

Universidade de São Paulo
Instituto de Química

Prof. Dr. Thiago C. Correra

Efeito da temperatura na velocidade das reações

Lei de velocidade

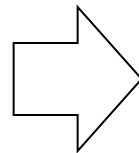
- Do que depende a velocidade de reação?

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

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

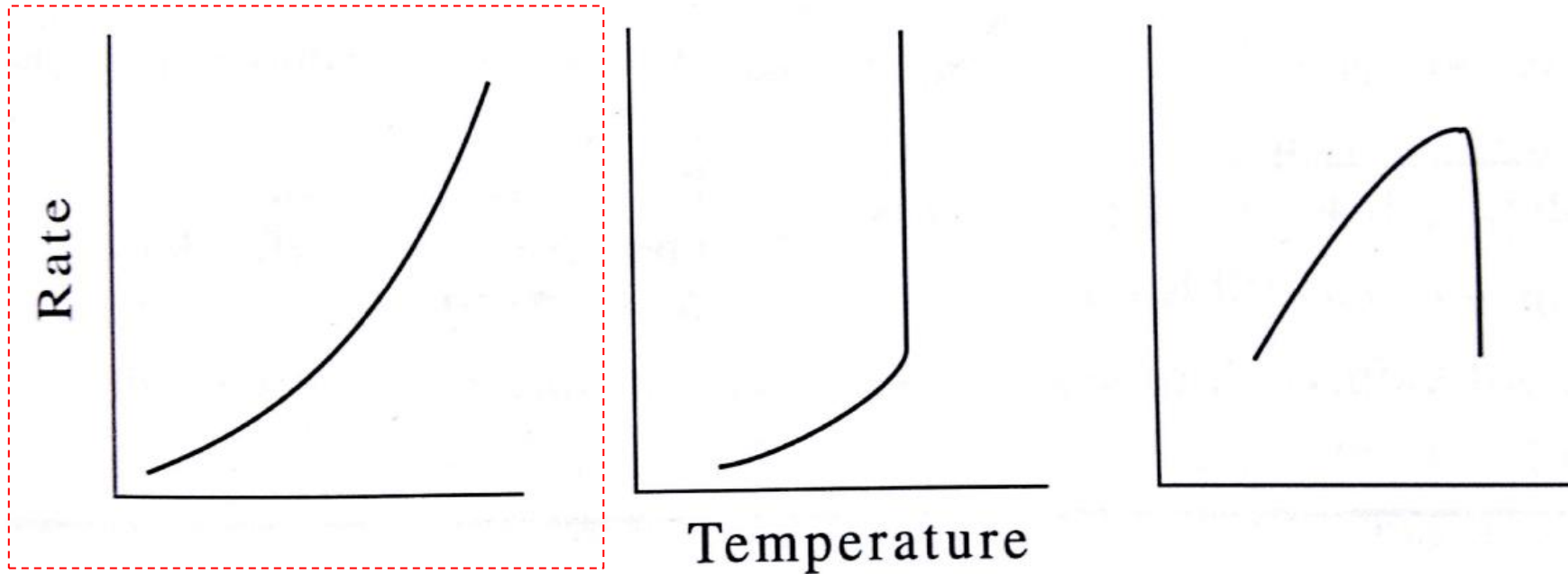
$$v = k(T)[A]^a[B]^b$$

Engloba
dependência de
temperatura



Avaliar
comportamento
de $k(T)$

Efeito da temperatura



(a)

maioria das
reações

(b)

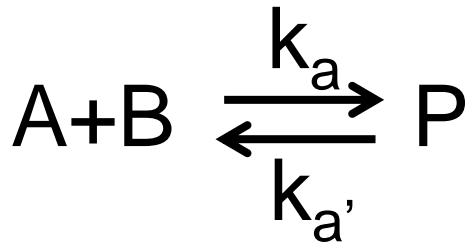
reações
explosivas

(c)

reações
enzimáticas

não é explicada pelo simples
aumento de colisões ...

Efeito da temperatura



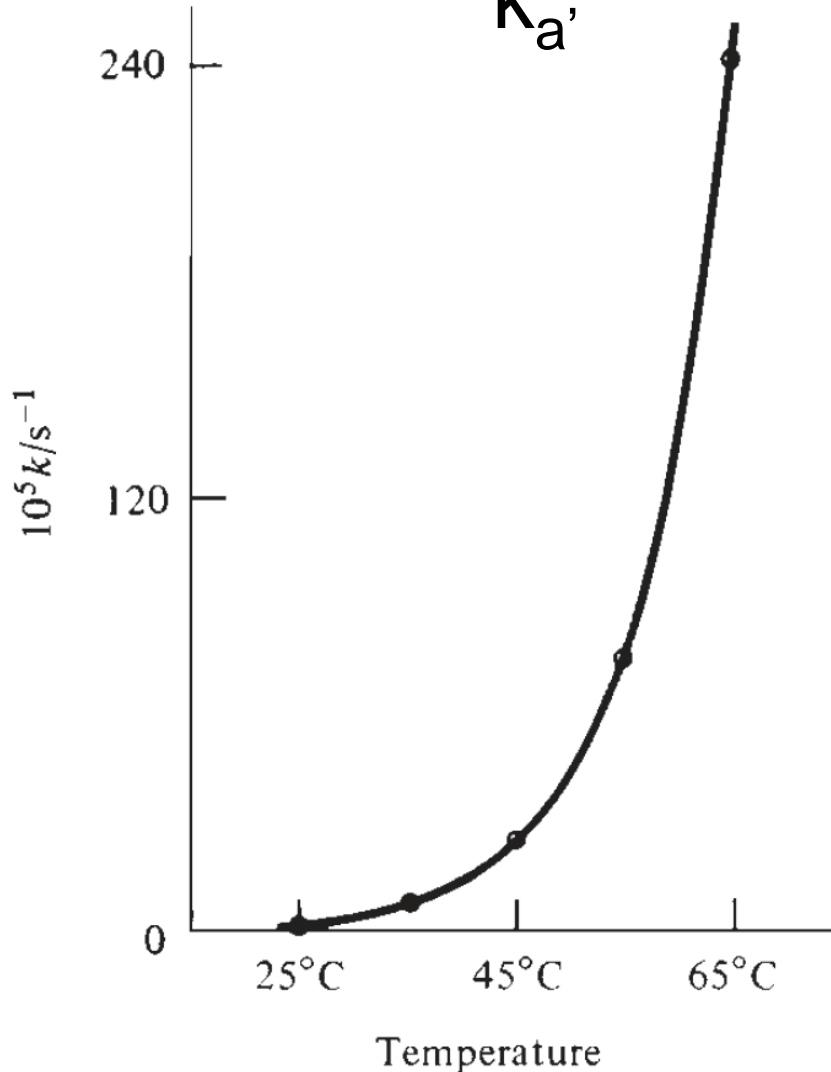
Qual usar pra “modelar” esses dados?

Do equilíbrios químico temos:

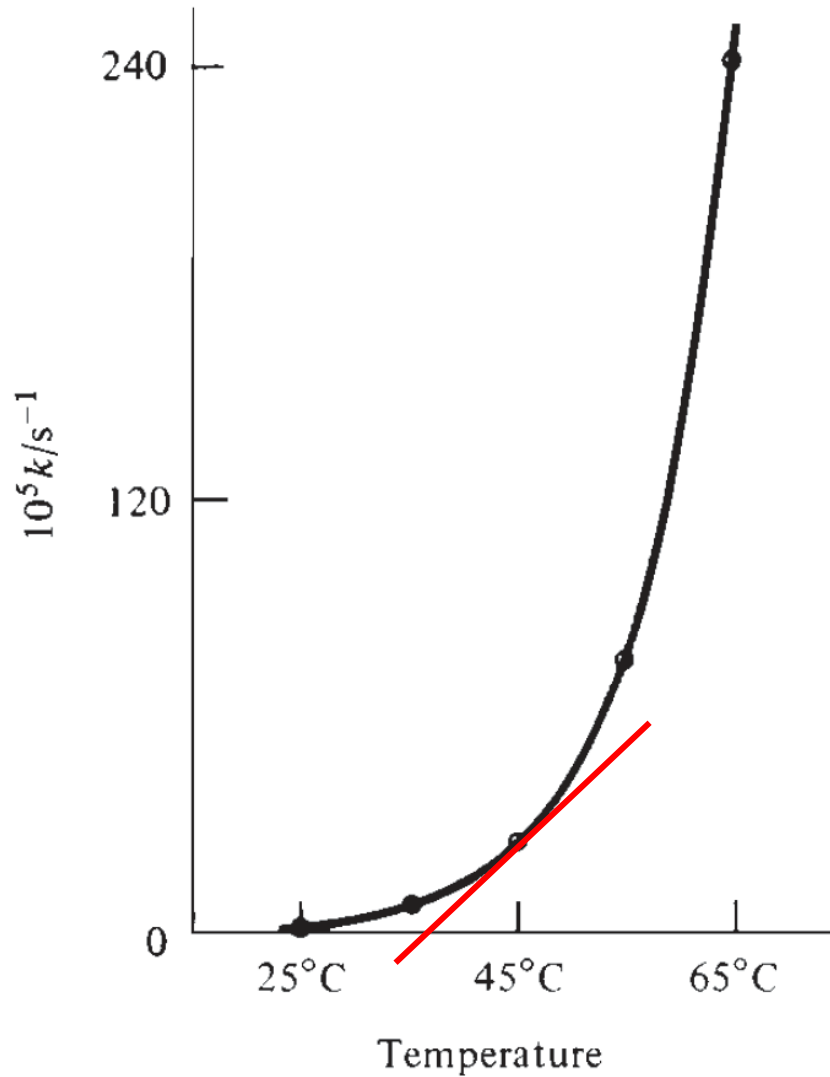
$$\frac{d \ln K}{dT} = \frac{\Delta G^0}{RT^2} \quad \rightarrow \quad \ln K = -\frac{\Delta G^0}{RT}$$

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

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



Efeito da temperatura



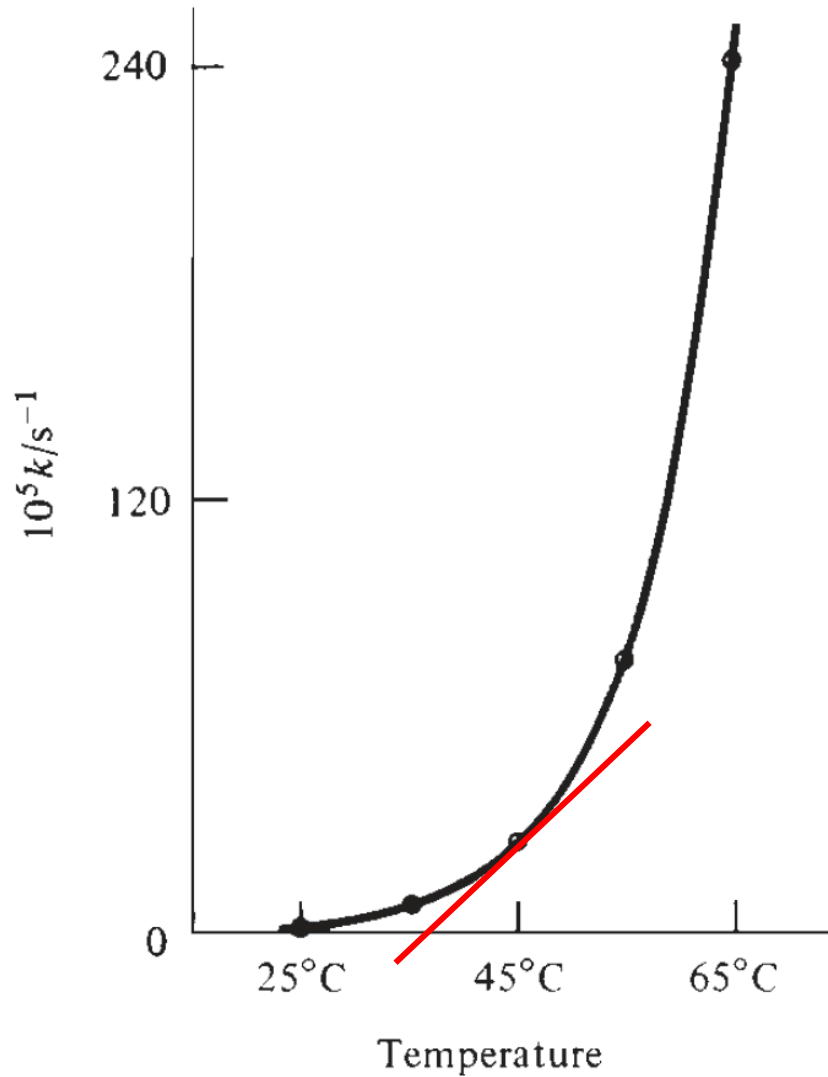
$$\frac{d \ln k}{dT} = C' \frac{1}{T^2}$$

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

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

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

Efeito da temperatura



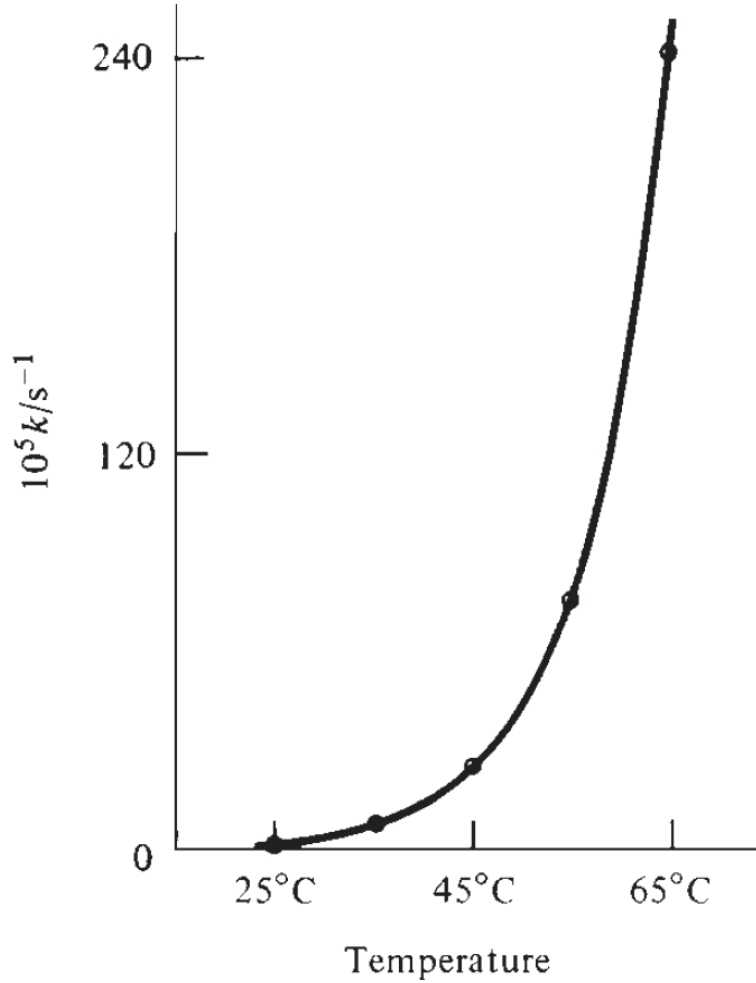
$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

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

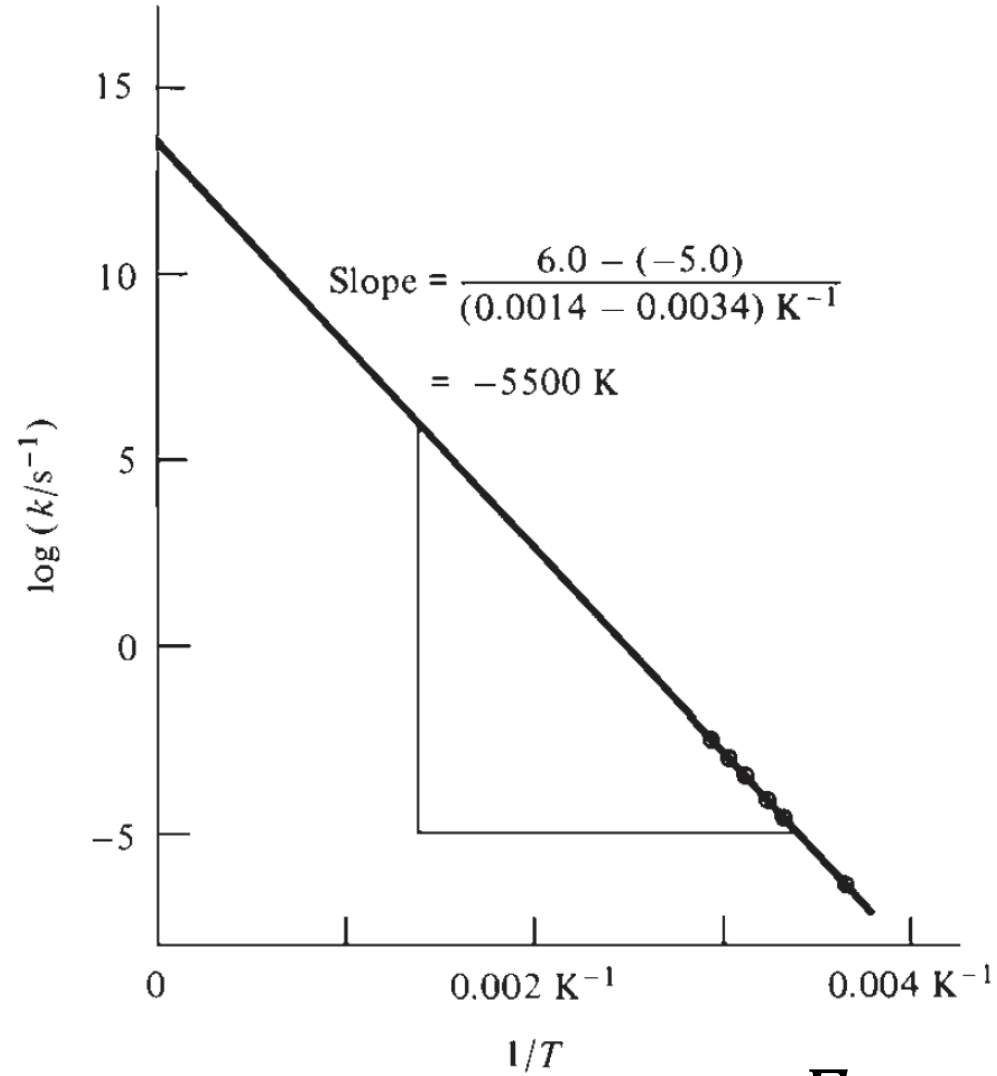
$$\ln k(T) = \ln A - \frac{E_a}{RT}$$

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

Efeito da temperatura

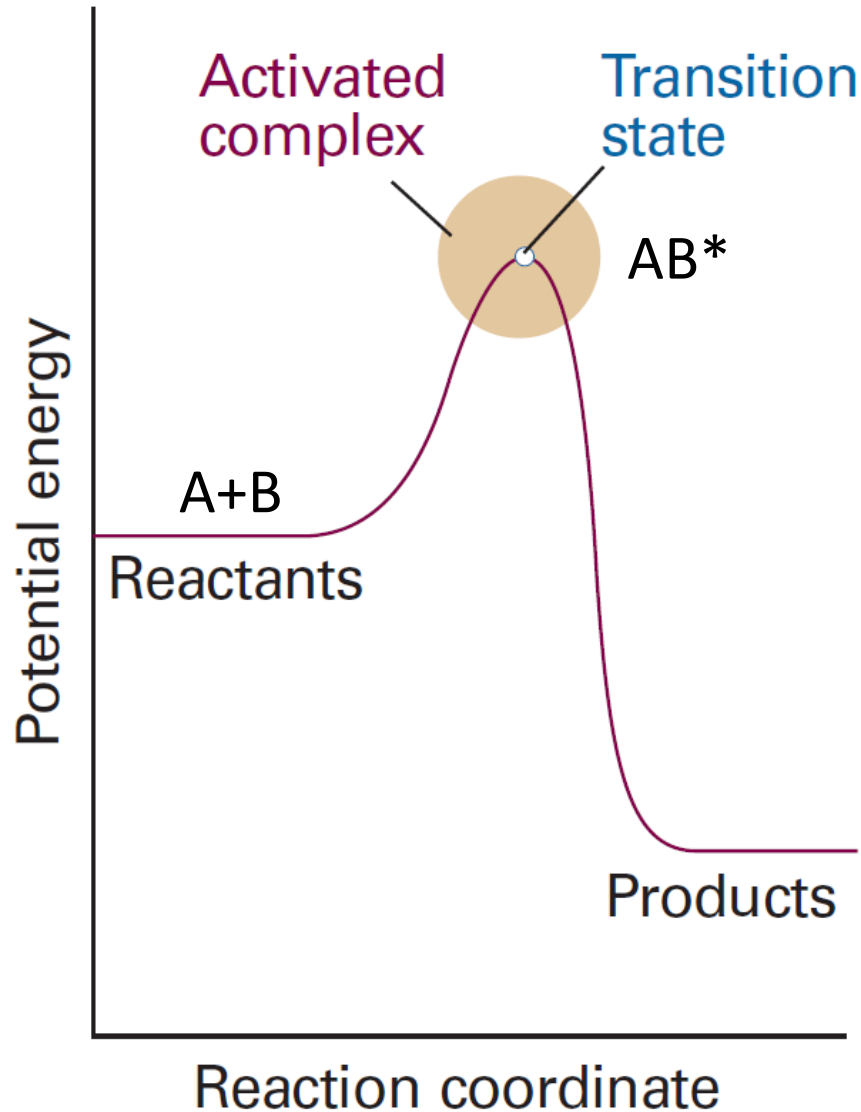


$$k(T) = A e^{-\frac{E_a}{RT}}$$



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

Origem da barreira energética



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

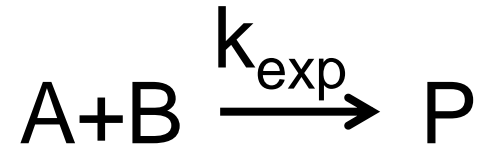
Colisões aumentam
com T ($A \propto T$)

Limite mínimo de
energia para reação
ocorrer

Formação de um complexo ativado!

Modelando por pré-equilíbrio

Experimental:

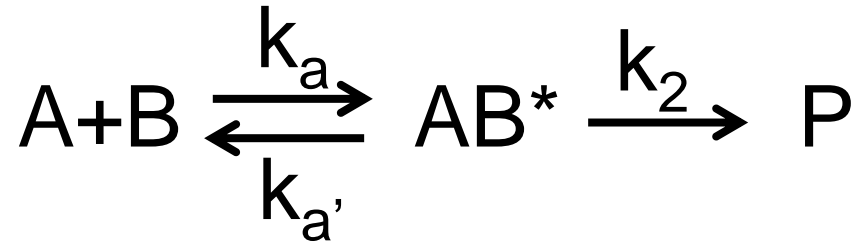


$$\frac{d[P]}{dt} = k_{exp} [A][B]$$



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

Considerando complexo ativado:



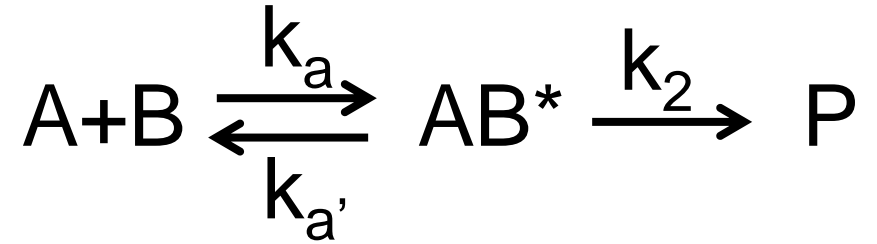
$$\frac{d[P]}{dt} = k_b [AB^*] \quad [AB^*] = \frac{k_a}{k_{a'}} [A][B]$$

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

Equação de Eyring

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

Pela mecânica estatística



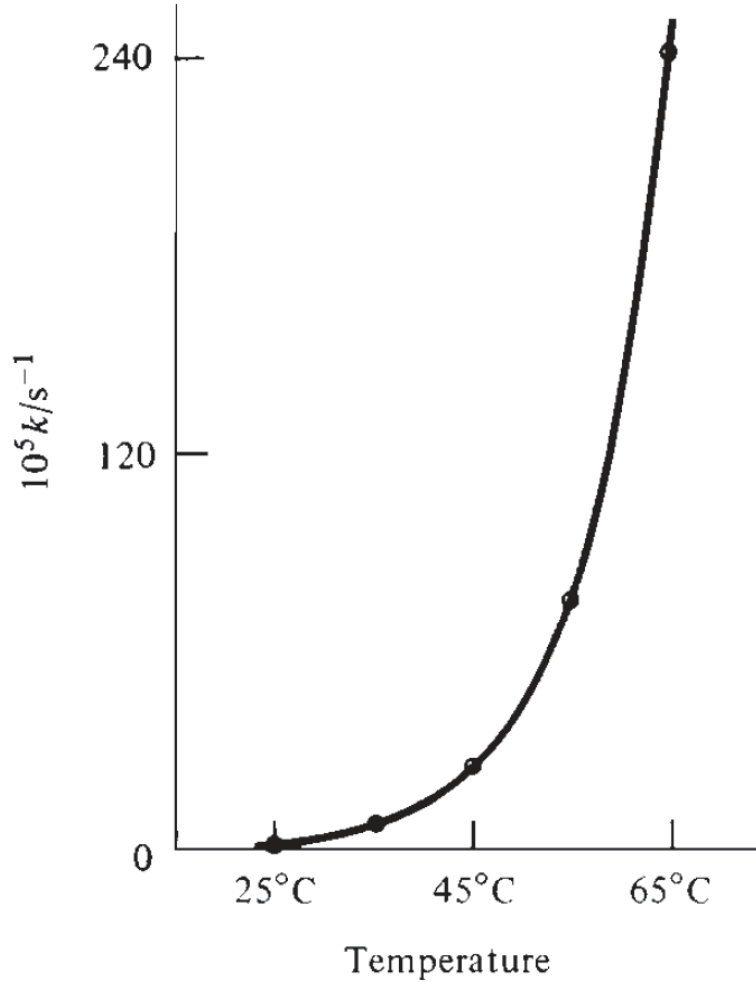
$$k_{exp} = \frac{k_b T}{h} \frac{k_a}{k_{a'}} = \frac{k_b T}{h} K^\ddagger = \frac{k_b T}{h} e^{-\frac{\Delta G^{0\ddagger}}{RT}}$$

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

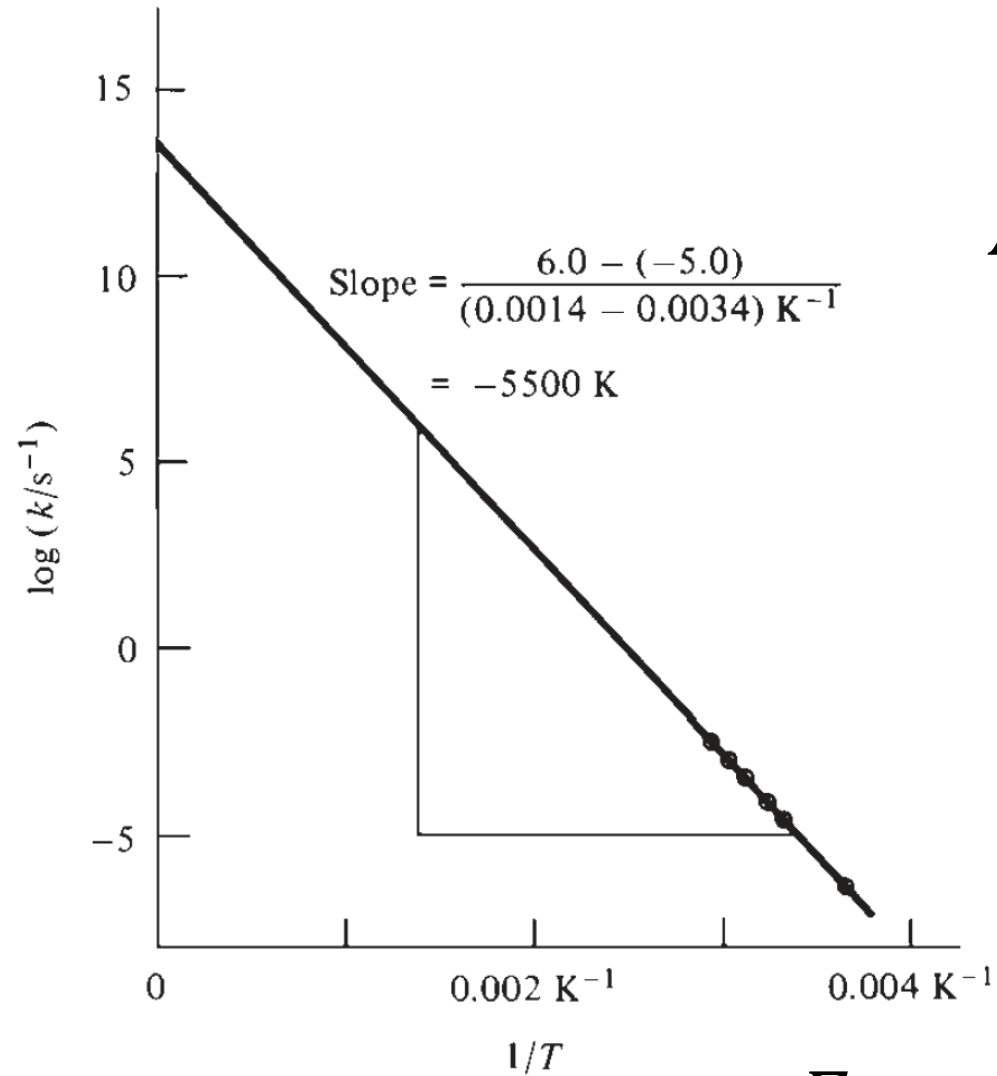
$$A = \frac{k_b T}{h} e^{\frac{\Delta S^{0\ddagger}}{R}}$$

Comparar com experimento ?

Efeito da temperatura



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



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

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

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

Comparação Eyring vs. Experimental

Reação	$A / \text{cm}^3 \text{mol}^{-1}\text{s}^{-1}$	
	Experimental	Calculado
$\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$	$5,4 \times 10^{13}$	$7,4 \times 10^{13}$
$\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$	3×10^{13}	10×10^{13}
$\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$	1×10^{13}	2×10^{13}
$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$	2×10^{12}	1×10^{12}
$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	6×10^{10}	10×10^{10}

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



Fator de Arrhenius

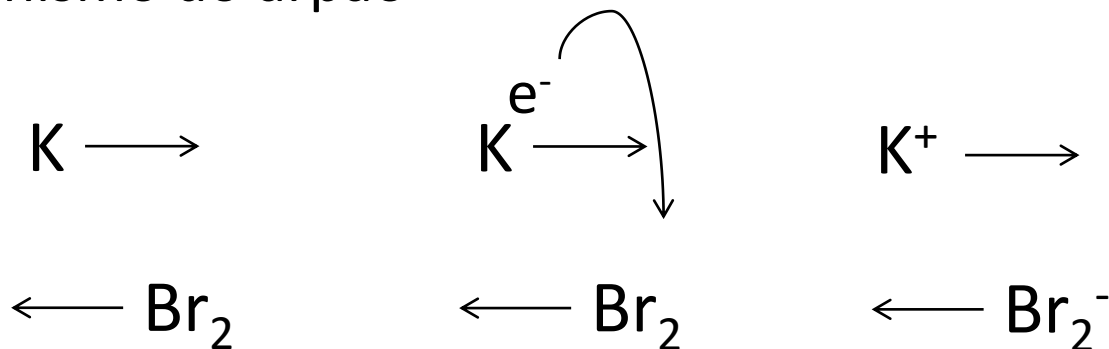
Comparação Eyring vs. Experimental

Synoptic table 24.1* Arrhenius parameters for gas-phase reactions

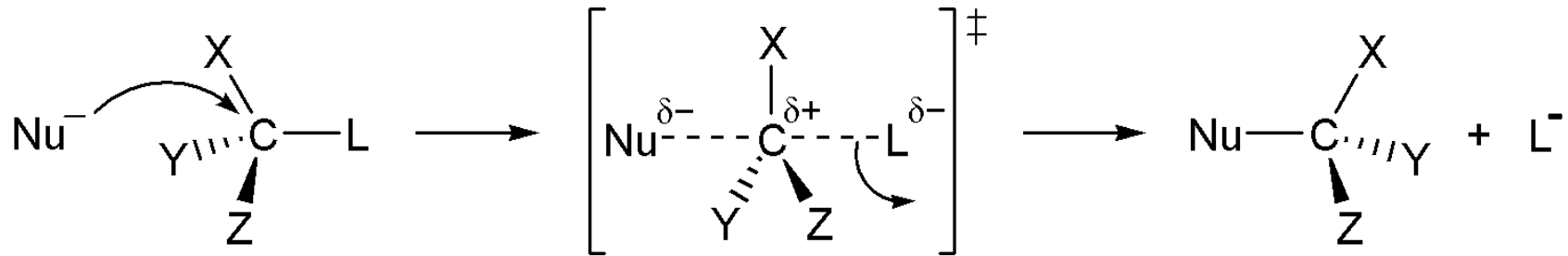
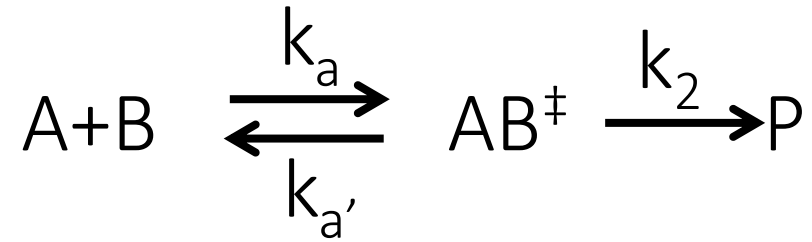
	$A/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$		$E_a/(\text{kJ mol}^{-1})$	P
	Experiment	Theory		
$2 \text{ NOCl} \rightarrow 2 \text{ NO} + 2 \text{ Cl}$	9.4×10^9	5.9×10^{10}	102	0.16
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	1.24×10^6	7.4×10^{11}	180	1.7×10^{-6}
$\text{K}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

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

Mecanismo do arpão

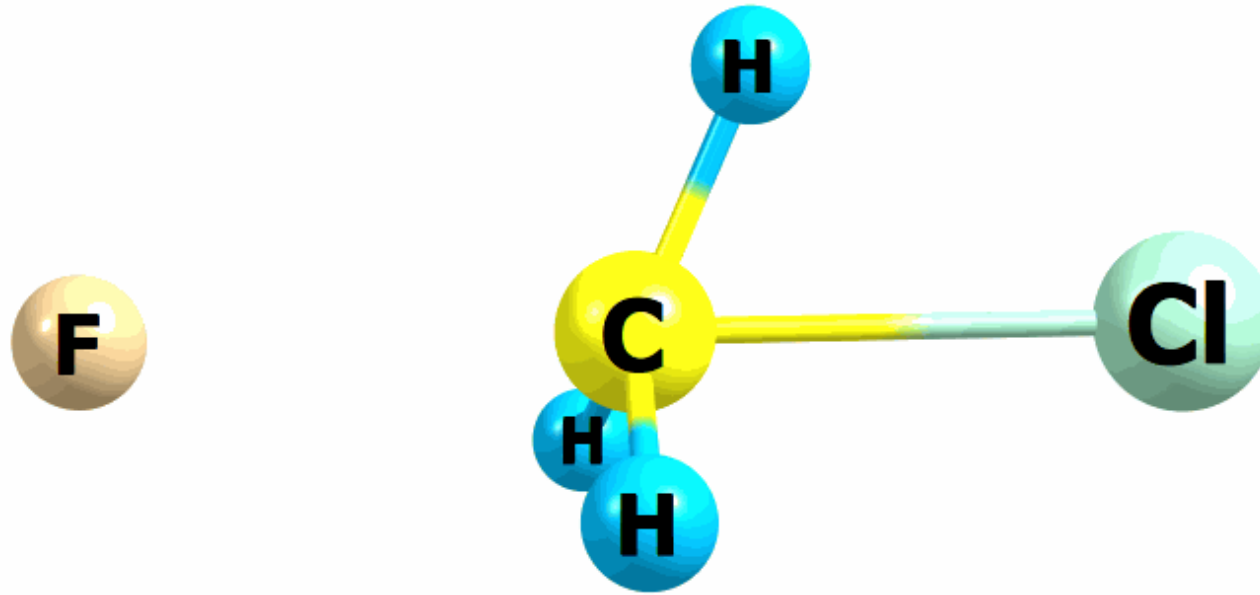
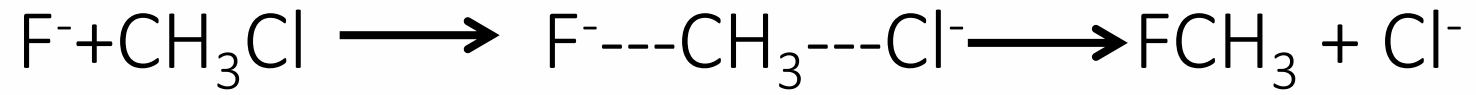


Coordenada de reação



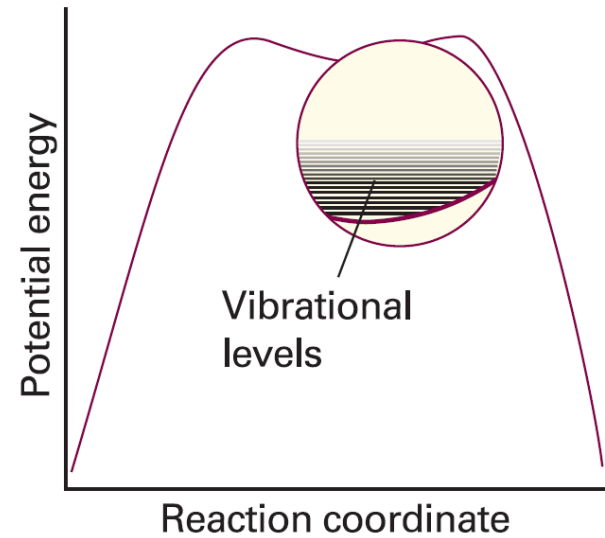
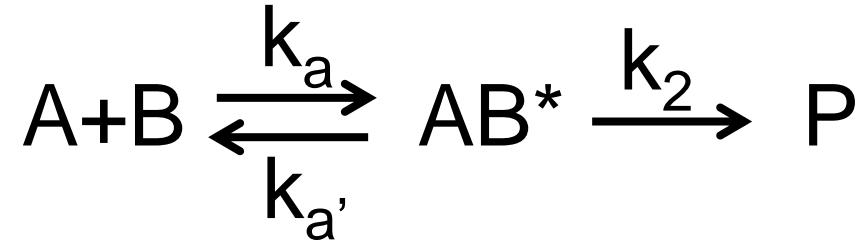
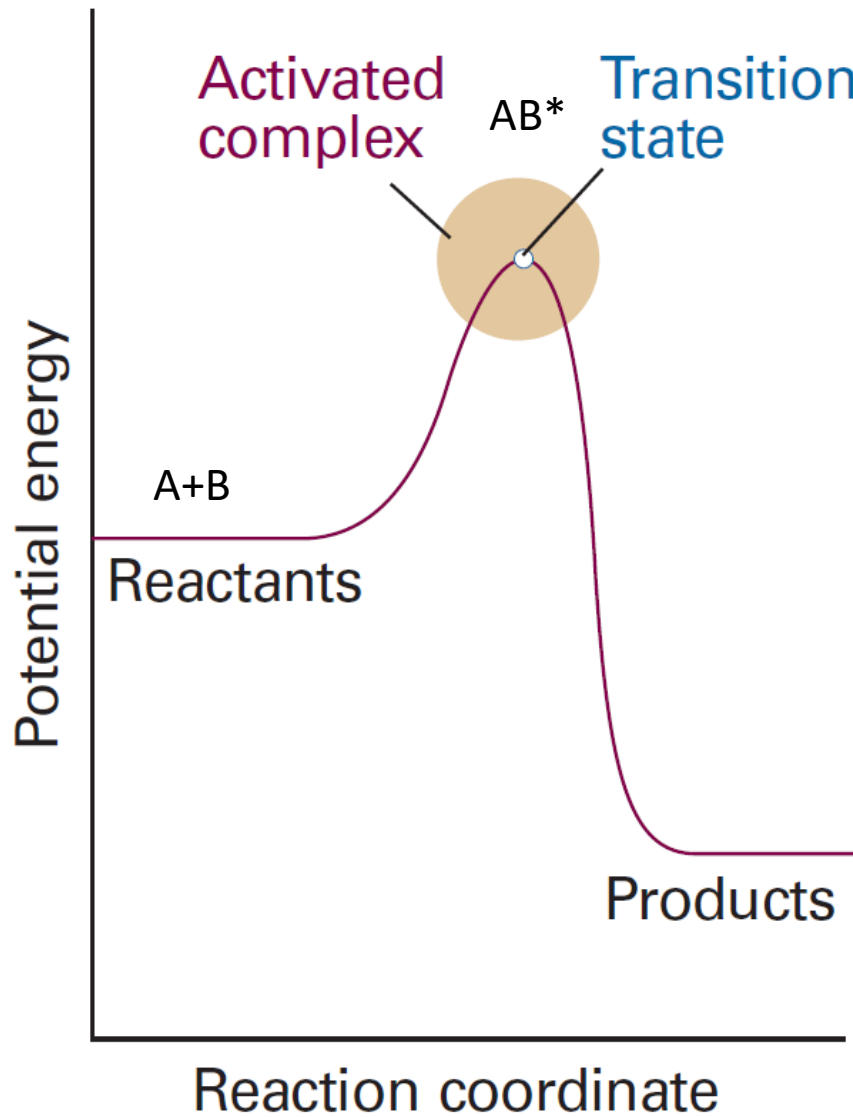
$$k_2 \propto \nu^\ddagger \sim 1/10^{-12} \text{ s}$$

Coordenada de reação

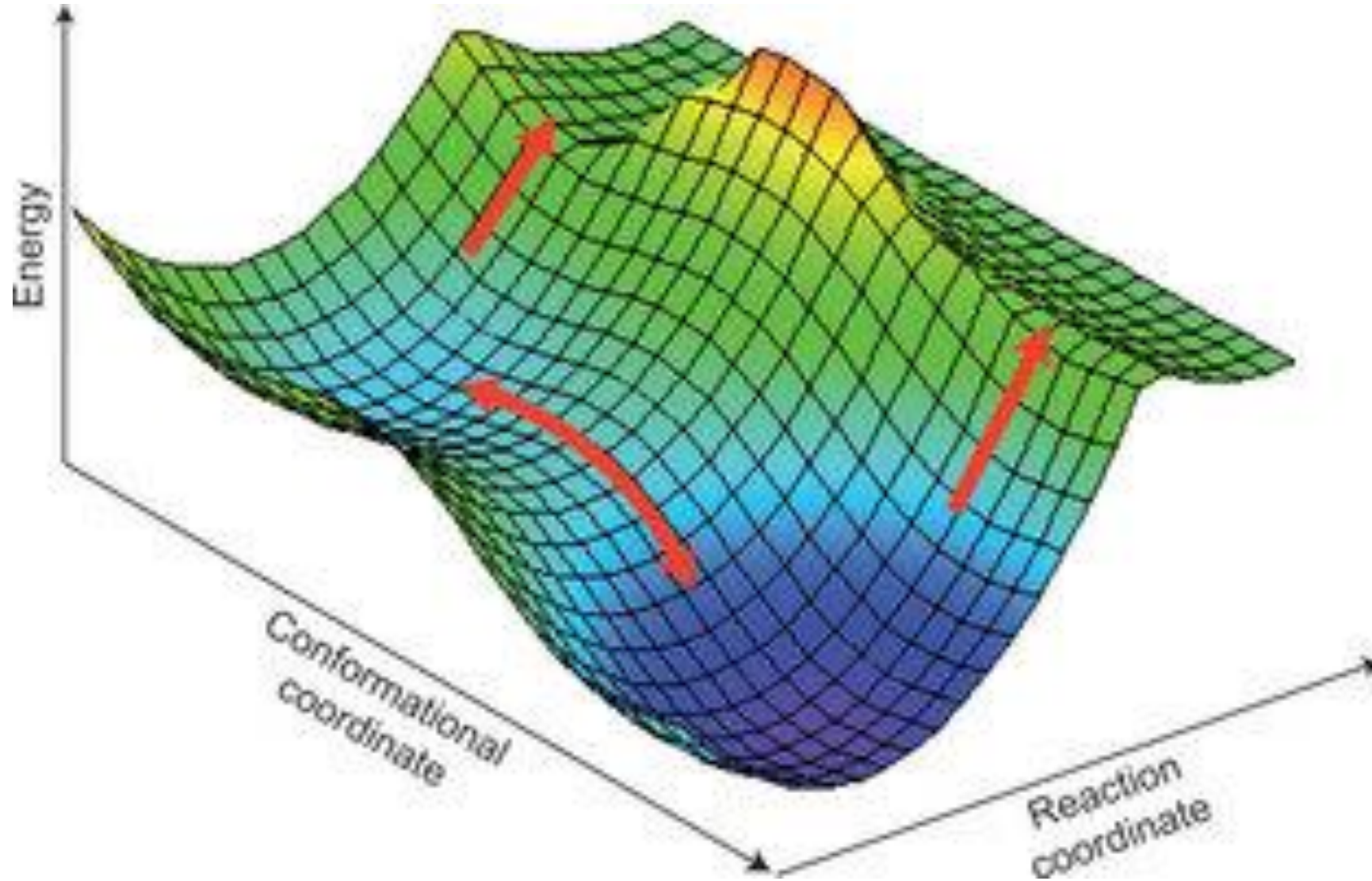


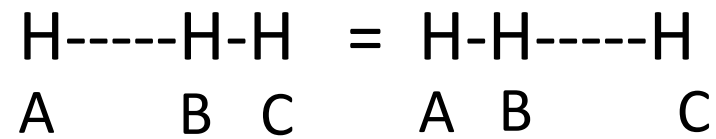
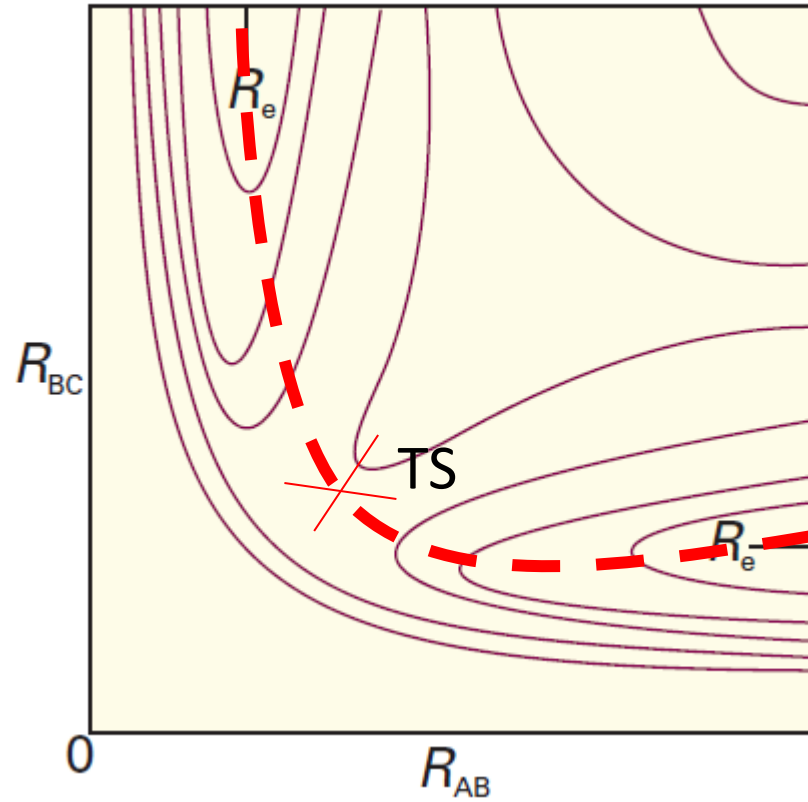
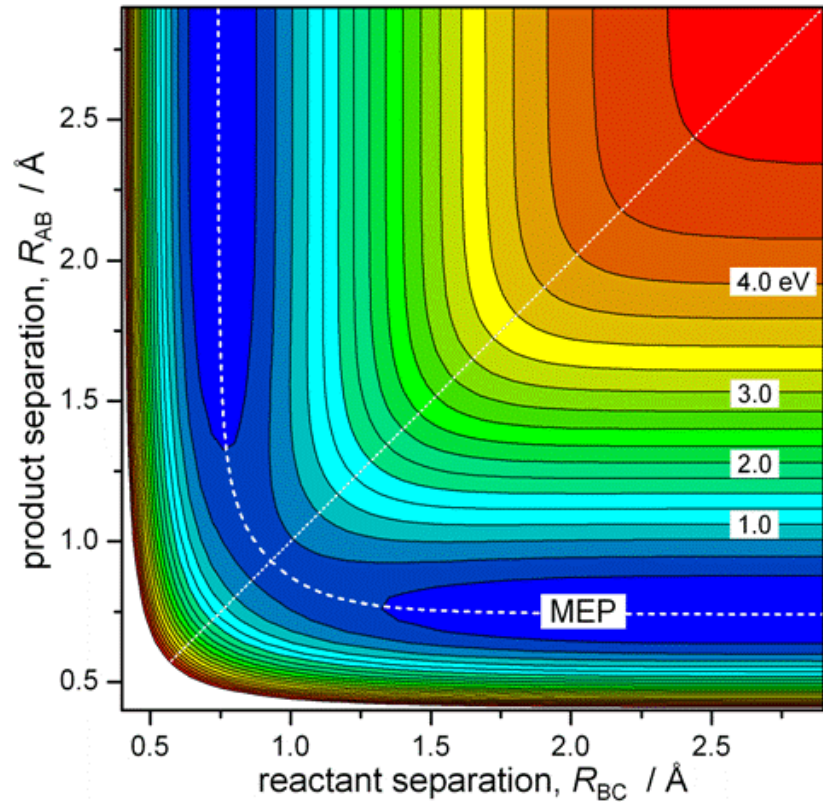
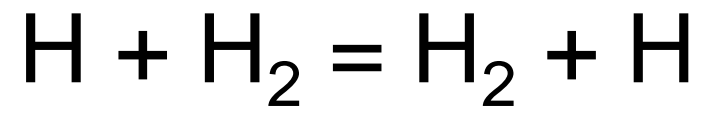
$$k_2 = 596,30 \text{ cm}^{-1} = 1,8 \cdot 10^{13} \text{ s}^{-1}$$

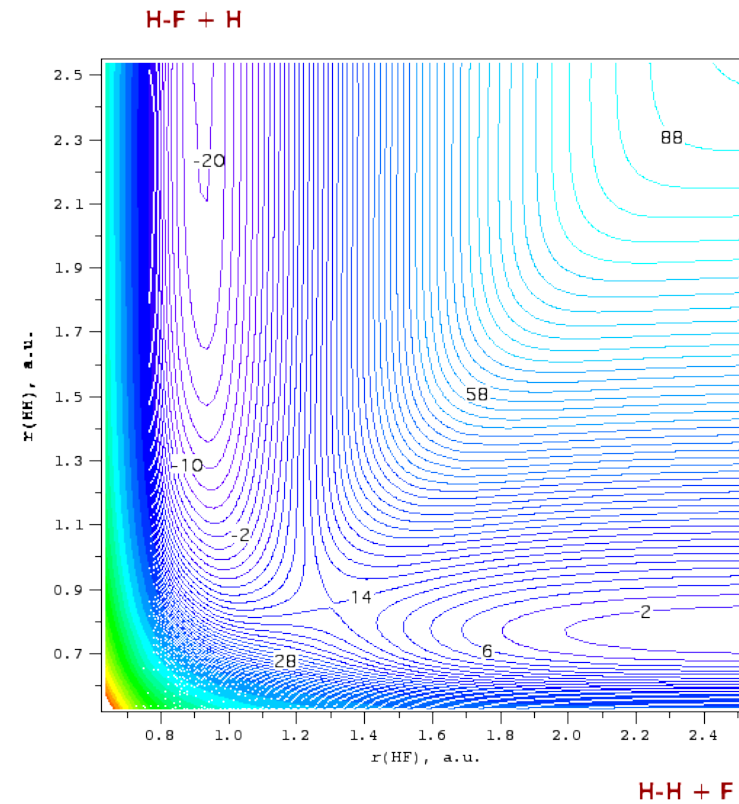
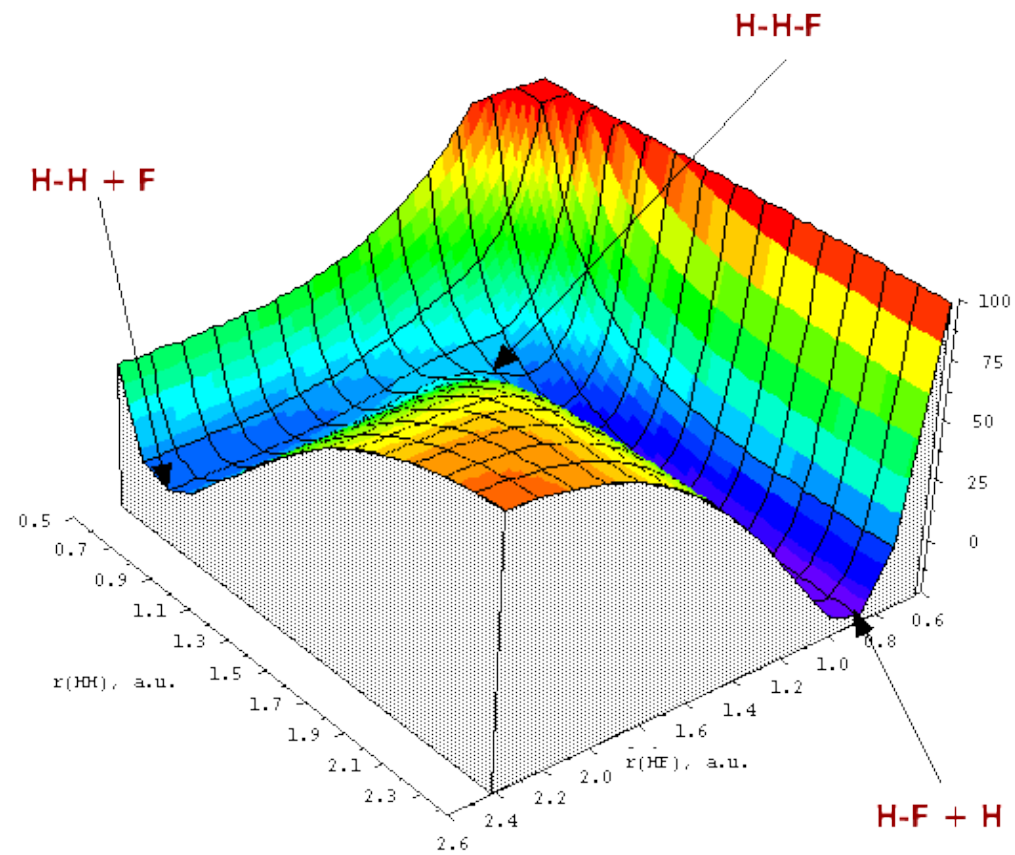
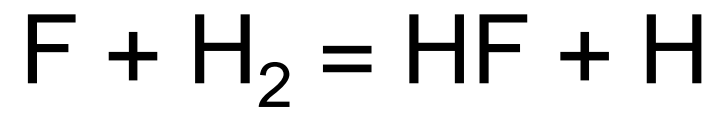
Estado de transição vs. Complexo ativado



Hipersuperfícies

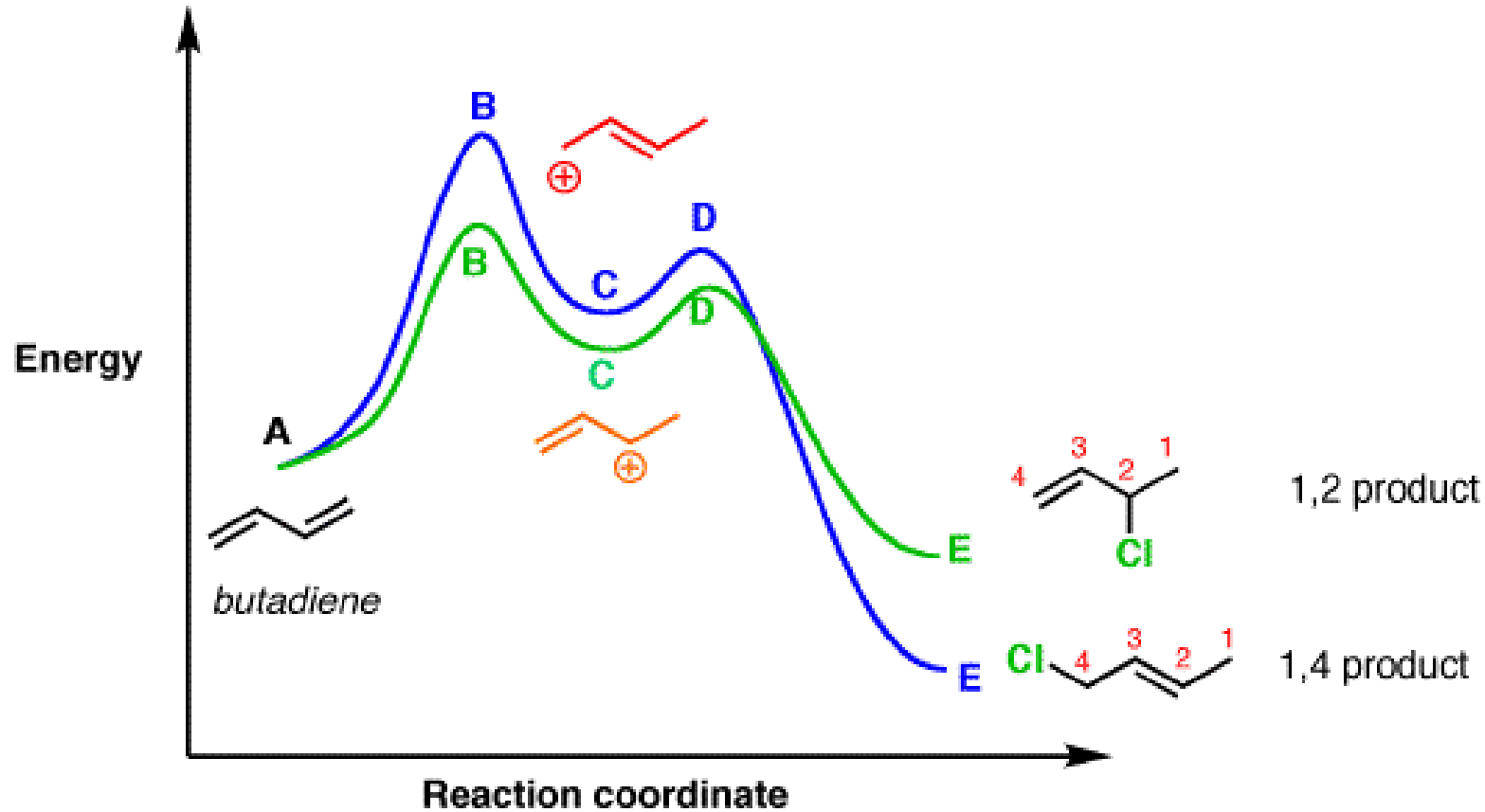






Controle cinético vs. termodinâmico

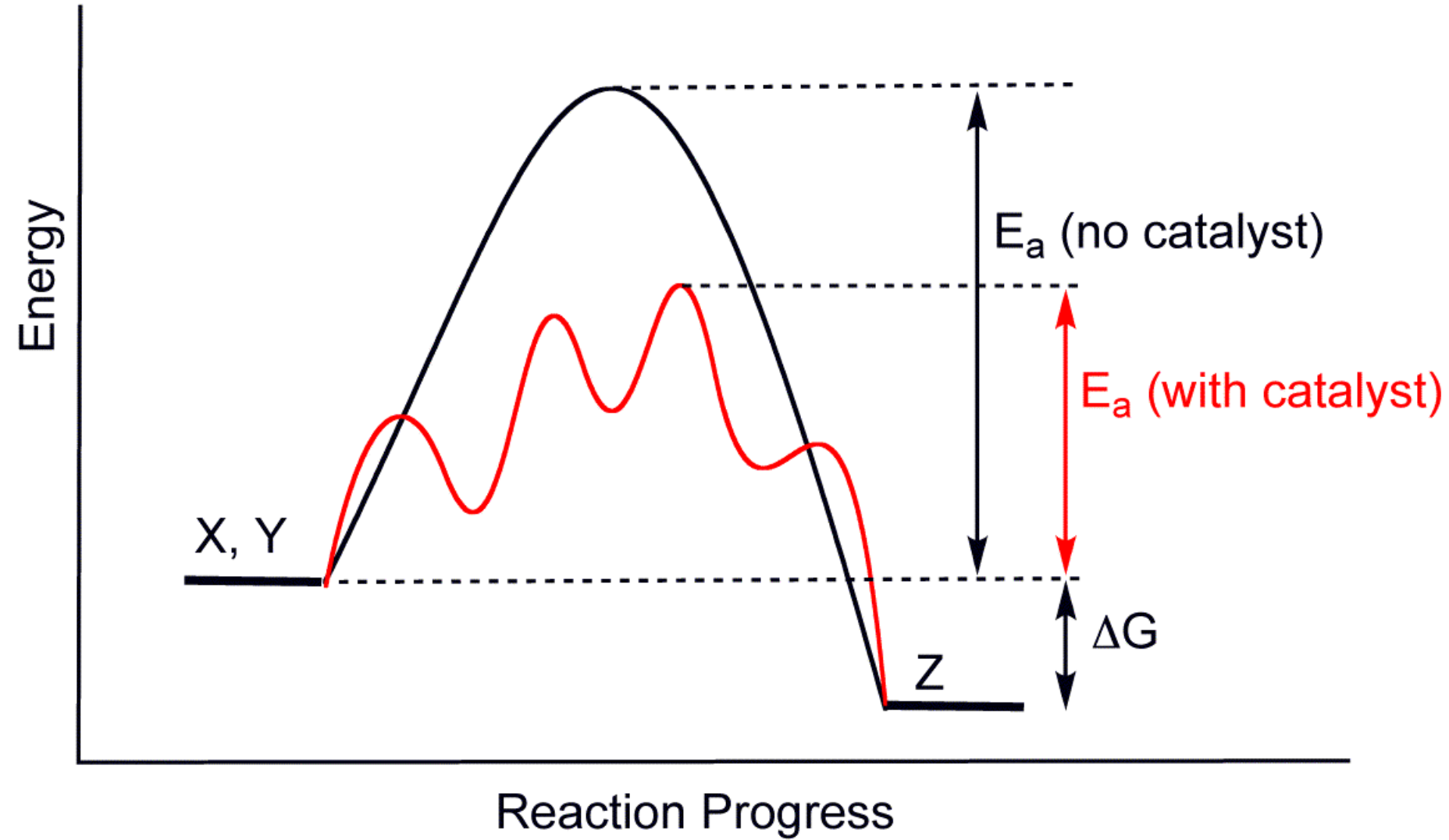
Energy coordinate for 1,2- versus 1,4- additions to butadiene



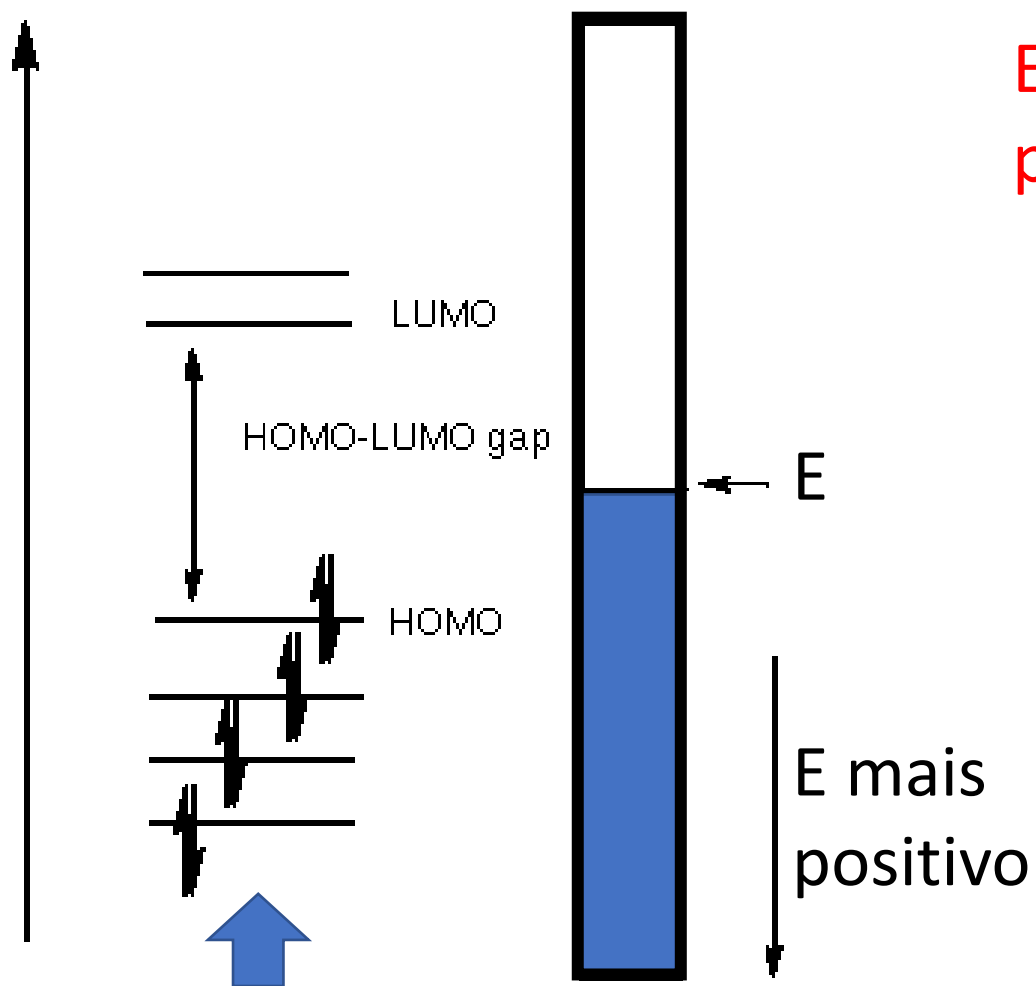
The energy of **C** and **C** (and therefore the height of transition states **B** and **B**) is related to carbocation stability (secondary more stable than primary here)

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

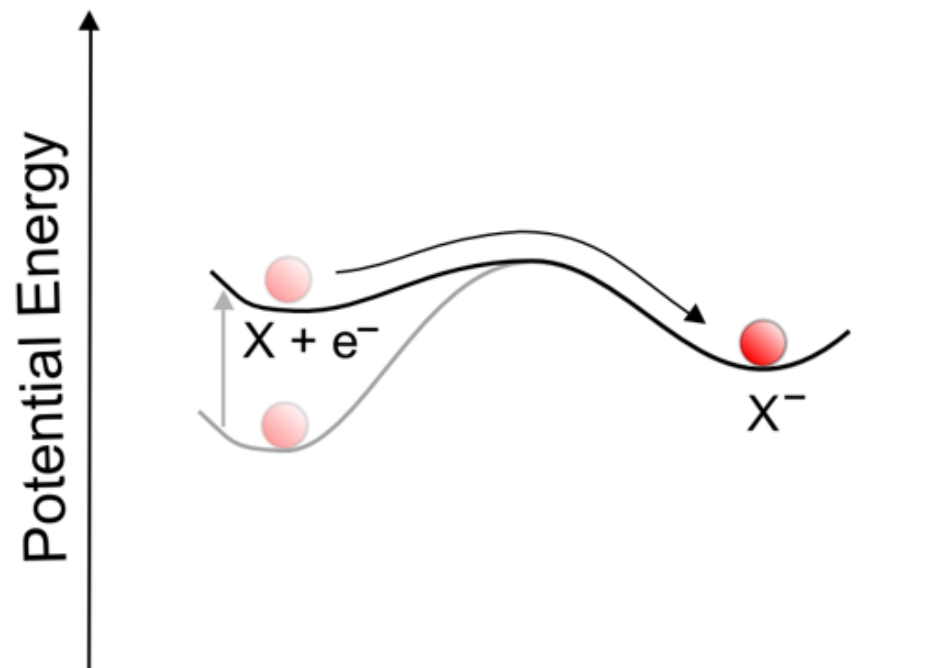
Superfícies de energia



Mudança da energia dos elétrons

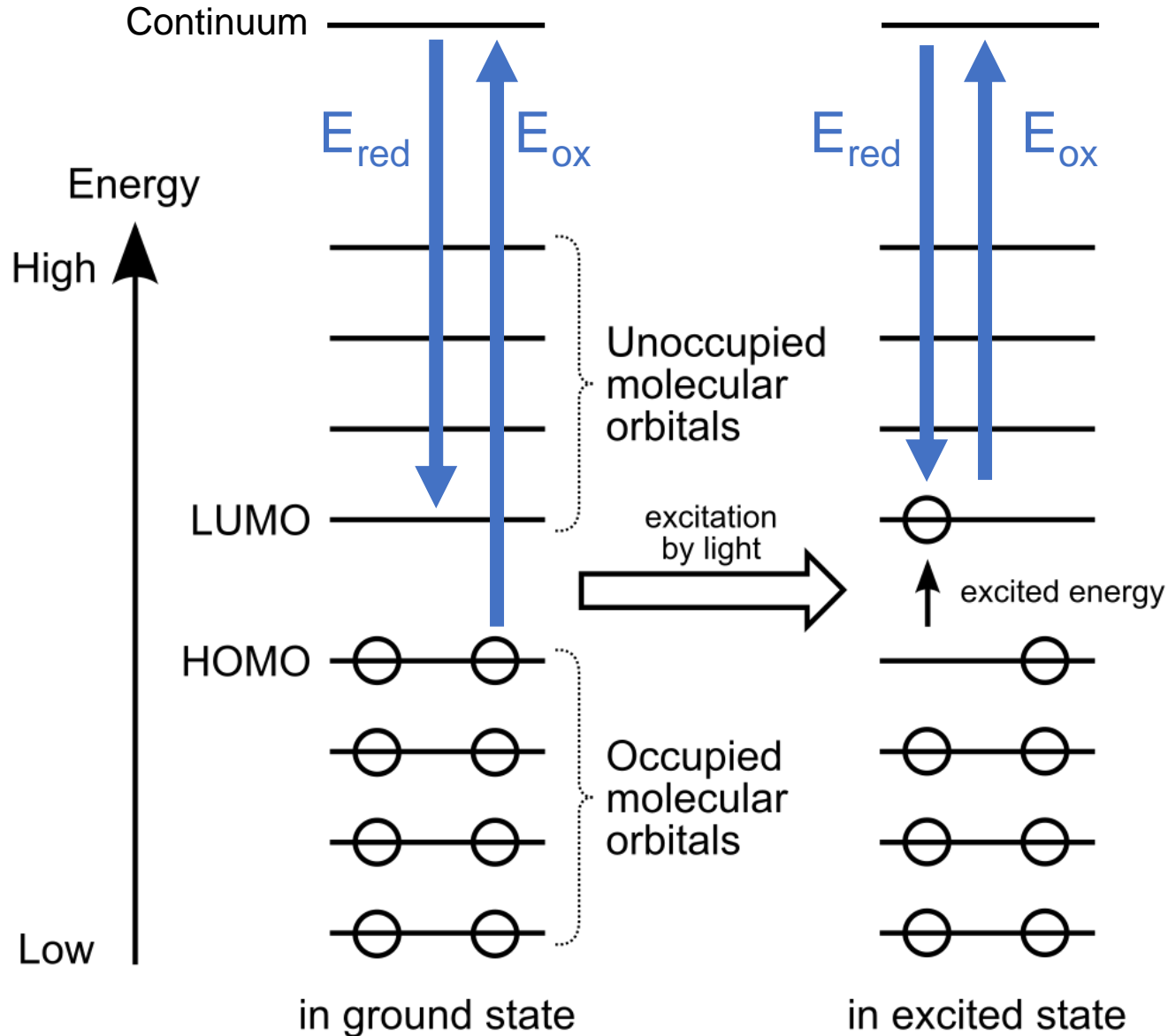


Energia dos elétrons pode ser ajustada para induzir processos químicos



Energia dos “reagentes” permanece inalterada

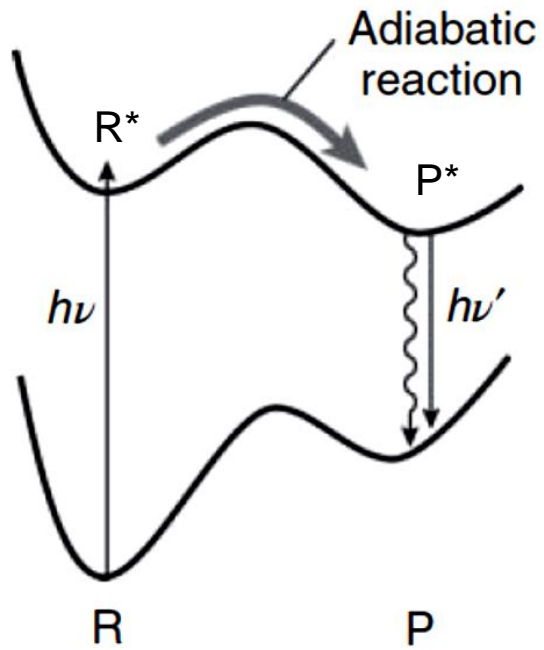
Mudança dos orbitais promovida por luz



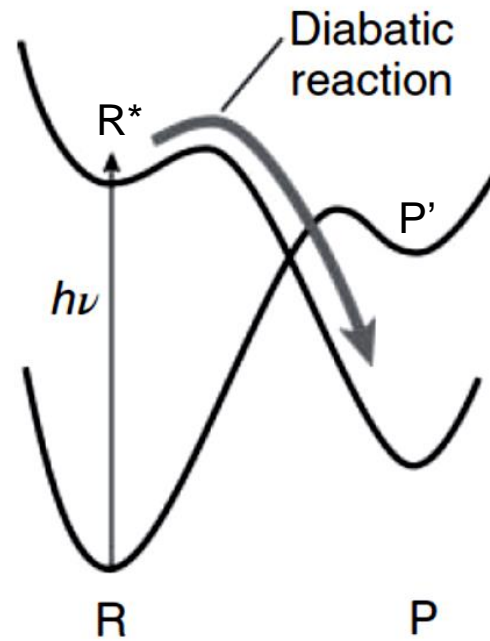
Reatividade do estado excitado é diferente do estado fundamental

Fótons como reagentes

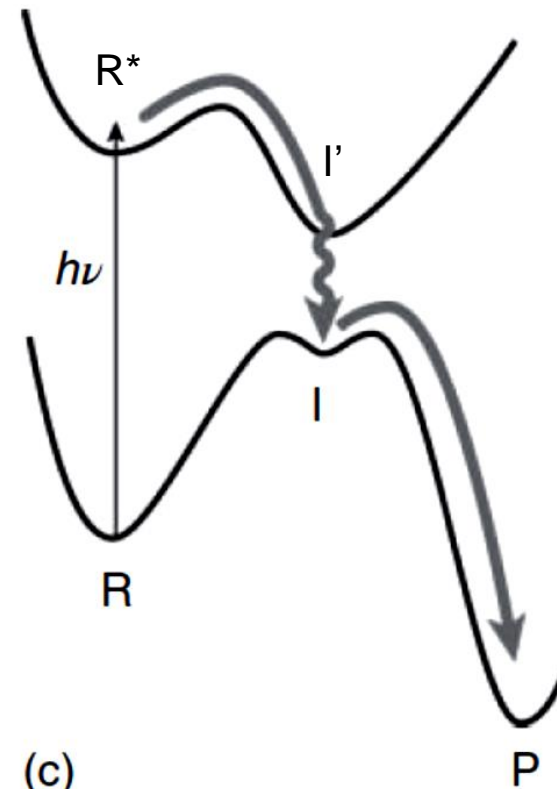
Natureza dos reagentes é alterada!



(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