(\mathrm{A}) - x)^2 \qquad \frac{dx}{\left(c_0(\mathrm{A}) - x\right)^2} = -k\,dt$$

Integrate: $\frac{1}{c_0(\mathrm{A}) - x} = \frac{1}{c(\mathrm{A})} = kt + C$

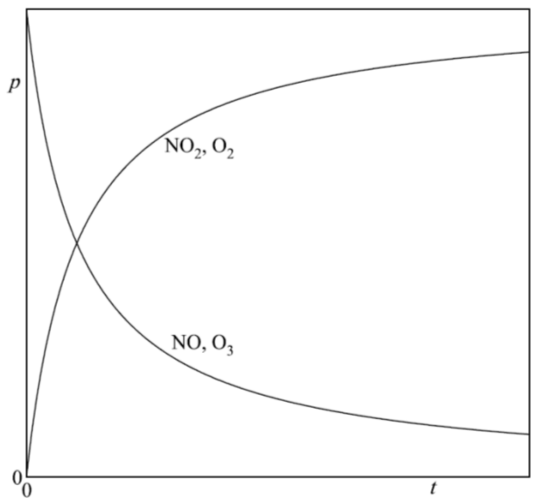
boundary condition: $t = 0: \quad C = \frac{1}{c_0(\mathrm{A})}$

$$\frac{1}{c(\mathrm{A})} = \frac{1}{c_0(\mathrm{A})} + kt$$



Active Figure 16-4 (a) Plot of concentration versus time for a first-order reaction. During the first half-life, 1.73 seconds, the concentration of A falls from 1.00 *M* to 0.50 *M*. An additional 1.73 seconds is required for the concentration to fall by half again, from 0.50 *M* to 0.25 *M*, and so on. For a first-order reaction, $t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{ak}$; $t_{1/2}$ does not depend on the concentration at the beginning of that time period. (b) Plot of concentration versus time for a second-order reaction. The same values are used for *a*, $[A]_0$, and *k* as in Part (a). During the first half-life, 2.50 seconds, the concentration of A falls from 1.00 *M* to 0.50 *M*. The concentration falls by half again from 2.50 to 7.50 seconds, so the second half-life is

example: $NO + O_3 \longrightarrow NO_2 + O_2$



Reaction 2^{nd} Order: plot $1/p$ against time