

Universidade de São Paulo  
**Instituto de Química**

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## **Efeito da temperatura na velocidade das reações**

# Lei de velocidade

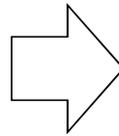
- Do que depende a velocidade de reação?

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

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

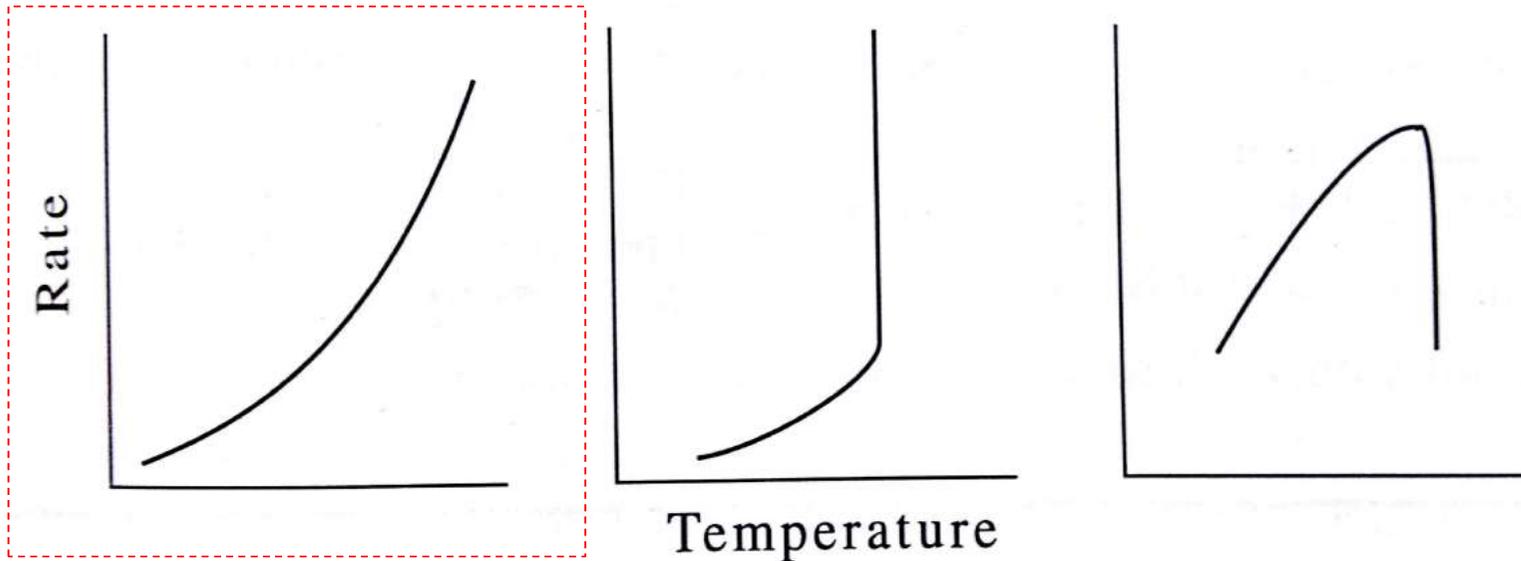
$$v = k(T)[A]^a[B]^b$$

Engloba  
dependência de  
temperatura



Avaliar  
comportamento  
de  $k(T)$

# Efeito da temperatura



(a)

maioria das  
reações

(b)

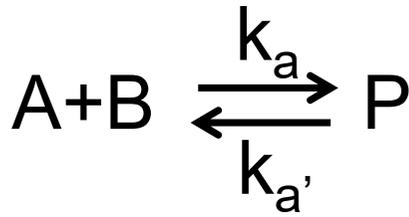
reações  
explosivas

(c)

reações  
enzimáticas

não é explicada pelo simples  
aumento de colisões ...

# Efeito da temperatura



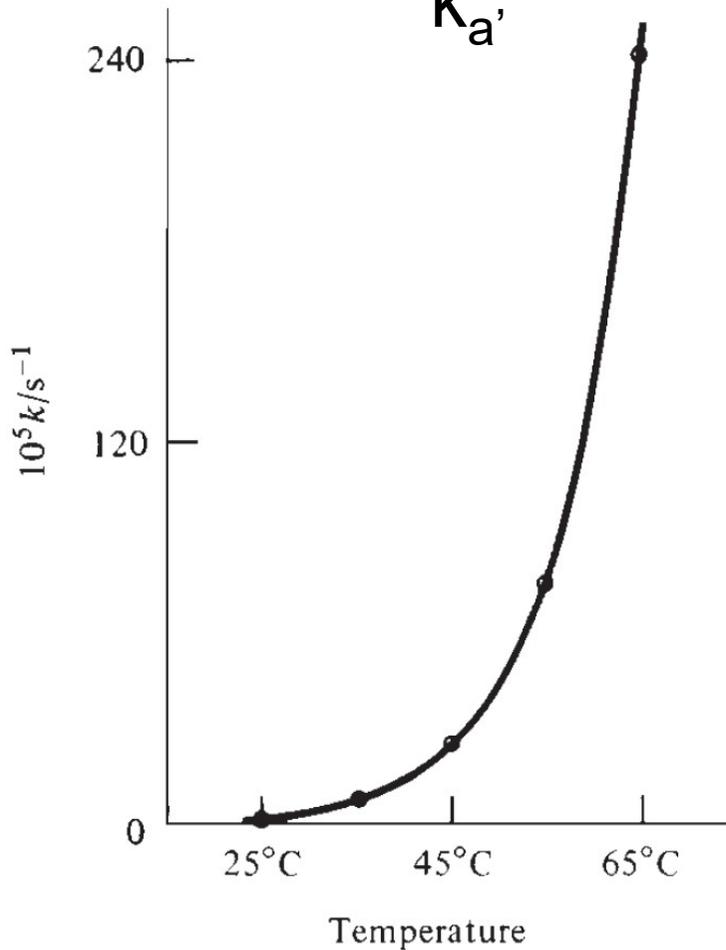
Qual usar pra “modelar” esses dados?

Do equilíbrios químico temos:

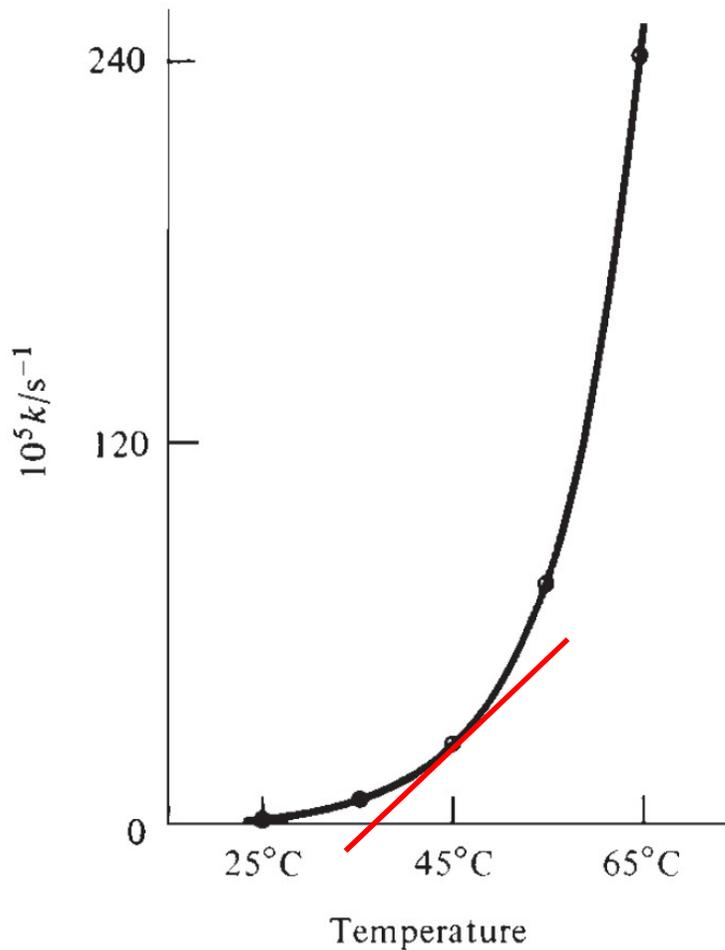
$$\frac{d \ln K}{dT} = \frac{\Delta G^0}{RT^2} \quad \rightarrow \quad \ln K = -\frac{\Delta G^0}{RT}$$

$$\text{No equilíbrio, } K = k_a/k_{a'}: \quad \ln k_a - \ln k_{a'} = -\frac{\Delta G^0}{RT}$$

$$\ln k_i = -\frac{\Delta G^\ddagger}{RT} + \text{constante}$$



# Efeito da temperatura



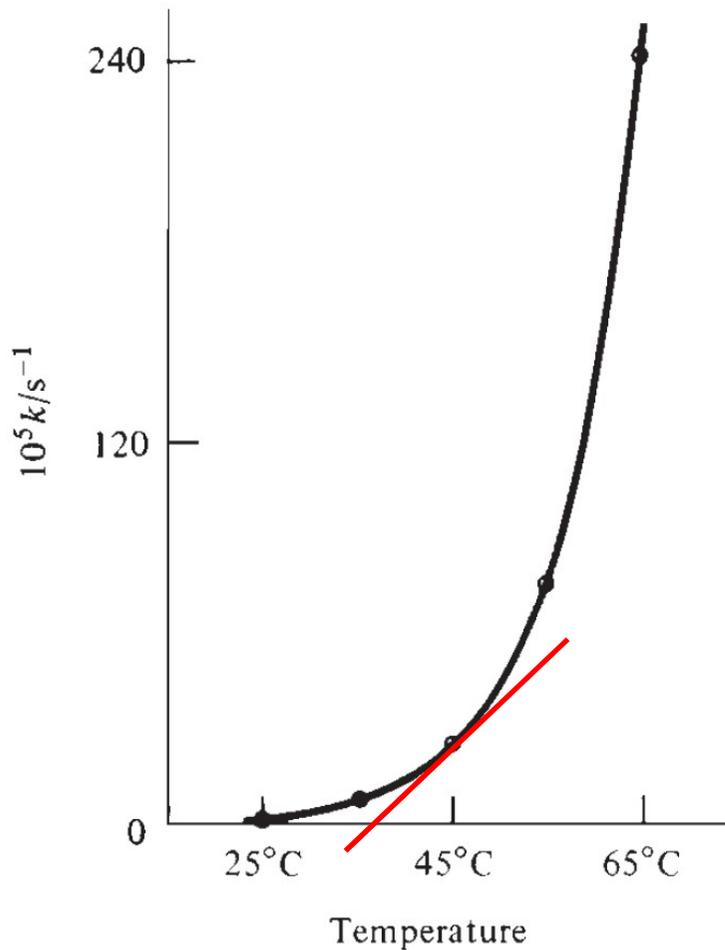
$$\frac{d \ln k}{dT} = C' \frac{1}{T^2}$$

$$\int_{k(\infty)}^{k(T)} d \ln k = C' \int_{\infty}^T \frac{1}{T^2} dT$$

$$\ln k(T) = \ln A - C' \frac{1}{T}$$

$$k(T) = A e^{-C' \frac{1}{T}}$$

# Efeito da temperatura



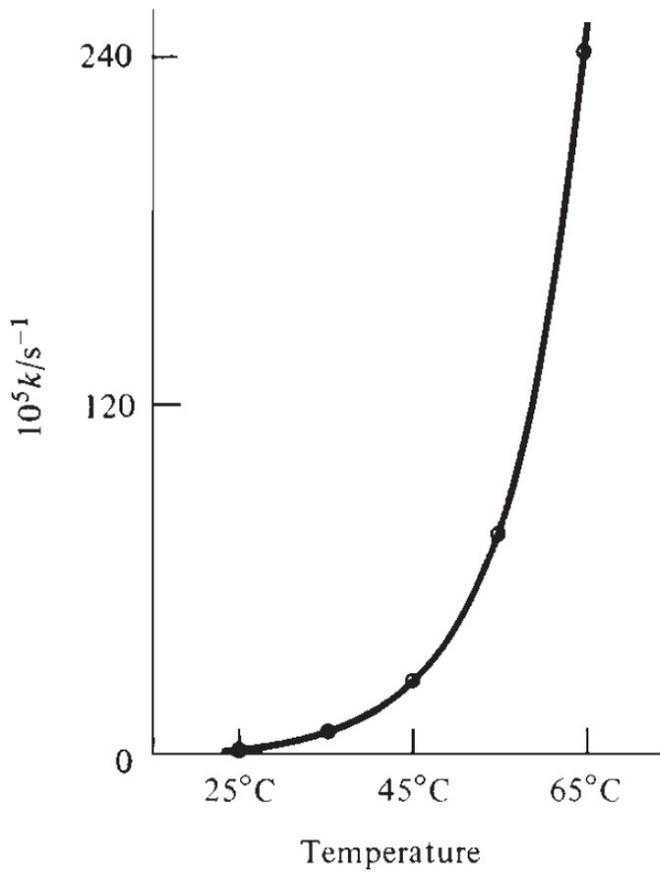
$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

$$\int_{k(\infty)}^{k(T)} d \ln k = \frac{E_a}{R} \int_{\infty}^T \frac{1}{T^2} dT$$

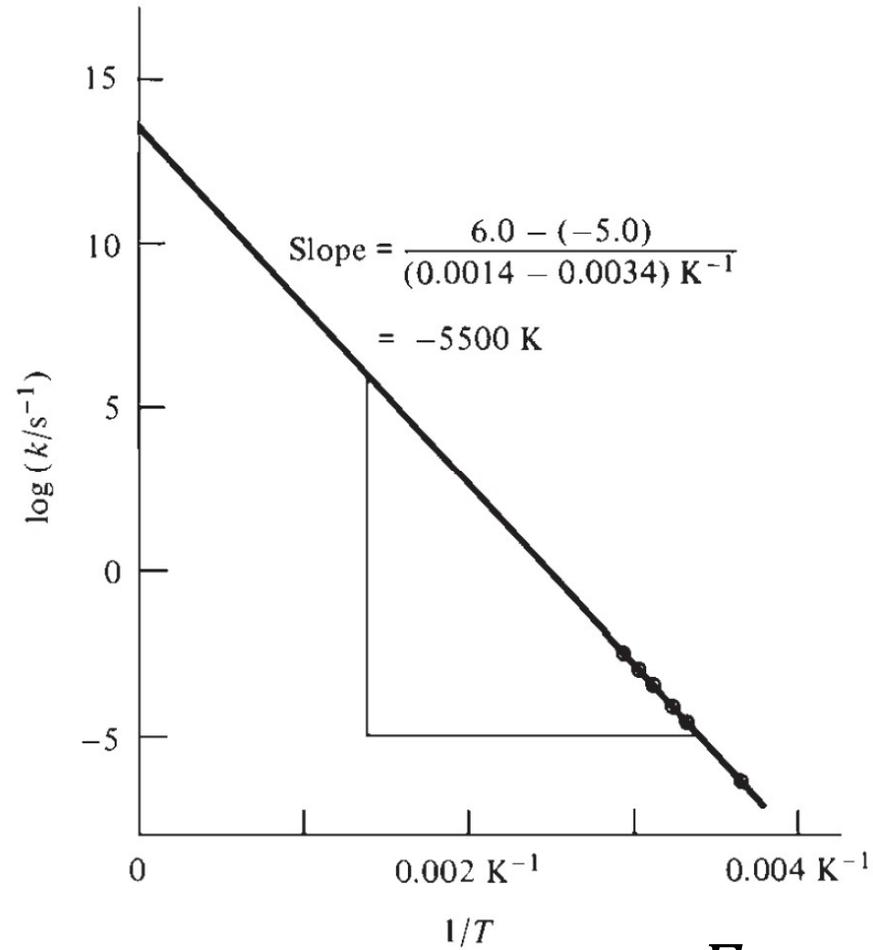
$$\ln k(T) = \ln A - \frac{E_a}{RT}$$

$$k(T) = A e^{-\frac{E_a}{RT}}$$

# Efeito da temperatura

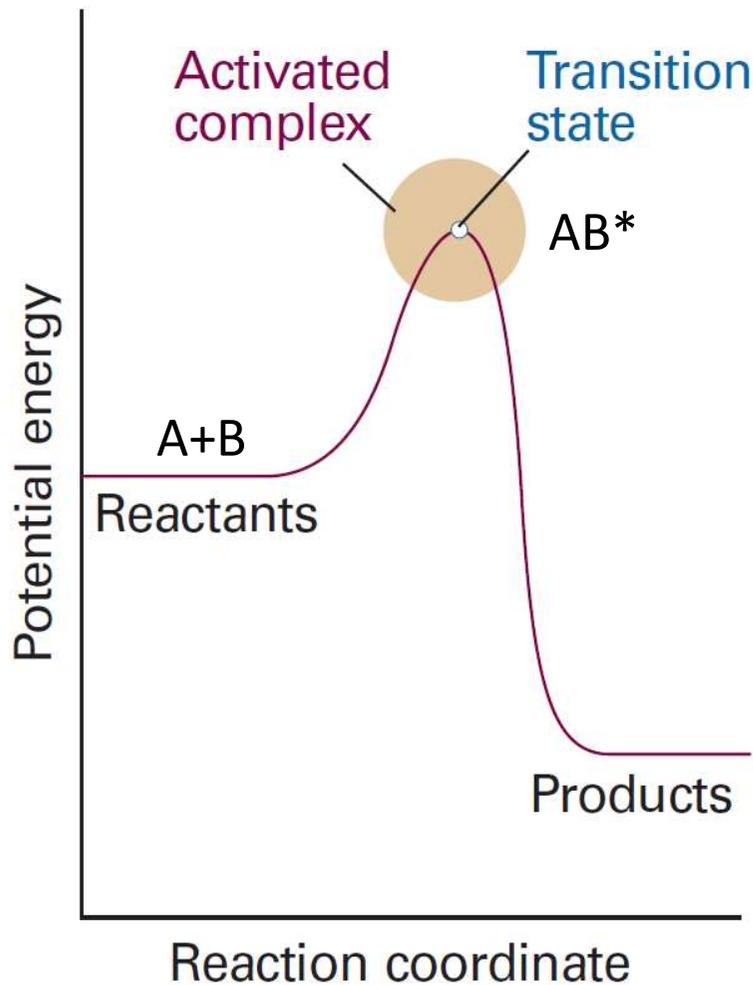


$$k(T) = Ae^{-\frac{E_a}{RT}}$$



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

# Origem da barreira energética



$$k(T) = A e^{-\frac{E_a}{RT}}$$

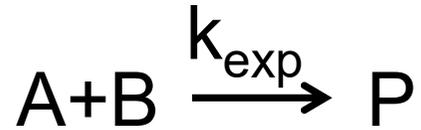
Colisões aumentam  
com T ( $A \propto T$ )

Limite mínimo de  
energia para reação  
ocorrer

Formação de um complexo ativado!

# Modelando por pré-equilíbrio

Experimental:

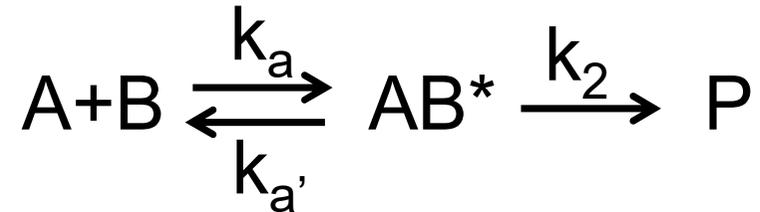


$$\frac{d[P]}{dt} = k_{exp}[A][B]$$



$$k_{exp} \propto \frac{k_a}{k_{a'}}$$

Considerando complexo ativado:



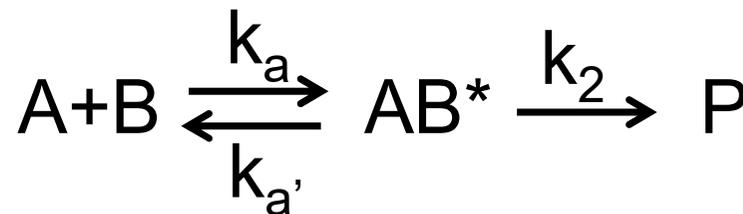
$$\frac{d[P]}{dt} = k_2[AB^*] \quad [AB^*] = \frac{k_a}{k_{a'}}[A][B]$$

$$\frac{d[P]}{dt} = k_2 \frac{k_a}{k_{a'}}[A][B]$$

# Equação de Eyring

$$k_{exp} \propto \frac{k_a}{k_{a'}}$$

Pela mecânica estatística



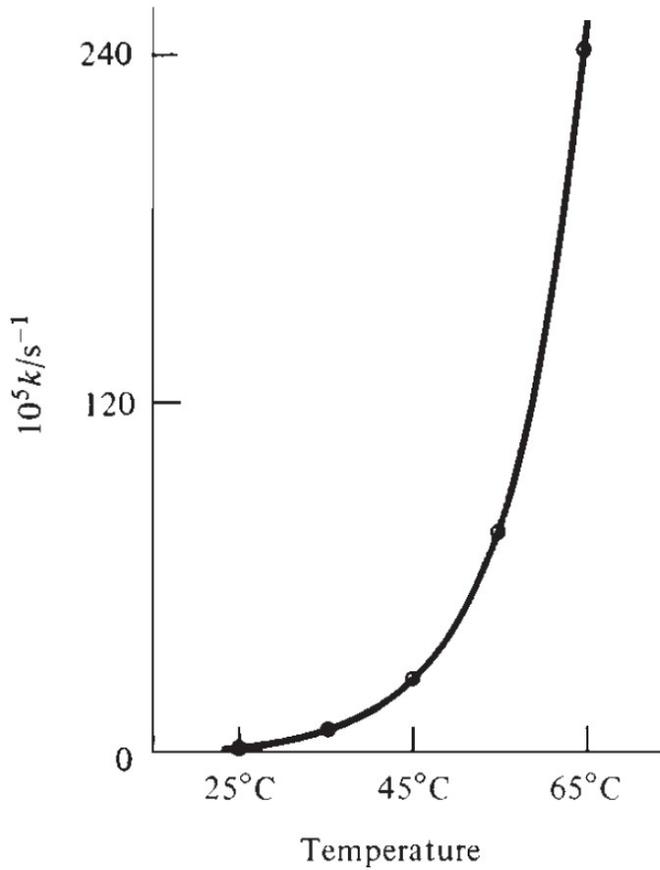
$$k_{exp} = \frac{k_b T}{h} \frac{k_a}{k_{a'}} = \frac{k_b T}{h} K^\ddagger = \frac{k_b T}{h} e^{-\frac{\Delta G^{0\ddagger}}{RT}}$$

$$k_{exp} = \frac{k_b T}{h} e^{\frac{\Delta S^{0\ddagger}}{R}} e^{-\frac{\Delta H^{0\ddagger}}{RT}} \quad k = A e^{-\frac{E_a}{RT}}$$

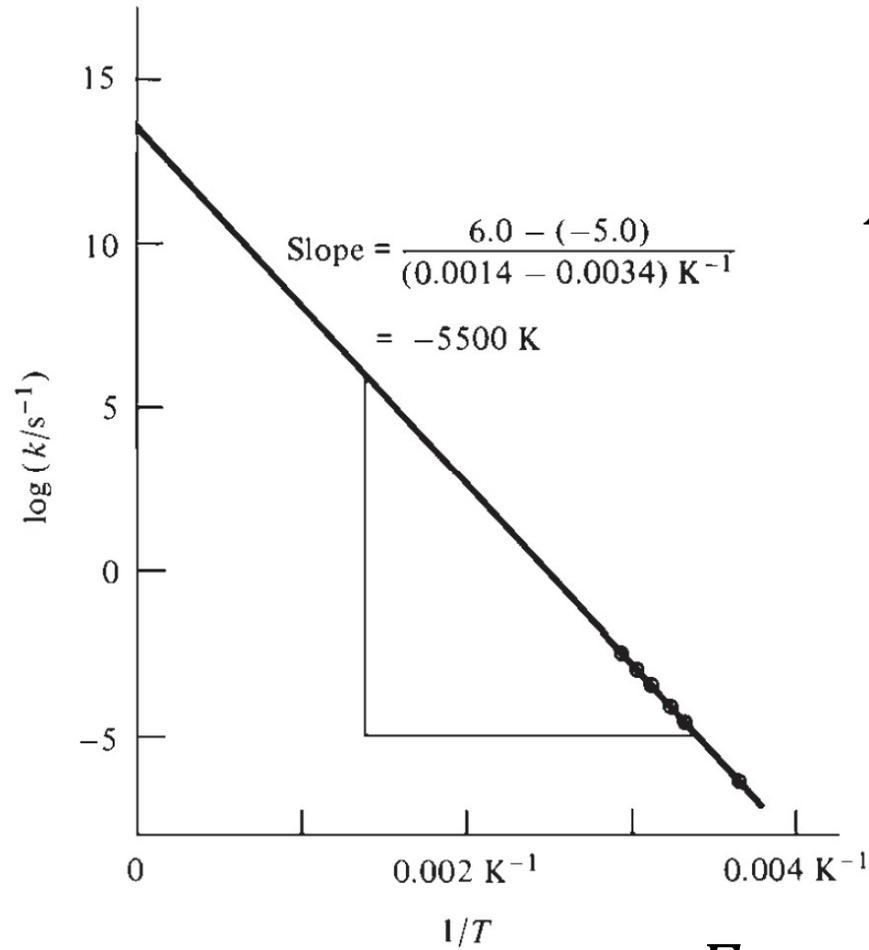
$$A = \frac{k_b T}{h} e^{\frac{\Delta S^{0\ddagger}}{R}}$$

Comparar com experimento ?

# Efeito da temperatura



$$k(T) = Ae^{-\frac{E_a}{RT}}$$



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

$$A = \frac{k_b T}{h} e^{\frac{\Delta S^{0\ddagger}}{R}}$$

$$E_a = \Delta H^{0\ddagger}$$

# Comparação Eyring vs. Experimental

Reação	A / cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	
	Experimental	Calculado
H + H <sub>2</sub> → H <sub>2</sub> + H	5,4 × 10 <sup>13</sup>	7,4 × 10 <sup>13</sup>
Br + H <sub>2</sub> → HBr + H	3 × 10 <sup>13</sup>	10 × 10 <sup>13</sup>
H + CH <sub>4</sub> → H <sub>2</sub> + CH <sub>3</sub>	1 × 10 <sup>13</sup>	2 × 10 <sup>13</sup>
CH <sub>3</sub> + H <sub>2</sub> → CH <sub>4</sub> + H	2 × 10 <sup>12</sup>	1 × 10 <sup>12</sup>
ClO + ClO → Cl <sub>2</sub> + O <sub>2</sub>	6 × 10 <sup>10</sup>	10 × 10 <sup>10</sup>

$$k = PAe^{-\frac{E_a}{RT}}$$



Fator de Arrhenius

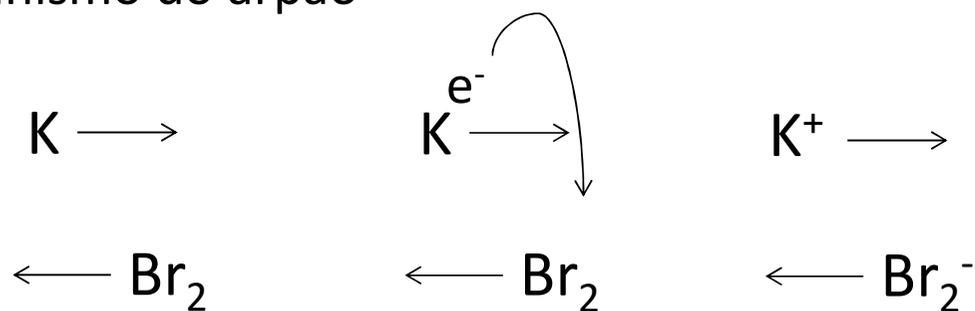
# Comparação Eyring vs. Experimental

Synoptic table 24.1\* Arrhenius parameters for gas-phase reactions

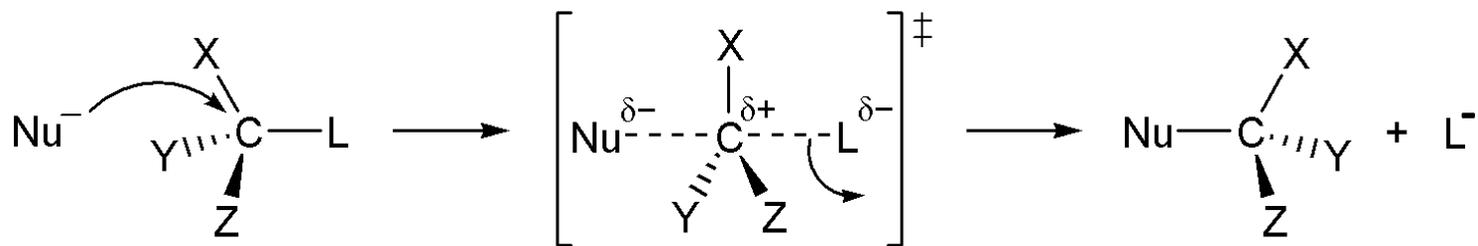
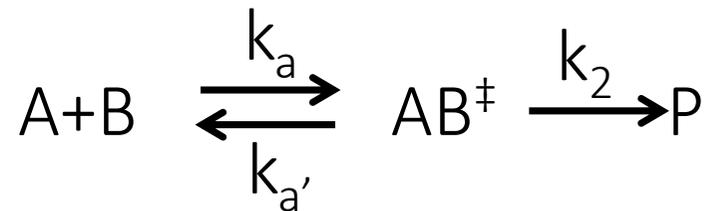
	$A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$		$E_a/(\text{kJ mol}^{-1})$	$P$
	Experiment	Theory		
$2 \text{NOCl} \rightarrow 2 \text{NO} + 2 \text{Cl}$	$9.4 \times 10^9$	$5.9 \times 10^{10}$	102	0.16
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	$1.24 \times 10^6$	$7.4 \times 10^{11}$	180	$1.7 \times 10^{-6}$
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	$1.0 \times 10^{12}$	$2.1 \times 10^{11}$	0	4.8

\* More values are given in the *Data section*.

Mecanismo do arpão

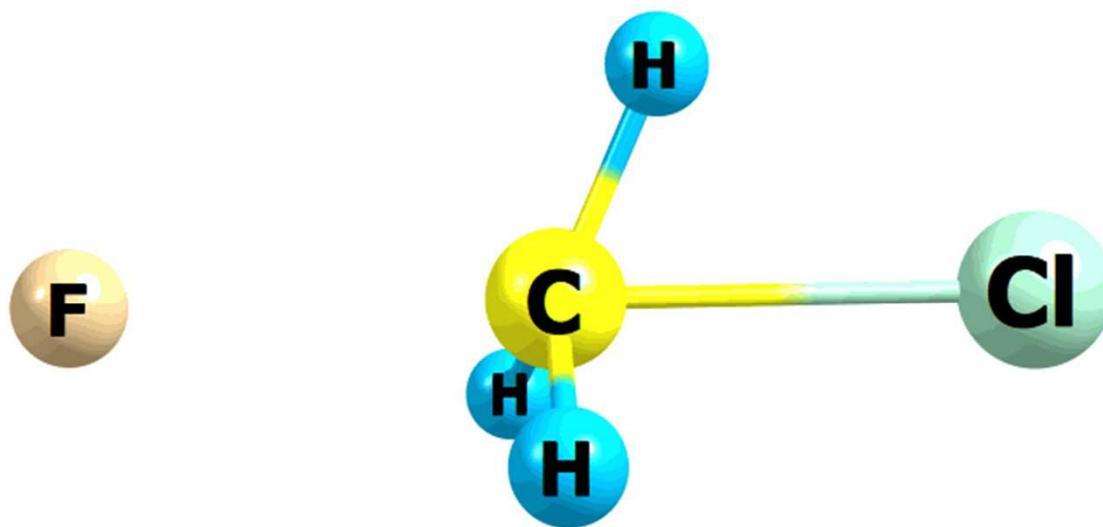


# Coordenada de reação



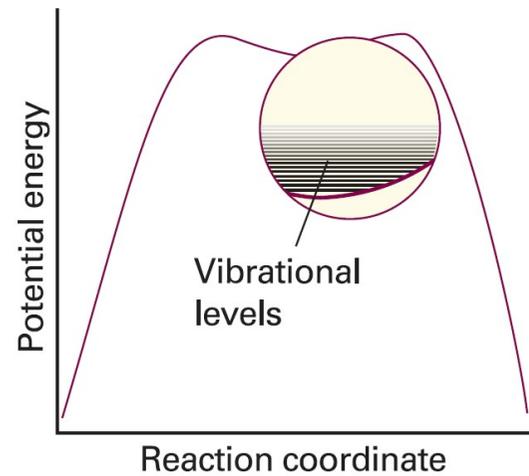
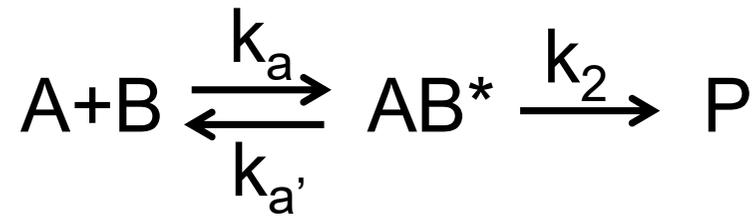
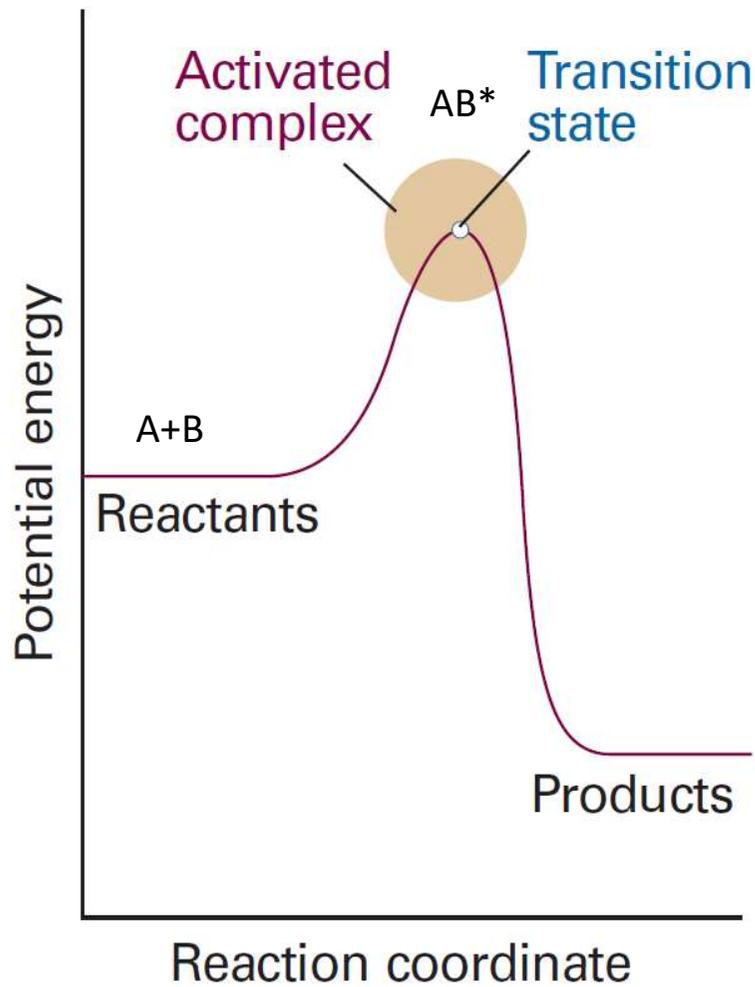
$$k_2 \propto \nu^\ddagger \sim 1/10^{-12} \text{ s}$$

## Coordenada de reação

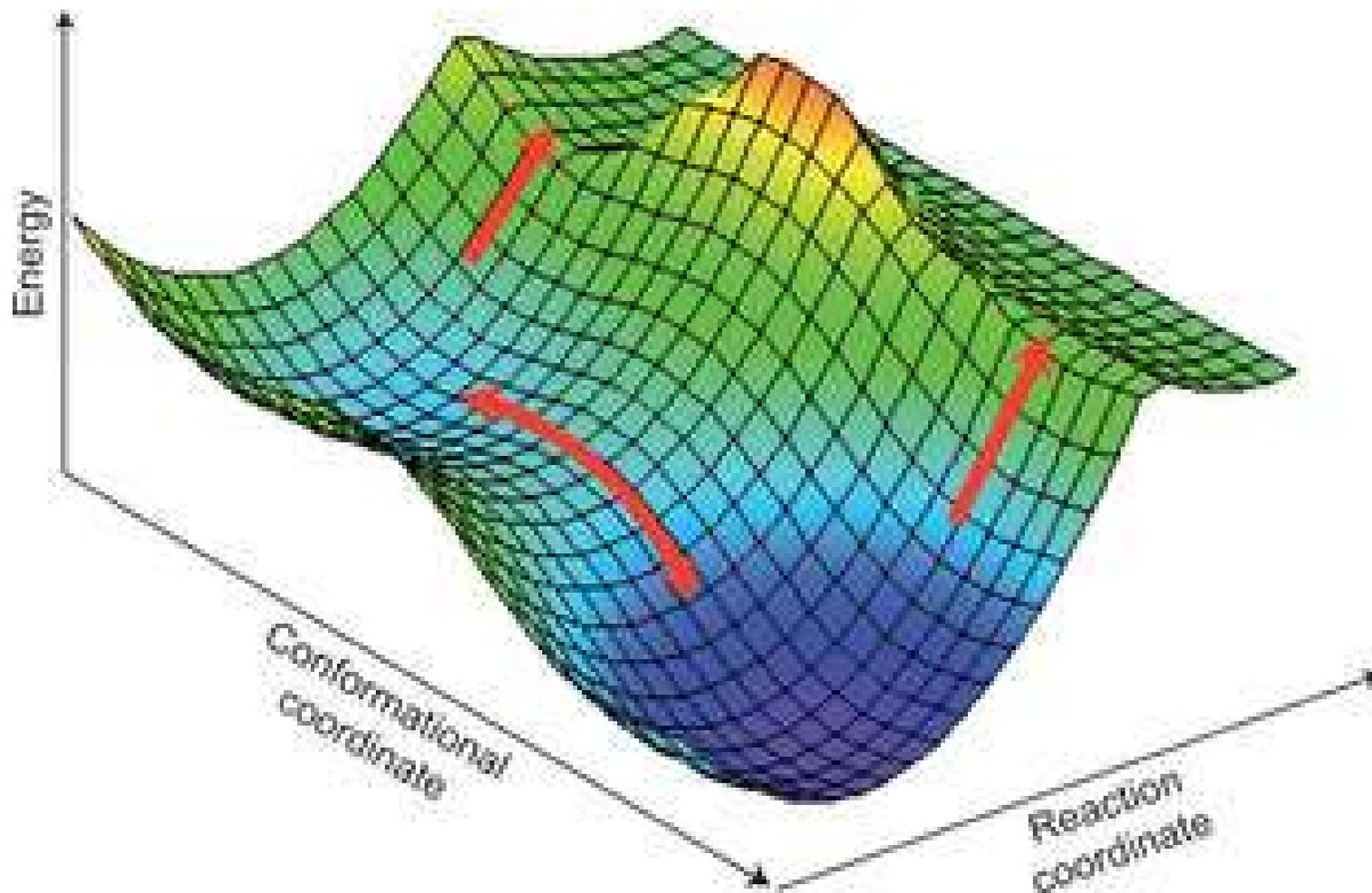


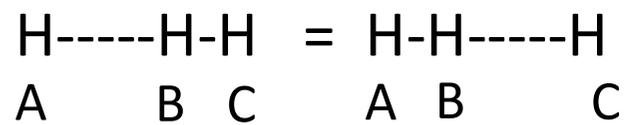
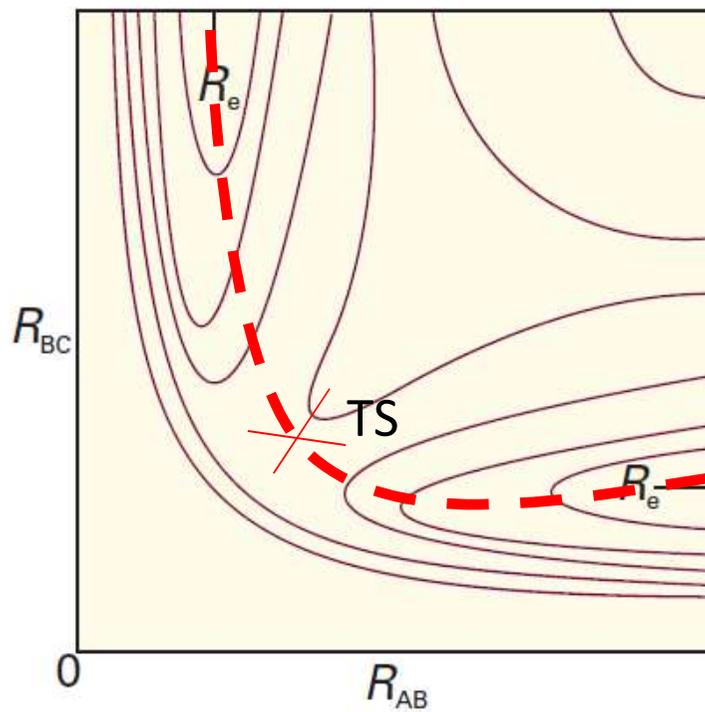
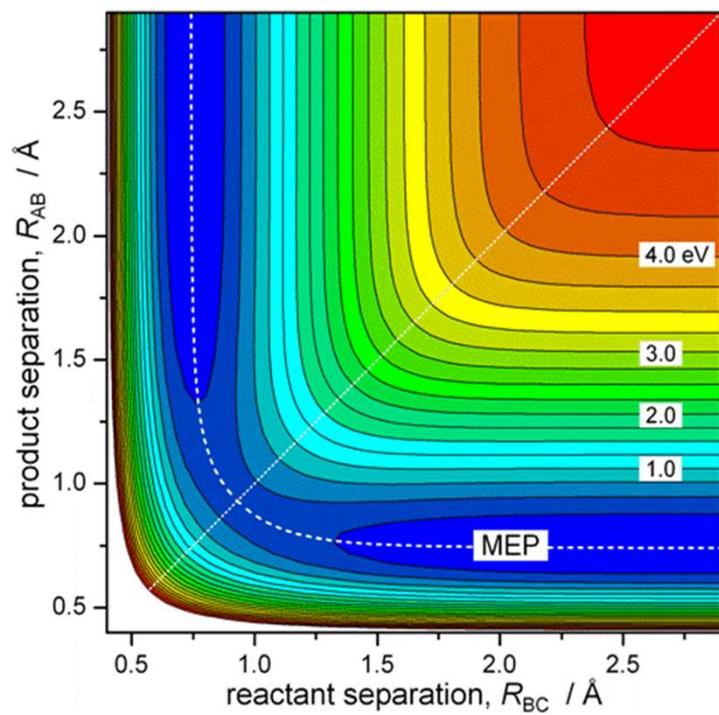
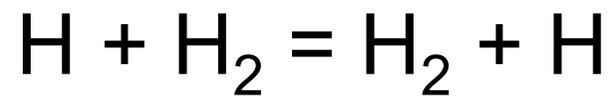
$$k_2 = 596,30 \text{ cm}^{-1} = 1,8 \cdot 10^{13} \text{ s}^{-1}$$

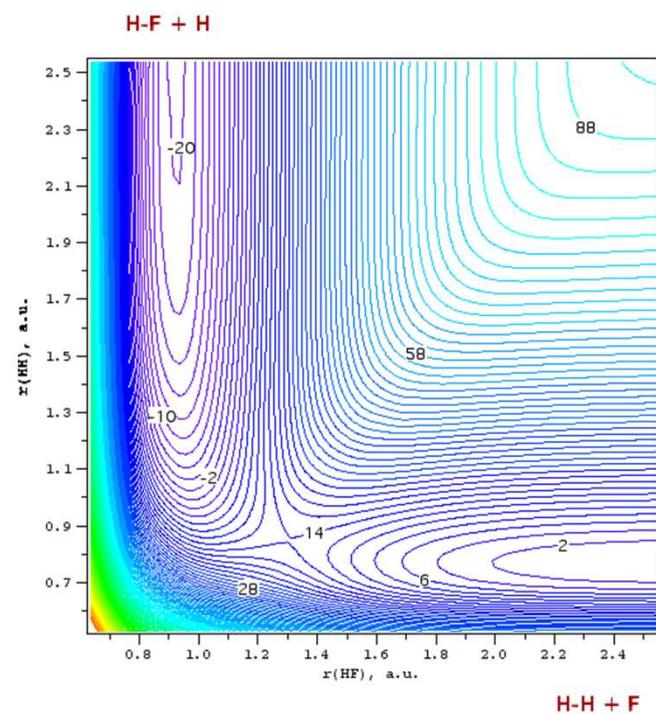
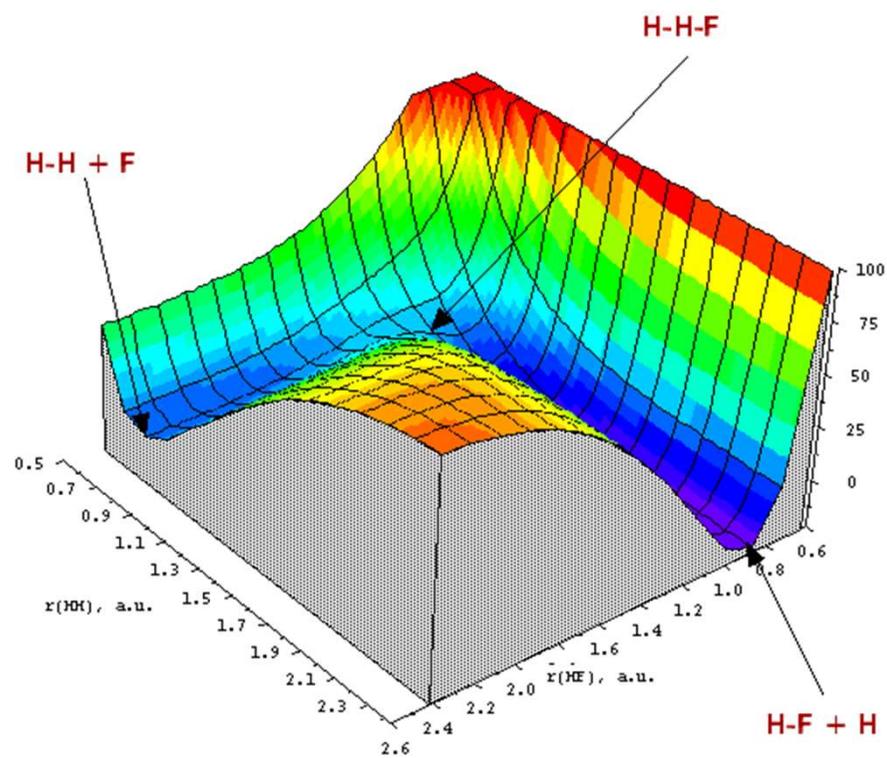
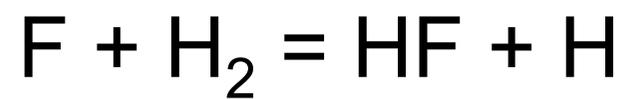
# Estado de transição vs. Complexo ativado



# Hipersuperfícies

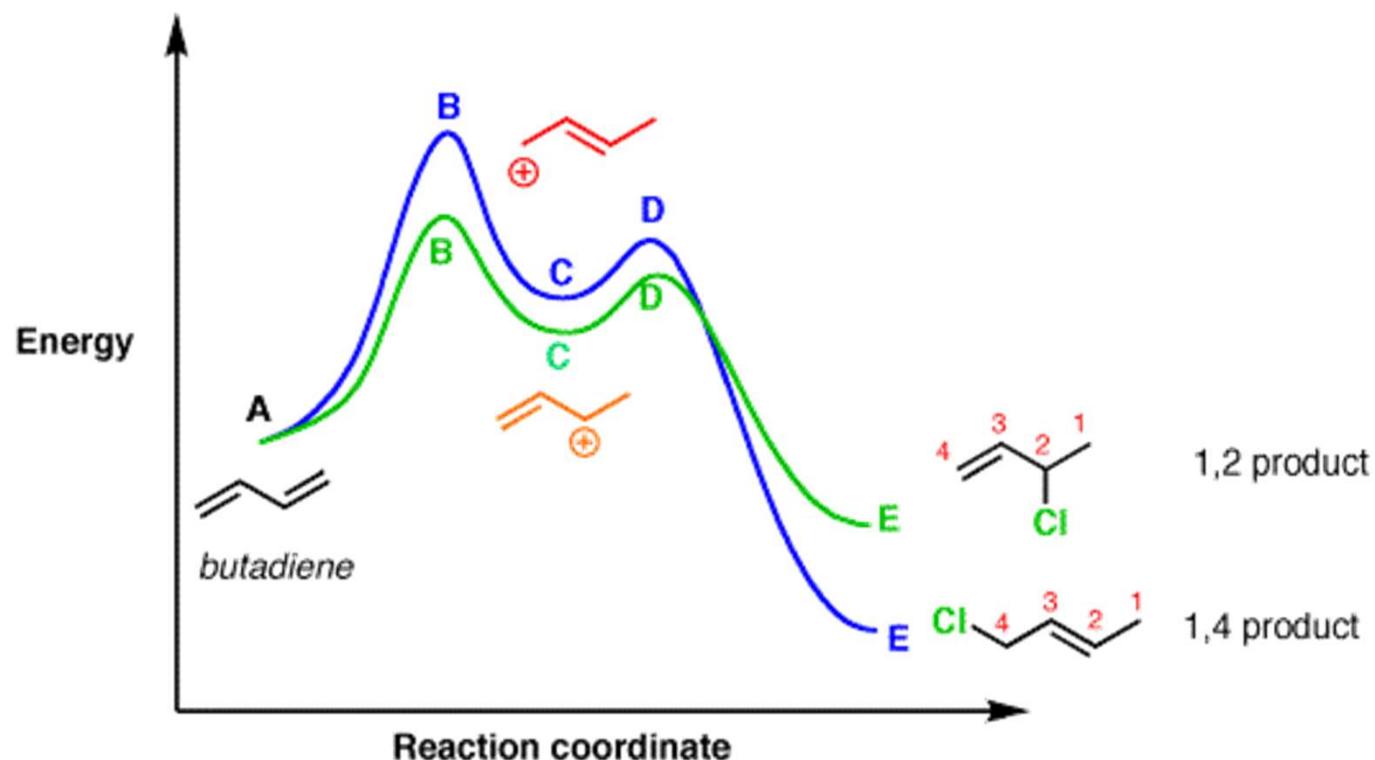






# Controle cinético vs. termodinâmico

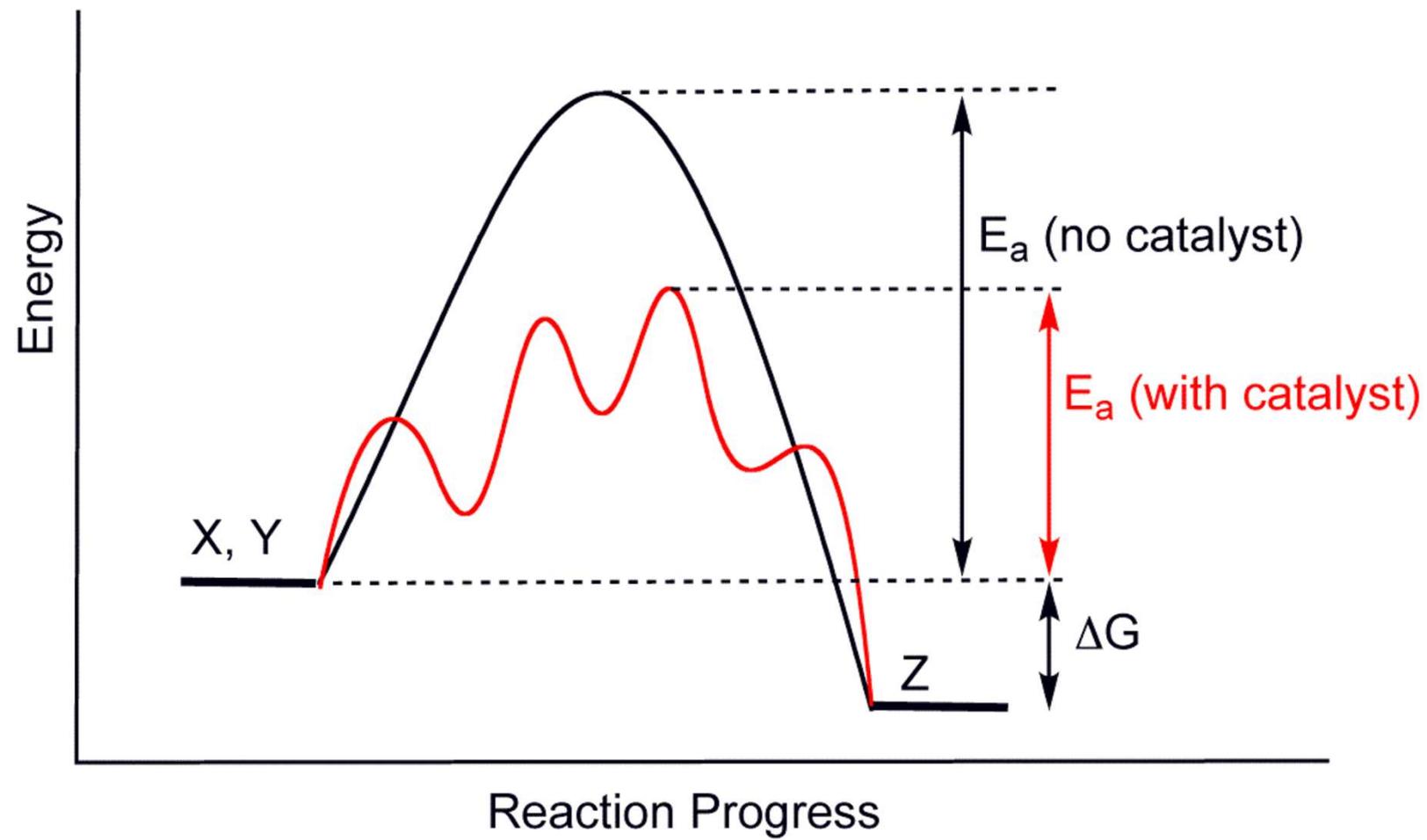
Energy coordinate for 1,2- versus 1,4- additions to butadiene



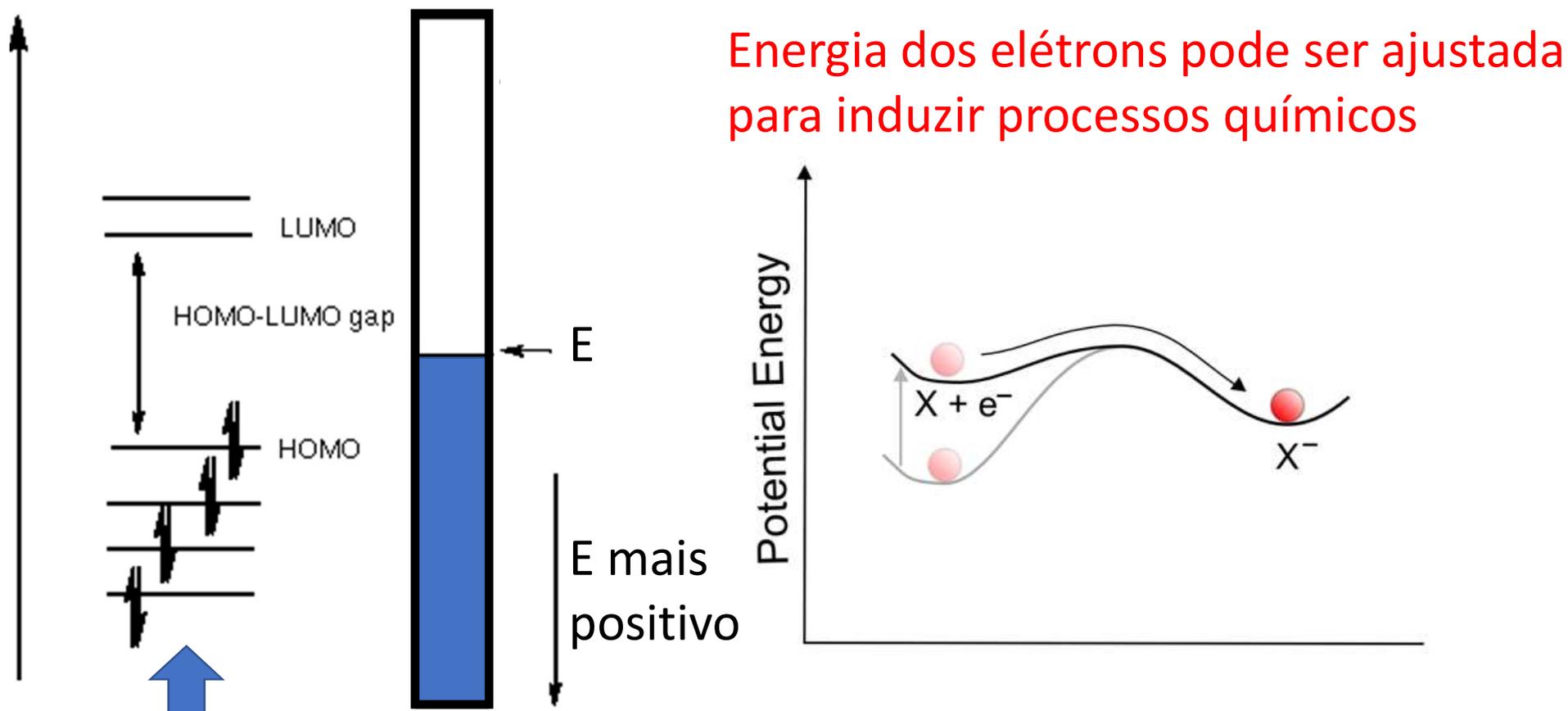
The energy of **C** and **C** (and therefore the height of transition states **B** and **B**) is related to carbocation stability (secondary more stable than primary here)

The energy of **E** and **E** is related to the greater stability of the 1,4 alkene in this case (disubstituted versus monosubstituted)

# Superfícies de energia



# Mudança da energia dos elétrons

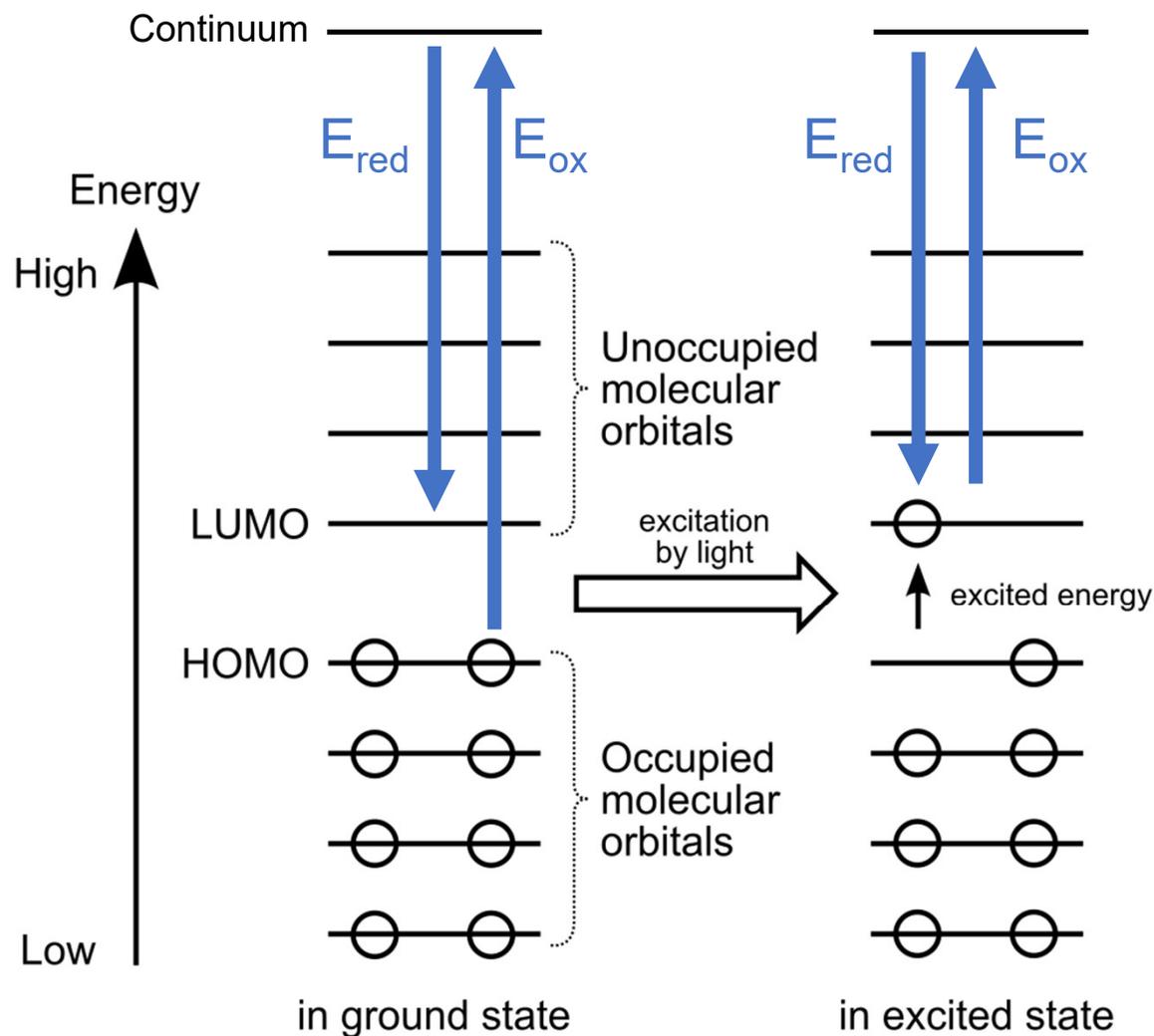


Energia dos “reagentes” permanece inalterada

<http://okbu.net/chemistry/mrjordan/inorganic1/electrochem/ECHEM1.HTML>

<https://sop4cv.com/chapters/ElectronTransferAtTheElectrode.html>

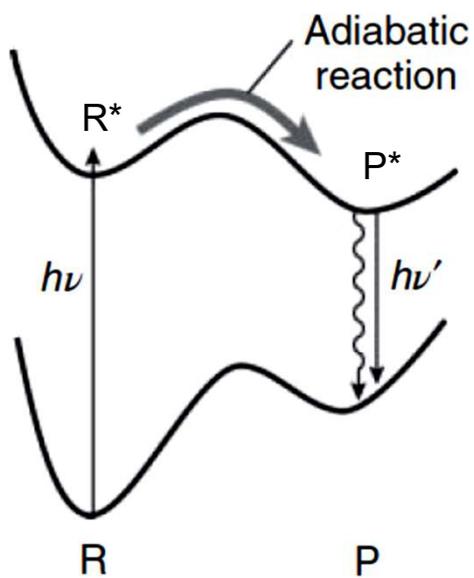
# Mudança dos orbitais promovida por luz



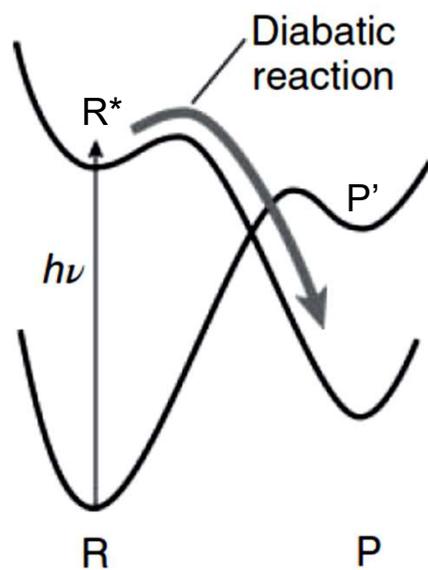
Reatividade do estado excitado é diferente do estado fundamental

# Fótons como reagentes

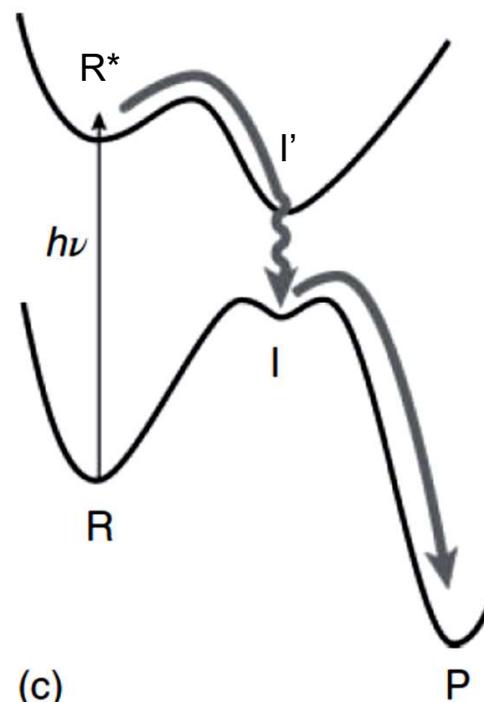
Natureza dos reagentes é alterada!



(a)



(b)



(c)

O que aprendemos com a dependência da temperature?

- Sabemos calcular  $k(T)$
- Criamos **um modelo para explicar a maioria das reações química** –  $E_a$  e colisões
  - Complexo ativado e do estado de transição
- Superfícies de energia:
  - Comparação de mecanismos
  - Ponte entre cinética e termodinâmica
  - Caminhos de reação mais favoráveis