

Universidade de São Paulo
Instituto de Química

Prof. Dr. Thiago C. Correra

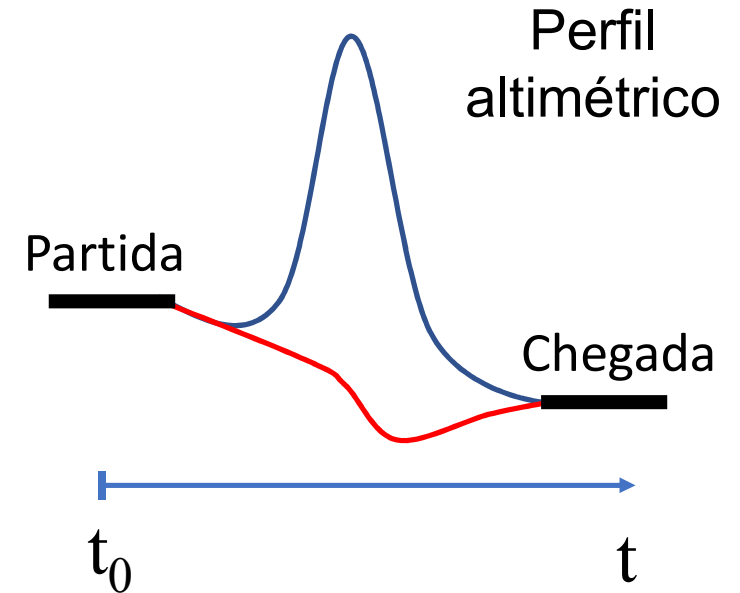
Cinética Química – Princípios e definições

Cinética química

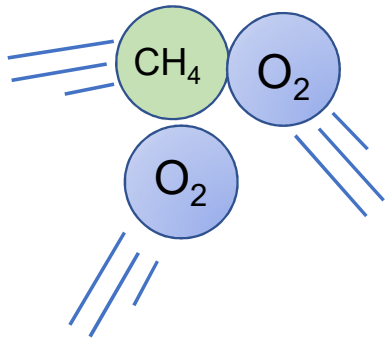
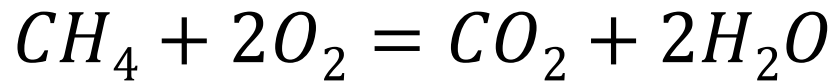
Cinética fenomenológica ↔ Mecanismos de reação

- Ciência que estuda a velocidade das reações e fatores que a influenciam
- Mecanismo de reação

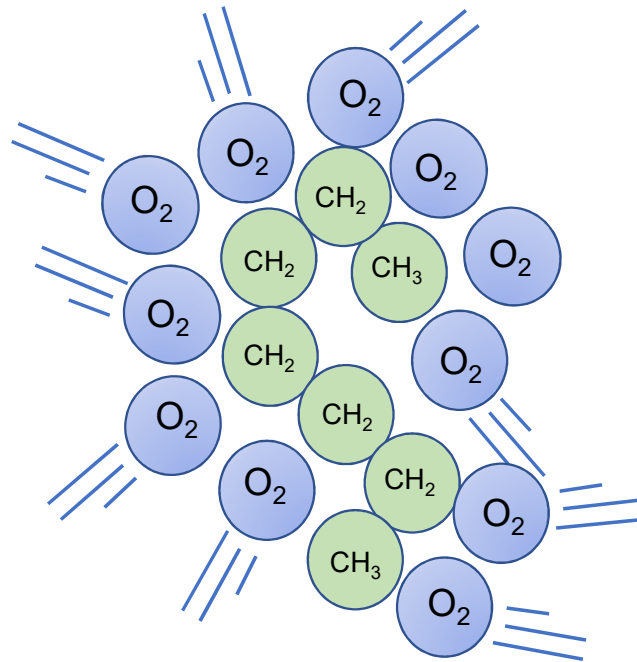
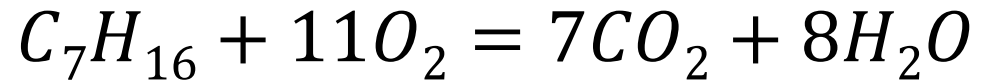
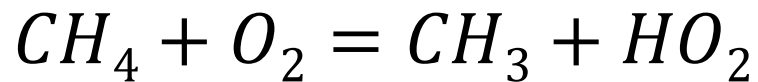
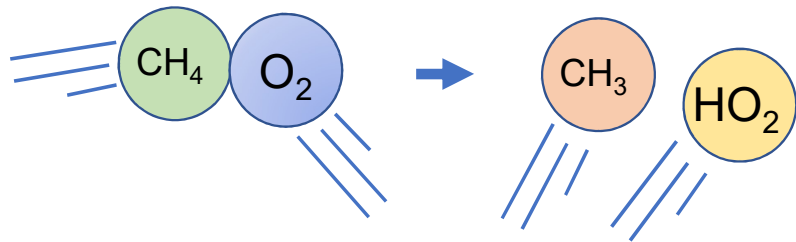
Mecanismos diferentes levam a cinéticas diferentes (velocidades diferentes)



Como a combustão de hidrocarbonetos?



Equações **podem** representar processos microscópicos



Um processo organizado com 22 corpos (ignorando a forma) é mais ou menos favorável do que com 3 corpos?

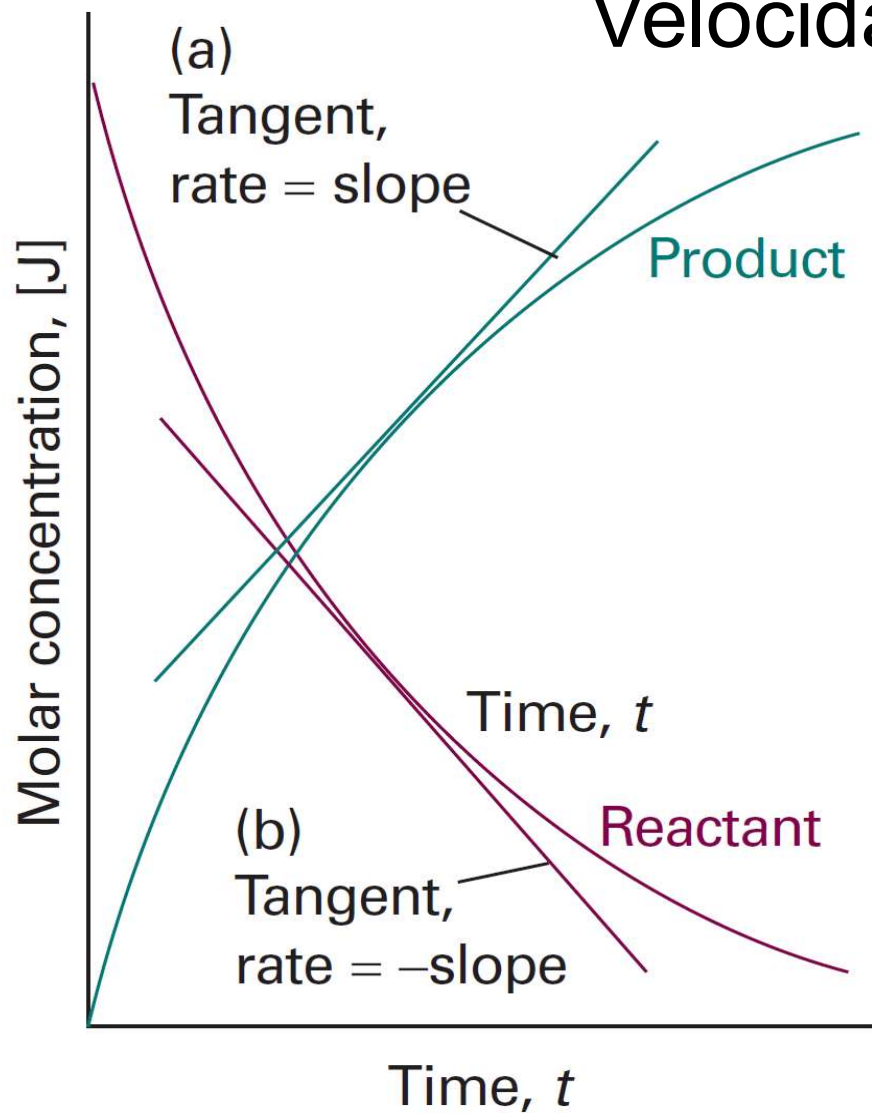
No.	Reaction	No.	Reaction	No.	Reaction
1	$C_7H_{16} + O_2 = C_7H_{15} + HO_2$	46	$C_7H_{15}O_2 + CH_3CHO = C_7H_{16}O_2 + CH_3CO$	91	$C_7H_{14}O + O = C_7H_{13}O + OH$
2	$C_7H_{16} + OH = C_7H_{15} + H_2O$	47	$C_7H_{15}O_2 + C_2H_5CHO = C_7H_{16}O_2 + C_2H_5CO$	92	$C_7H_{14}O + HO_2 = C_7H_{13}O + H_2O_2$
3	$C_7H_{16} + H = C_7H_{15} + H_2$	48	$C_7H_{15}O_2 + C_4H_8O = C_7H_{16}O_2 + C_4H_7O$	93	$C_6H_{13} + HCO = C_7H_{14}O$
4	$C_7H_{16} + O = C_7H_{15} + OH$	49	$C_7H_{15}O_2 + C_5H_{10}O = C_7H_{16}O_2 + C_5H_9O$	94	$C_6H_{13} + CO = C_7H_{13}O$
5	$C_7H_{16} + HO_2 = C_7H_{15} + H_2O_2$	50	$C_7H_{15}O_2 + C_6H_{12}O = C_7H_{16}O_2 + C_6H_{11}O$	95	$C_7H_{13}O + H = C_6H_{13} + HCO$
6	$C_7H_{14} + H = C_7H_{15}$	51	$C_7H_{15}O_2 + C_7H_{14}O = C_7H_{16}O_2 + C_7H_{13}O$	96	$C_7H_{13}O + O = C_6H_{13}O + CO$
7	$C_7H_{15} + O_2 = C_7H_{14} + HO_2$	52	$C_7H_{15} + HO_2 = C_7H_{15}O + OH$	97	$C_7H_{14} + OH = C_7H_{13} + H_2O$
8	$C_7H_{15} + OH = C_7H_{14} + H_2O$	53	$C_7H_{15} + O_2 = C_7H_{14}O + OH$	98	$C_7H_{13} + H_2 = C_7H_{14} + H$
9	$C_7H_{16} = H + C_7H_{15}$	54	$C_7H_{15} + C_2H_5 = C_7H_{16} + C_2H_4$	99	$C_7H_{13} + O_2 = C_5H_{11}O_2 + C_2H_2$
10	$C_7H_{16} = CH_3 + C_6H_{13}$	55	$C_7H_{15} + C_3H_7 = C_7H_{16} + C_3H_6$	100	$C_7H_{14} + HCO = C_7H_{13} + H_2CO$
11	$C_7H_{16} = C_2H_5 + C_5H_{11}$	56	$C_7H_{15} + C_4H_9 = C_7H_{16} + C_4H_8$	101	$C_7H_{14} + CH_3 = C_7H_{13} + CH_4$
12	$C_7H_{16} = C_3H_7 + C_4H_9$	57	$C_7H_{15} + C_5H_{11} = C_7H_{16} + C_5H_{10}$	102	$C_7H_{14} + C_2H_5 = C_7H_{13} + C_2H_6$
13	$C_7H_{15} + H = C_7H_{14} + H_2$	58	$C_7H_{15} + C_6H_{13} = C_7H_{16} + C_6H_{12}$	103	$C_7H_{14} + C_3H_7 = C_7H_{13} + C_3H_8$
14	$C_7H_{15} + CH_3 = C_7H_{14} + CH_4$	59	$C_7H_{15} + C_7H_{15} = C_7H_{16} + C_7H_{14}$	104	$C_7H_{14} + C_4H_9 = C_7H_{13} + C_4H_{10}$
15	$C_7H_{15} + C_2H_5 = C_7H_{14} + C_2H_6$	60	$C_7H_{15} + O_2 = H_2CO + C_6H_{13}O$	105	$C_7H_{14} + C_5H_{11} = C_7H_{13} + C_5H_{12}$
16	$C_7H_{15} + C_3H_7 = C_7H_{14} + C_3H_8$	61	$C_7H_{15} + O_2 = CH_3CHO + C_5H_{11}O$	106	$C_7H_{14} + C_6H_{13} = C_7H_{13} + C_6H_{14}$
17	$C_7H_{15} + C_4H_9 = C_7H_{14} + C_4H_{10}$	62	$C_7H_{15} + O_2 = C_2H_5CHO + C_4H_9O$	107	$C_5H_{11} + C_2H_2 = C_7H_{13}$
18	$C_7H_{15} + C_5H_{11} = C_7H_{14} + C_5H_{12}$	63	$C_7H_{15} + O_2 = C_4H_8O + C_3H_7O$	108	$C_7H_{14} = C_2H_3 + C_5H_{11}$
19	$C_7H_{15} + C_6H_{13} = C_7H_{14} + C_6H_{14}$	64	$C_7H_{15} + O_2 = C_3H_{10}O + C_2H_5O$	109	$C_7H_{14} = C_3H_5 + C_4H_9$
20	$C_7H_{15} + O = C_7H_{14} + OH$	65	$C_7H_{15} + O_2 = C_6H_{12}O + CH_3O$	110	$C_7H_{14} = C_4H_7 + C_3H_7$
21	$C_7H_{15} + O_2 = C_7H_{15}O_2$	66	$C_7H_{15} + OH = CH_3 + C_6H_{13}O$	111	$C_7H_{14} = C_5H_9 + C_2H_5$
22	$C_7H_{16} + CH_3O_2 = C_7H_{15} + CH_3O_2H$	67	$C_7H_{15} + OH = C_2H_5 + C_5H_{11}O$	112	$C_7H_{14} = C_6H_{11} + CH_3$
23	$C_7H_{16} + C_2H_5O_2 = C_7H_{15} + C_2H_5O_2H$	68	$C_7H_{15} + OH = C_3H_7 + C_4H_9O$	113	$C_7H_{14} + O_2 = C_7H_{13} + HO_2$
24	$C_7H_{16} + C_3H_7O_2 = C_7H_{15} + C_3H_7O_2H$	69	$C_7H_{15} + OH = C_4H_9 + C_3H_7O$	114	$C_7H_{14} + O = C_6H_{13} + HCO$
25	$C_7H_{16} + C_4H_9O_2 = C_7H_{15} + C_4H_9O_2H$	70	$C_7H_{15} + OH = C_5H_{11} + C_2H_5O$	115	$C_7H_{13} + OH = C_6H_{13} + HCO$
26	$C_7H_{16} + C_5H_{11}O_2 = C_7H_{15} + C_5H_{11}O_2H$	71	$C_7H_{15} + OH = C_6H_{13} + CH_3O$	116	$C_7H_{13} + H = C_5H_{12} + C_2H_2$
27	$C_7H_{16} + C_6H_{13}O_2 = C_7H_{15} + C_6H_{13}O_2H$	72	$C_7H_{15} + H = CH_3 + C_6H_{13}$	117	$C_7H_{13} + O = C_6H_{13} + CO$
28	$C_7H_{16} + C_7H_{15}O_2 = C_7H_{15} + C_7H_{16}O_2$	73	$C_7H_{15} + H = C_2H_5 + C_5H_{11}$	118	$C_7H_{13} + O = C_5H_{11}O + C_2H_2$
29	$C_7H_{16}O_2 = C_7H_{15}O + OH$	74	$C_7H_{15} + H = C_3H_7 + C_4H_9$	119	$CH_3 + C_6H_{13} = C_7H_{14} + H_2$
30	$C_7H_{15}O = H_2CO + C_6H_{13}$	75	$C_7H_{15} + H = CH_2 + C_6H_{14}$	120	$C_2H_5 + C_5H_{11} = C_7H_{14} + H_2$
31	$C_7H_{15}O = CH_3CHO + C_5H_{11}$	76	$C_7H_{15} + H = C_2H_4 + C_5H_{12}$	121	$C_3H_7 + C_4H_9 = C_7H_{14} + H_2$
32	$C_7H_{15}O = C_2H_5CHO + C_4H_9$	77	$C_7H_{15} + H = C_3H_6 + C_4H_{10}$	122	$C_7H_{14} + H + H = CH_3 + C_6H_{13}$
33	$C_7H_{15}O = C_4H_8O + C_3H_7$	78	$C_7H_{15} + H = C_4H_8 + C_3H_8$	123	$C_7H_{14} + H + H = C_2H_3 + C_5H_{11}$
34	$C_7H_{15}O = C_5H_{10}O + C_2H_5$	79	$C_7H_{15} + H = C_5H_{10} + C_2H_6$	124	$C_7H_{14} + H + H = C_3H_7 + C_4H_9$
35	$C_7H_{15}O = C_6H_{12}O + CH_3$	80	$C_7H_{15} + H = C_6H_{12} + CH_4$		
36	$C_7H_{15}O = C_7H_{14}O + H$	81	$C_7H_{15} + O = H + C_7H_{14}O$		
37	$C_7H_{15}O_2 + H = C_7H_{15}O + OH$	82	$C_7H_{15} + O = CH_3 + C_6H_{12}O$		
38	$C_7H_{15}O_2 + CH_3 = C_7H_{15}O + CH_3O$	83	$C_7H_{15} + O = C_2H_5 + C_5H_{10}O$		
39	$C_7H_{15}O_2 + C_2H_5 = C_7H_{15}O + C_2H_5O$	84	$C_7H_{15} + O = C_3H_7 + C_4H_8O$		
40	$C_7H_{15}O_2 + C_3H_7 = C_7H_{15}O + C_3H_7O$	85	$C_7H_{15} + O = C_4H_9 + C_3H_5CHO$		
41	$C_7H_{15}O_2 + C_4H_9 = C_7H_{15}O + C_4H_9O$	86	$C_7H_{15} + O = C_5H_{11} + CH_3CHO$		
42	$C_7H_{15}O_2 + C_5H_{11} = C_7H_{15}O + C_5H_{11}O$	87	$C_7H_{15} + O = C_6H_{13} + H_2CO$		
43	$C_7H_{15}O_2 + C_6H_{13} = C_7H_{15}O + C_6H_{13}O$	88	$C_7H_{13}O + HO_2 = C_7H_{14}O + O_2$		
44	$C_7H_{15}O_2 + C_7H_{15} = C_7H_{15}O + C_7H_{15}O$	89	$C_7H_{14}O + OH = C_7H_{13}O + H_2O$		
45	$C_7H_{15}O_2 + H_2CO = C_7H_{16}O_2 + HCO$	90	$C_7H_{14}O + H = C_7H_{13}O + H_2$		

Oxidação do heptano

(followed by the mechanism of the oxidation and combustion of C_1-C_6)

No.	Reaction
1	$C_7H_{16} + O_2 = C_7H_{15} + HO_2$
2	$C_7H_{16} + OH = C_7H_{15} + H_2O$
3	$C_7H_{16} + H = C_7H_{15} + H_2$
4	$C_7H_{16} + O = C_7H_{15} + OH$

Velocidades instantâneas



$$\frac{d[D]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt}$$

$$\xi = \frac{n_J - n_{J,0}}{\nu_J}$$

$$v = \frac{1}{\nu_J} \times \frac{1}{V} \frac{dn_J}{dt}$$

Velocidades instantâneas

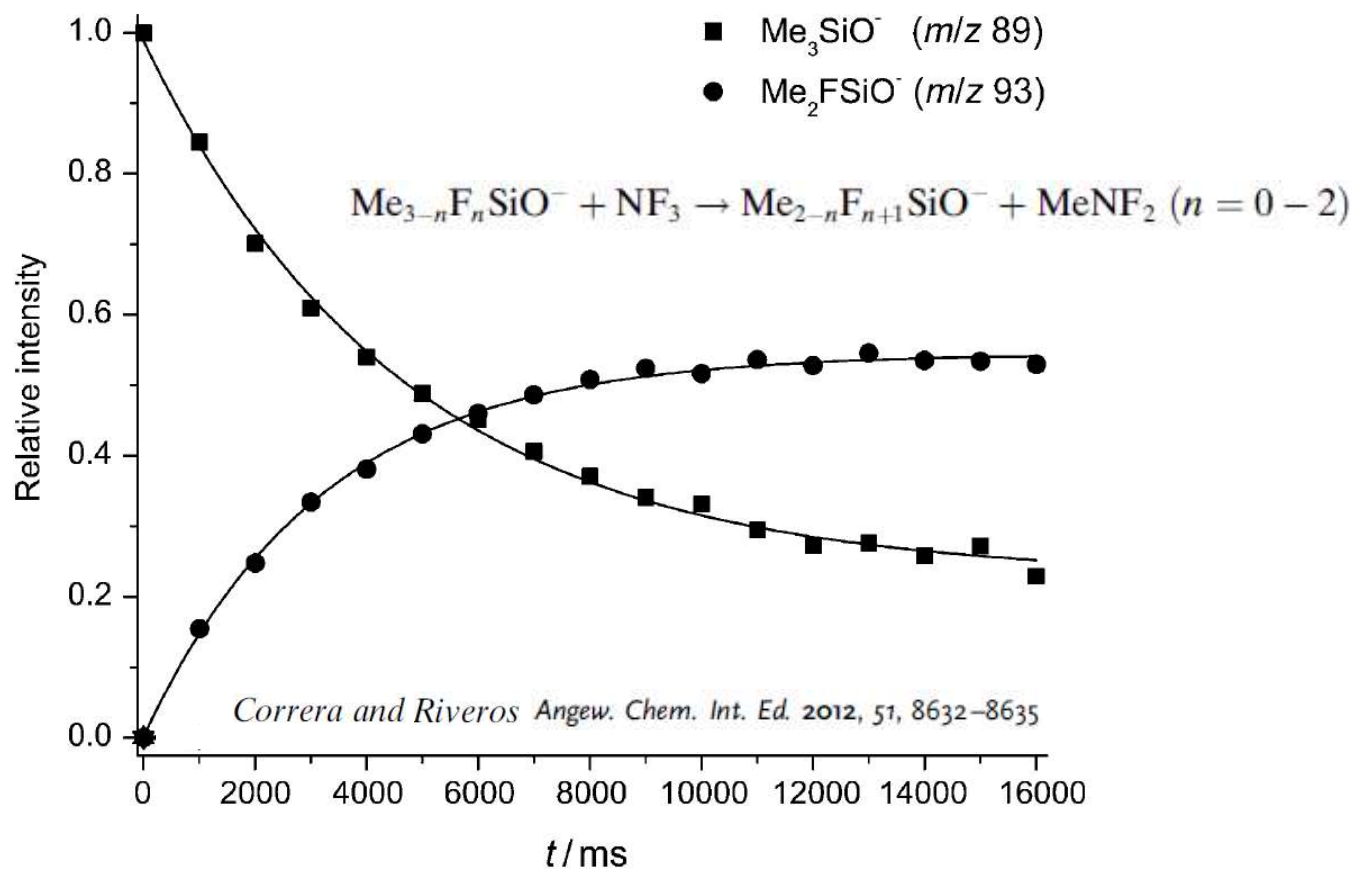


Figure 1. Reaction kinetics of NF_3 (2.12×10^{-8} Torr) reacting with Me_3SiO^- (m/z 89), which is generated from the reaction of F^- and Me_3SiOEt (7.8×10^{-9} Torr). The partial pressures are nominal values measured with an ionization gauge.

Reações complexas

W. Piang-Siong et al. / Industrial Crops and Products 35 (2012) 203–210

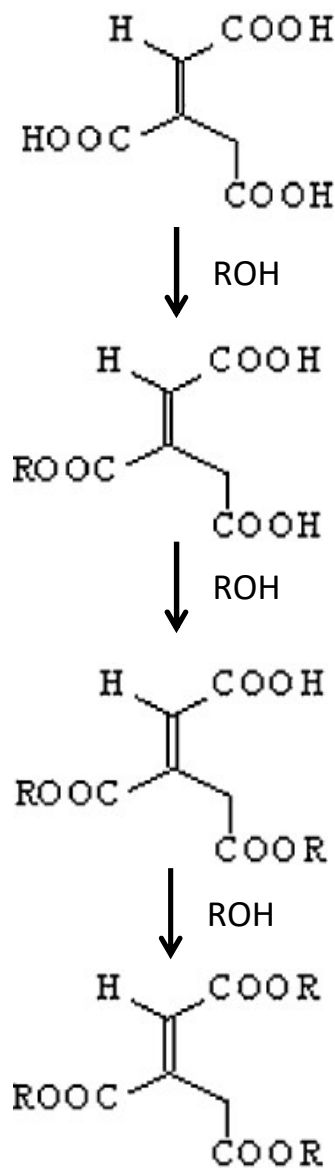
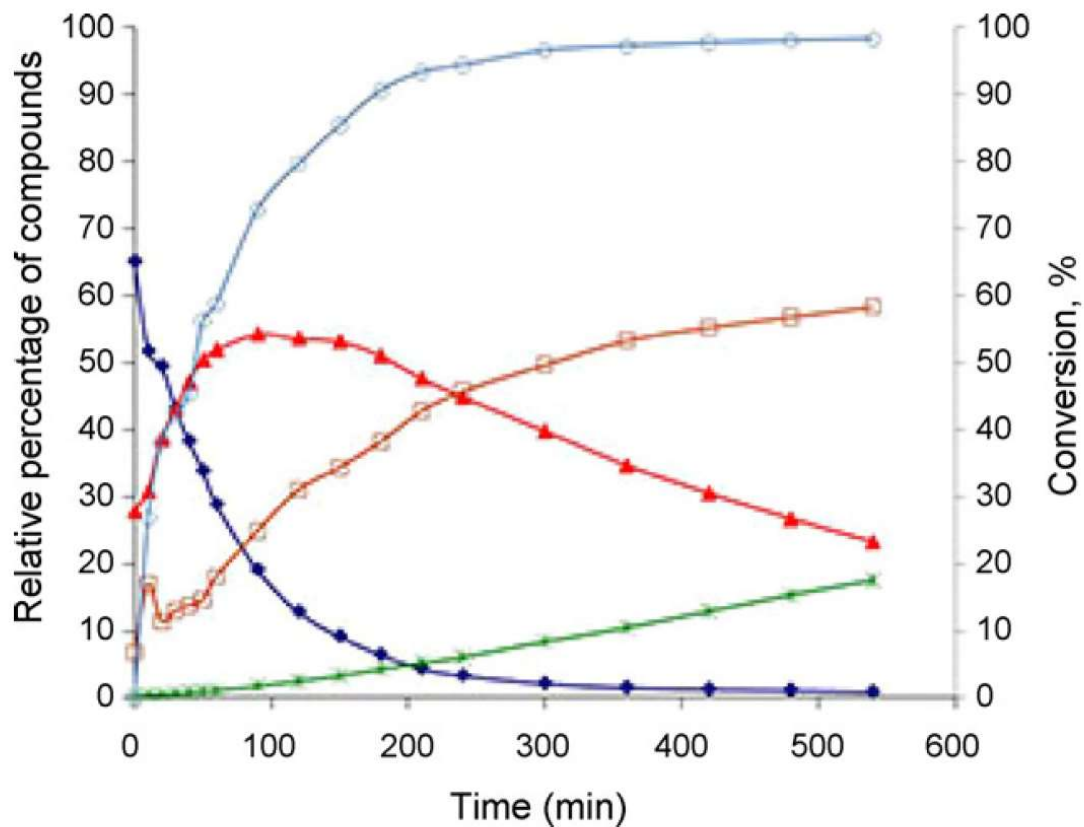


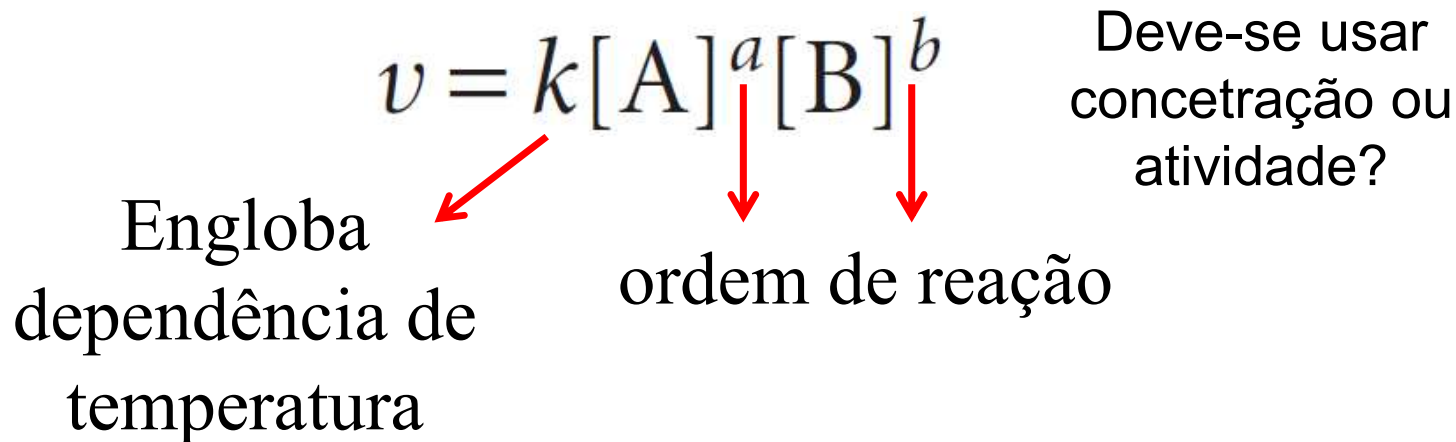
Fig. 8. Esterification of aconitic acid catalyzed by ion-exchange resin, according to method 2 (\blacklozenge : AA; \blacktriangle : MIA; \square : DIA; \times : TIA; \circ : conversion).

Lei de velocidade

- Do que depende a velocidade de reação?

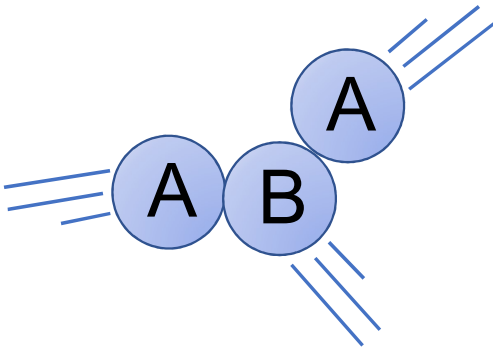
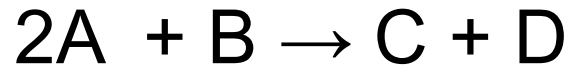
$$v = f(T, [\text{Reagentes}], \text{molecularidade, etc})$$

- Normalmente, para $aA + bB = \text{produtos}$



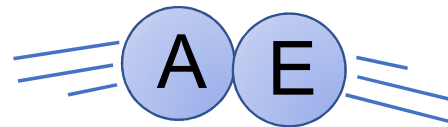
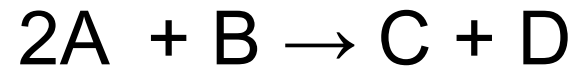
Molecularidade

Reação: Elementar



$$v(t) = k(T)[A]^2[B]^1$$

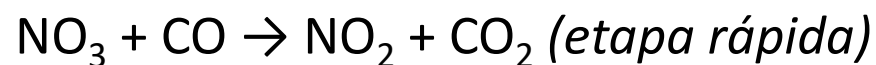
Não-Elementar



$$v(t) = k'(T)[A]^1[E]^1$$

etapa determinante
de velocidade?

Como reconhecer a etapa determinante de velocidade?



$$v \propto [\text{NO}_2]^2 [\text{CO}]^0$$

Etapas
elementares

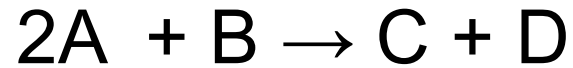
$$v \propto [\text{NO}_2]^2$$

$$v \propto [\text{NO}_3]^1 [\text{CO}]^1$$

Permite “determinar” mecanismo da reação

Escrevendo velocidades de reação

Escrever a variação em forma diferencial:



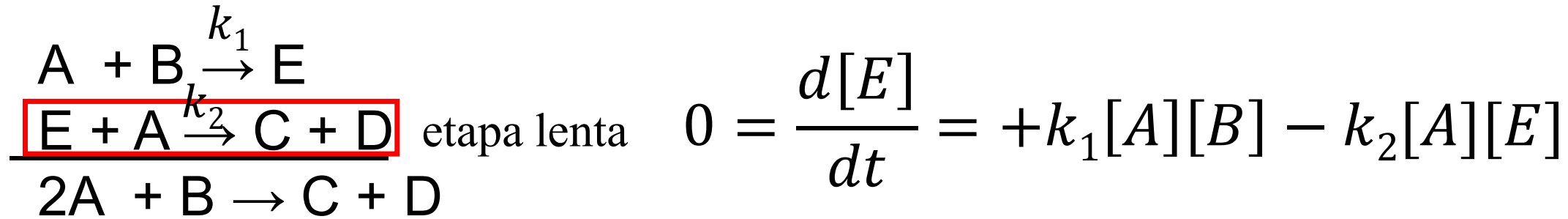
$$v(t) = k(T)[A]^2[B]^1$$

$$\frac{d[B]}{dt} = -k[A]^2[B]$$

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

Escrevendo velocidades de reação

Escrever a variação em forma diferencial:



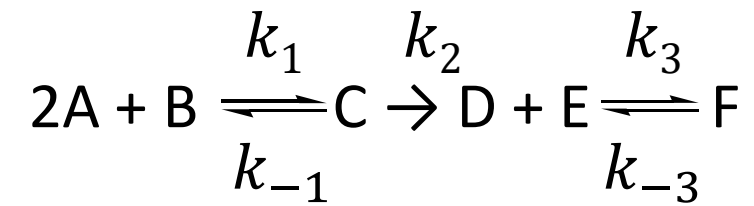
$$v(t) = k'(T)[A]^1[E]^1$$

$$\frac{d[B]}{dt} = -k_1[A][B]$$

$$\frac{d[E]}{dt} = +k_1[A][B] - k_2[A][E]$$

$$\frac{d[B]}{dt} = -k_2[A][E]$$

Para reações genéricas:



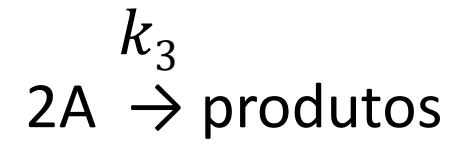
Reações não elementares (empíricas)

- (1) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ $r = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + j[\text{HBr}]/[\text{Br}_2]}$
- (2) $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ $r = k[\text{N}_2\text{O}_5]$
- (3) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ $r = k[\text{H}_2][\text{I}_2]$
- (4) $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ $r = k[\text{NO}]^2[\text{O}_2]$
- (5) $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$ $r = k[\text{CH}_3\text{CHO}]^{3/2}$
- (6) $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{NO}} 2\text{SO}_3$ $r = k[\text{O}_2][\text{NO}]^2$
- (7) $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2$ $r = k_1[\text{H}_2\text{O}_2][\text{I}^-] + k_2[\text{H}_2\text{O}_2][\text{I}^-][\text{H}^+]$
- (8) $\text{Hg}_2^{2+} + \text{Tl}^{3+} \rightarrow 2\text{Hg}^{2+} + \text{Tl}^+$ $r = k \frac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$

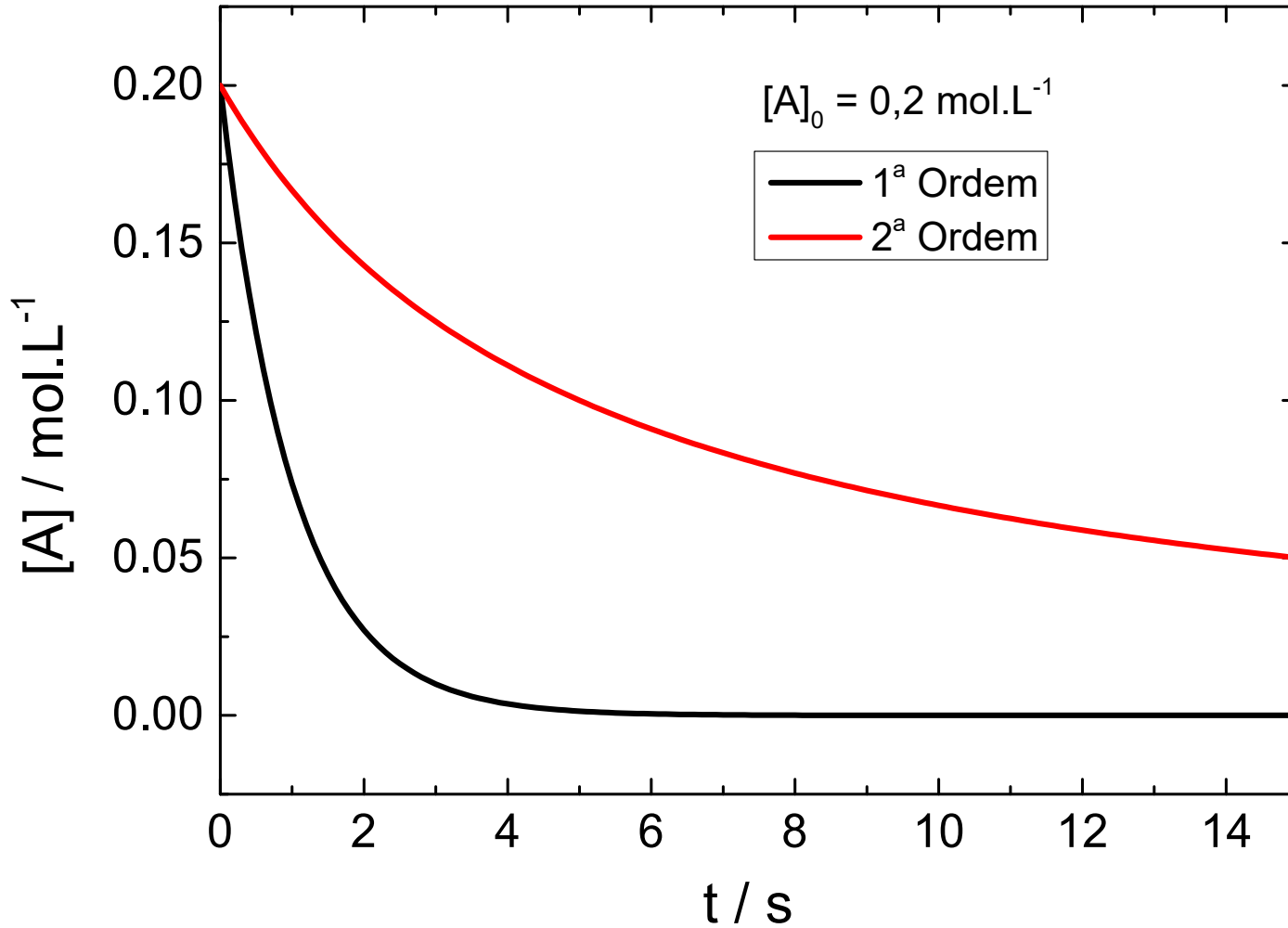
Casos interessantes



Leis integradas

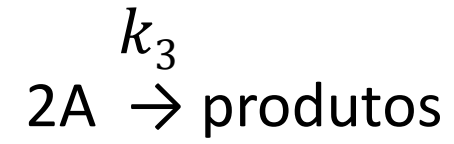


Primeira vs. Segunda ordem



Dependendo do mecanismo,
mais tempo pode ser
necessário para atingir a
mesma concentração de um
reagente!

Meia-vida



Quando a velocidade independe da concentração

