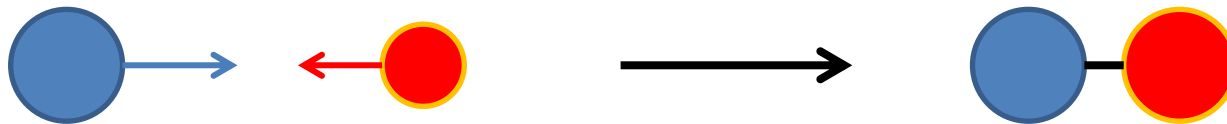
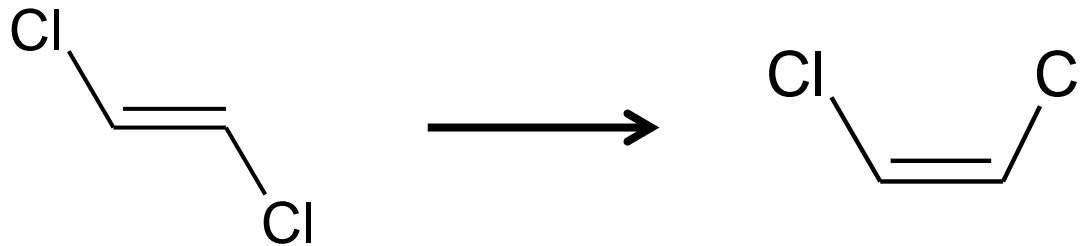


# REACCIONES UNIMOLECULARES Y DE ASOCIACIÓN

# Reacciones unimoleculares



encuentro



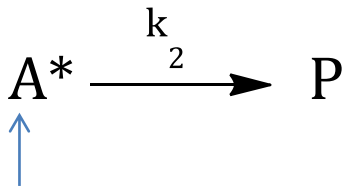
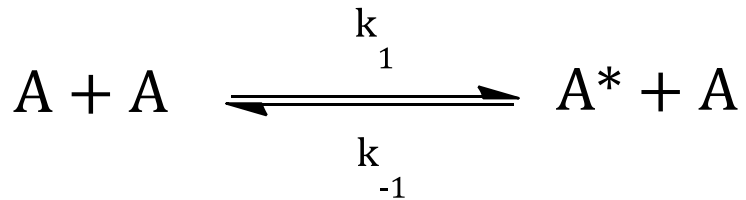
Isomerización ¿Cómo sucede?

1919 Teoría radiativa (Perrin)

1921 Lindemann-Christiansen

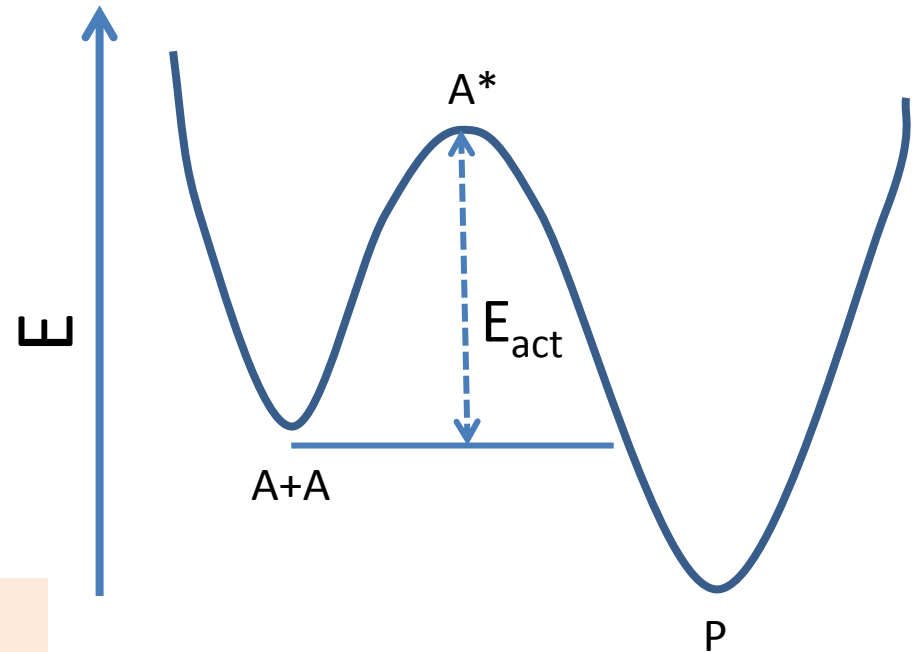
Base de teoría para reacciones unimoleculares

# Teoría de Lindemann-Christiansen



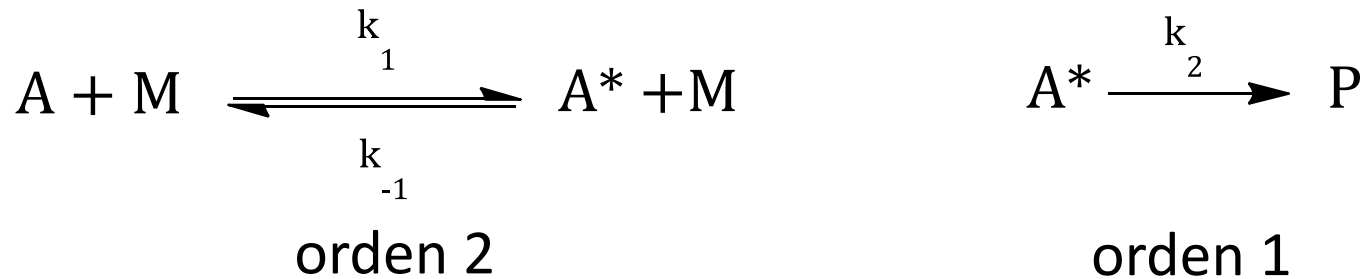
molécula o átomo energizado

- $k_1$  y  $k_{-1}$  relacionados con colisiones
- $k_{-1}$  y  $k_2$  no depende de  $E$  (ver más adelante)



Activación colisional

# T. Lindemann: Análisis de mecanismo



$$\frac{d[A^*]}{dt} = 0 = k_1[A][M] - k_{-1}[M][A^*] - k_2[A^*] \quad (\text{supongo EE})$$

$$v = \frac{d[P]}{dt} = k_2[A^*]$$

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

$$\text{o} \quad [A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \quad ([M] = [A])$$

$$v_0 = \frac{k_2 k_1 [M][A]_0}{k_{-1}[M] + k_2}$$

$$v_0 = \frac{k_2 k_1 [A]_0^2}{k_{-1}[A]_0 + k_2}$$

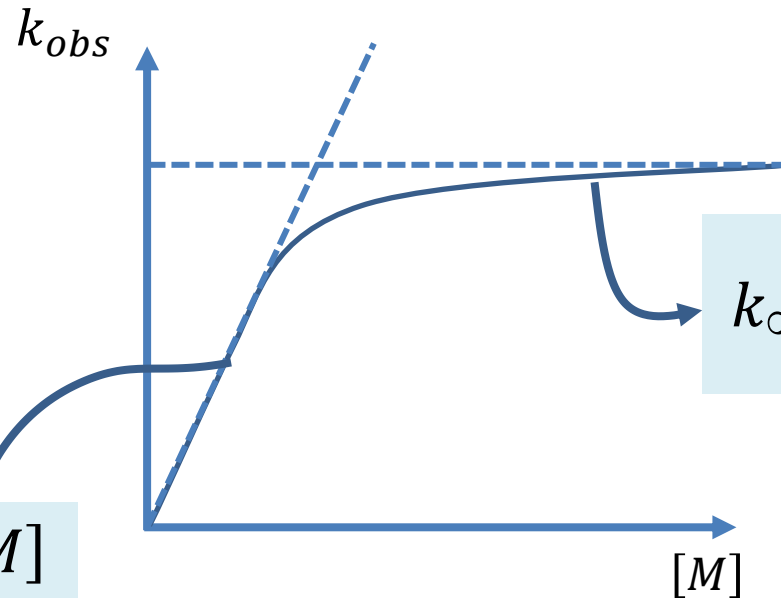
# $k_{obs}$ depende de $[M]$

$$v_0 = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2} [A]_0$$

$$k_{obs} = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2}$$

$$v_0 = k_1 [A]_0^2$$

$$v_0 = \frac{k_1 k_2 [A]_0}{k_{-1}}$$



↓  $[M]$

↑  $[M]$

$k_{obs} = k_1 [M]$

↓↓  $[M]$

$k_{\infty} = \frac{k_1 k_2}{k_{-1}}$

↑↑  $[M]$

( $[A]_0$  fijo)

# $k_{obs}$ depende de $[A]_0$

$$v_0 = \frac{k_2 k_1 [A]_0}{k_{-1} [A]_0 + k_2} [A]_0$$

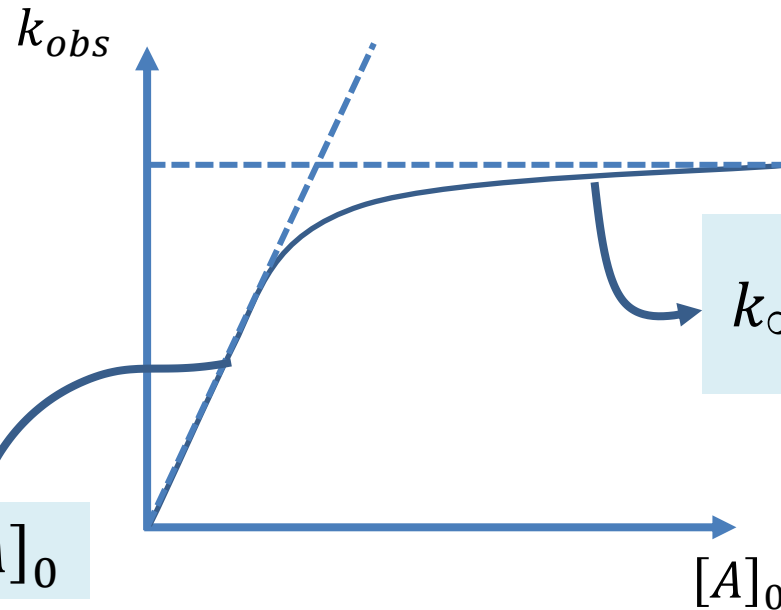
$$v_0 = k_1 [A]_0^2$$

↓  $[A]_0$

↑  $[A]_0$

$$v_0 = \frac{k_1 k_2 [A]_0}{k_{-1}}$$

$$k_{obs} = \frac{k_1 k_2 [A]_0}{k_{-1} [A]_0 + k_2}$$



$$k_{\infty} = \frac{k_1 k_2}{k_{-1}}$$

↑↑  $[A]_0$

$$k_{obs} = k_1 [A]_0$$

↓↓  $[A]_0$

# $k_{\infty}$ experimental vs $k_{\infty}$ teórico

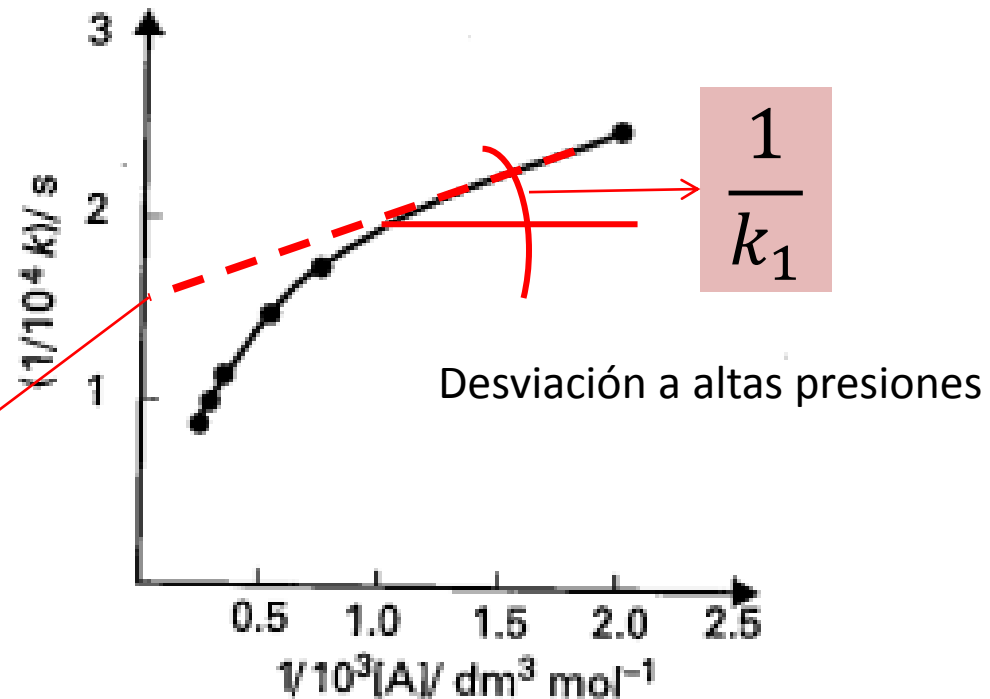
$$k_{obs} = \frac{k_1 k_2 [A]_0}{k_{-1} [A]_0 + k_2}$$

$$\frac{1}{k_{obs}} = \frac{k_{-1} [A]_0 + k_2}{k_1 k_2 [A]_0}$$

$$\frac{1}{k_{obs}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [A]_0}$$

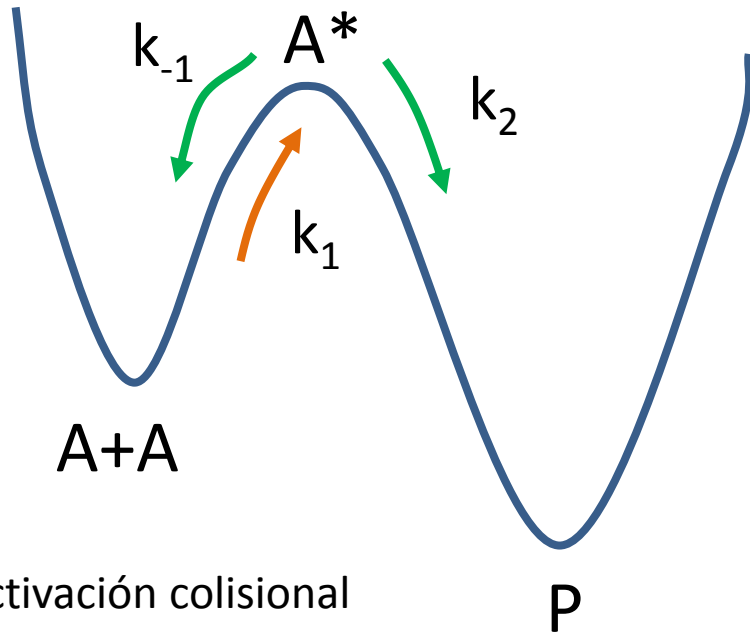
$$\frac{1}{k_{\infty}} = \frac{k_{-1}}{k_1 k_2}$$

$$\frac{1}{k_{\infty,teo}} > \frac{1}{k_{\infty,exp}}$$



Isomerización  $trans\text{-C}_2\text{H}_2\text{D}_2 \rightarrow cis\text{-C}_2\text{H}_2\text{D}_2$  @ 794 K

# $k_{\infty}$ experimental ¿por qué falla?



→ activación colisional

$$\frac{1}{k_{\infty,teo}} > \frac{1}{k_{\infty,exp}}$$

$$\frac{1}{k_{\infty}} = \frac{k_{-1}}{k_1 k_2}$$

estaríamos subestimando  $k_1$

$$k_1 \sim Z_{AM} e^{-E^*/kT}$$

## Hipótesis

- $k_1$  y  $k_{-1}$  colisiones
- $k_1$  depende de  $E$
- $k_{-1}$  y  $k_2$  no dependen de  $E$

$$k_{-1} \sim Z_{A^*M} \approx \pi (r_{A^*} + r_M)^2$$

$$k_{-1} \sim 10^{11} \text{ M}^{-1} \text{ s}^{-1}$$

A altas presiones  $k_{-1} [M] \gg k_2$   
“de-energización”  $\gg$  conversión

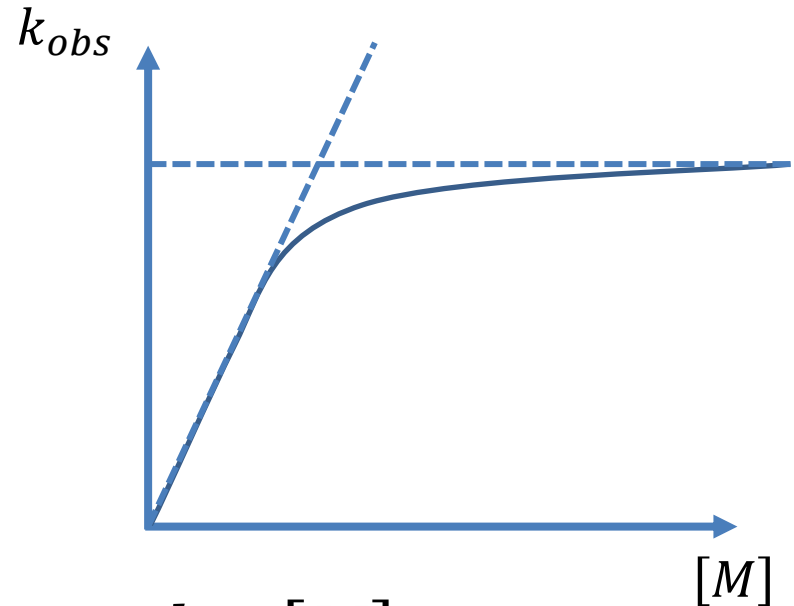
$$v_0 = \frac{k_1 k_2 [A]_0}{k_{-1}}$$



# Reordenando y expresando $k_{obs} - k_{\infty}$

$$k_{obs} = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2}$$

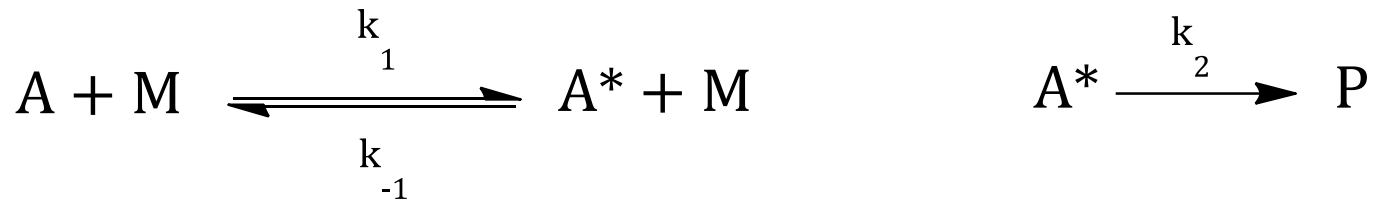
$$k_{\infty} = \frac{k_1 k_2}{k_{-1}}$$



$$\frac{k_{obs}}{k_{\infty}} = \frac{k_1 k_2 [M]}{(k_{-1} [M] + k_2)} \cdot \frac{k_{-1}}{k_1 k_2} = \frac{k_{-1} [M]}{k_{-1} [M] + k_2}$$

$$\frac{k_{obs}}{k_{\infty}} = \frac{k_{-1} [M]}{k_{-1} [M] + k_2}$$

# Cambio de orden: bimolecular-unimolecular



Velocidad de desactivación de  $A^*$  = formación de  $P$  ( $v_{-1} = v_2$ )

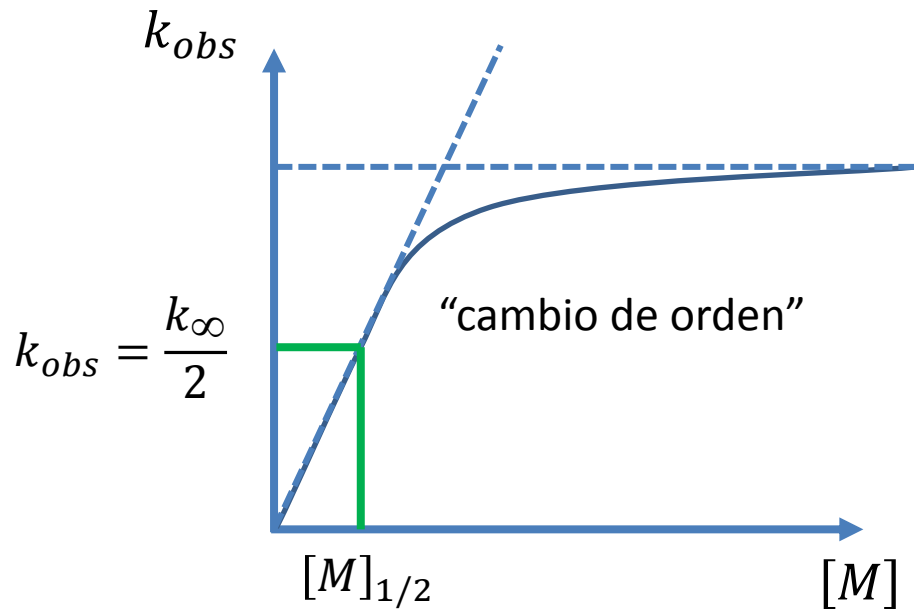
$$k_{-1}[A^*][M] = k_2[A^*] \quad [M]_{1/2} = \frac{k_2}{k_{-1}}$$

$A^*$  tiene un 50 % de chance de ir a productos o reactivos

$$\frac{k_{obs}}{k_{\infty}} = \frac{k_{-1}[M]}{k_{-1}[M] + k_2} \longrightarrow \frac{k_{obs}}{k_{\infty}} = \frac{1}{2}$$

$$k_{obs} = \frac{k_{\infty}}{2} ; [M]_{1/2}$$

# Bimolecular - Unimolecular



$$[M]_{1/2} = \frac{k_2}{k_{-1}} \quad k_{\infty} = \frac{k_1 k_2}{k_{-1}}$$

$$[M]_{1/2} = \frac{k_{\infty}}{k_1} \quad k_1 = Z_{AM} e^{-E^*/kT}$$

Suponiendo teoría colisional para especie activada

Reaction	$A / s^{-1}$	$E / kJ mol^{-1}$	$[M]_{1/2}^{expt} / mol dm^{-3}$	$[M]_{1/2}^{calc} / mol dm^{-3}$	$T / K$
Cyclopropane $\rightarrow$ propene	$3 \times 10^{15}$	275	$3 \times 10^{-4}$	$1.5 \times 10^4$	760
Cyclobutane $\rightarrow$ 2 ethene	$4 \times 10^{15}$	267	$10^{-5}$	$2 \times 10^4$	720
Methylcyclobutane $\rightarrow$ ethene + propene	$2.5 \times 10^{15}$	256	$10^{-6}$	$10^4$	670
$CH_3NC \rightarrow CH_3CN$	$4 \times 10^{13}$	161	$4 \times 10^{-3}$	$2 \times 10^2$	500
$C_2H_5NC \rightarrow C_2H_5CN$	$6 \times 10^{13}$	160	$3.5 \times 10^{-5}$	$3.5 \times 10^2$	500
$N_2O \rightarrow N_2 + O$	$8 \times 10^{11}$	256	0.8	4	890

Estimo valores de  $[M]_{1/2}$  de experimentos



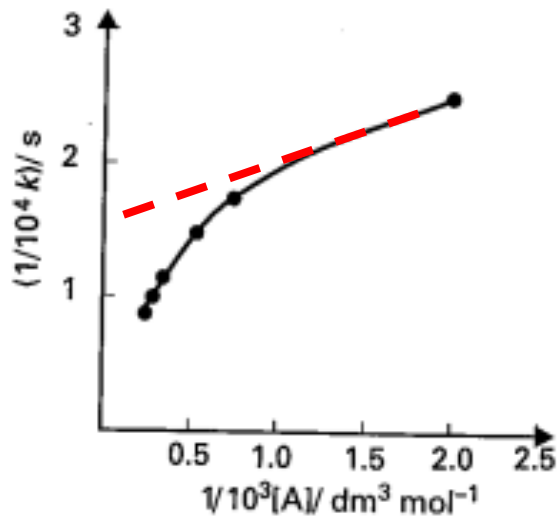
$k_1$  subestimada



subestima  $E^*$   
(niega modos internos)

# Teoría Lindemann: Hinshelwood

## Limitaciones



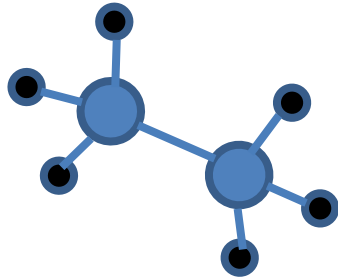
desviaciones a presiones altas

Reaction	$A / s^{-1}$	$E / kJ mol^{-1}$	$[M]_3^{expt} / mol dm^{-3}$	$[M]_3^{calc} / mol dm^{-3}$	$T / K$
Cyclopropane $\rightarrow$ propene	$3 \times 10^{15}$	275	$3 \times 10^{-4}$	$1.5 \times 10^4$	760
Cyclobutane $\rightarrow$ 2 ethene	$4 \times 10^{15}$	267	$10^{-5}$	$2 \times 10^4$	720
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$N_2O \rightarrow N_2 + O$	$8 \times 10^{11}$	256	0.8	4	890

depende del tipo de molécula

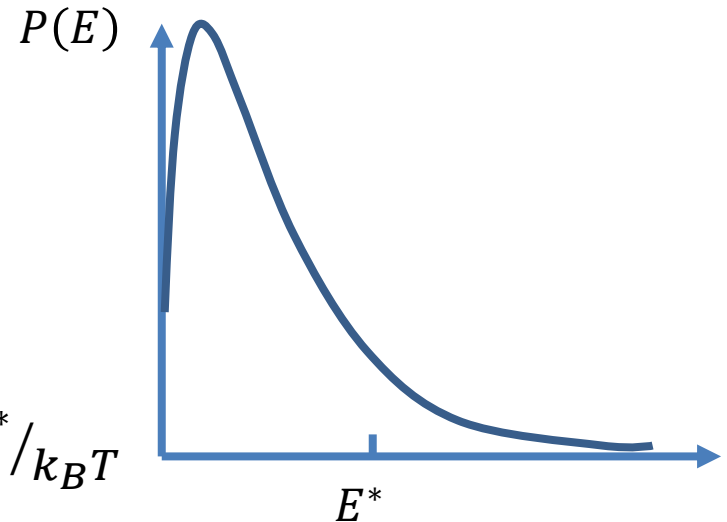
# Teoría Lindemann: Hinshelwood

Subestimar  $k_1$



subestimar  $E^*$

modos vibracionales pueden contribuir a  $E^*$   
(interna además de cinética)



Considero  $\mathbf{S}$  osciladores armónicos; misma  $\mathbf{v}$

$$P(E > E^*) = \frac{1}{(s-1)!} \left( \frac{E^*}{k_B T} \right)^{s-1} e^{-E^*/k_B T}$$

$$k_1 = Z_1 \frac{1}{(s-1)!} \left( \frac{E^*}{k_B T} \right)^{s-1} e^{-E^*/k_B T}$$

$$k_{1,H} > k_{1,L}$$

siempre  $> 1$ ;  $E^* \gg k_B T$

# Comparación $k_1$

$$k_{1,L} = Z_1 e^{-E^*/k_B T}$$

Lindemann  
Christiansen

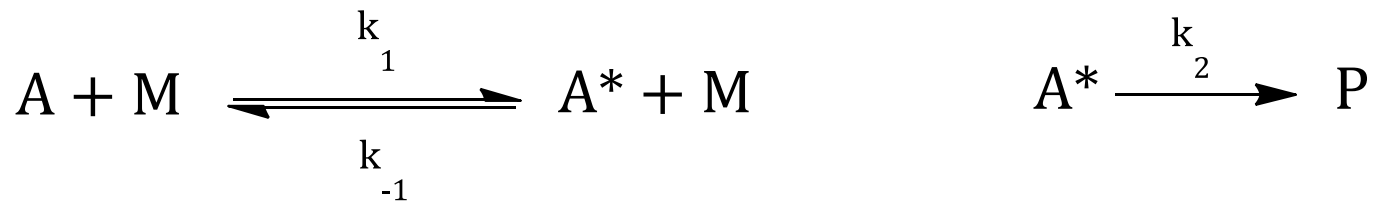
$$k_{-1,L} = Z_1$$

$$k_{1,LH} = Z_1 \frac{1}{(s-1)!} \left( \frac{E^*}{k_B T} \right)^{s-1} e^{-E^*/k_B T}$$

Lindemann  
Hinshelwood

$$k_{-1,LH} = Z_1$$

# Estimación $k_2$ - Lindemann



$$k_{\infty} = \frac{k_1 k_2}{k_{-1}} \Rightarrow k_2 = \frac{k_{-1} k_{\infty}}{k_1}$$

$$k_{\infty} = A_{\infty} e^{-E_{\infty}/k_B T}$$

$$k_2 = \frac{Z_{-1} A_{\infty} e^{-E_{\infty}/k_B T}}{Z_1 e^{-E_0/k_B T}}$$

$$E_{\infty} \simeq E_0 ; Z_1 \simeq Z_{-1}$$

$$k_2 = A_{\infty}$$

experimentalmente se encuentra  $10^{13.5} \text{ s}^{-1}$

$k_2$  parecido a una vibración molecular

# Estimación $k_2$ - Hinshelwood

$$k_2 = \frac{k_{-1}k_{\infty}}{k_1} \quad k_2 = \frac{Z_{-1}A_{\infty}e^{-E_{\infty}/k_B T}}{Z_1 \frac{1}{(s-1)!} \left(\frac{E^*}{k_B T}\right)^{s-1} e^{-E_0/k_B T}}$$

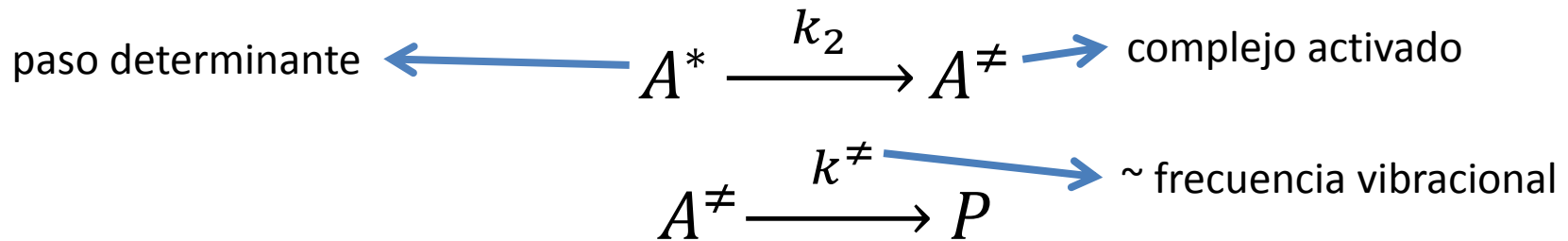
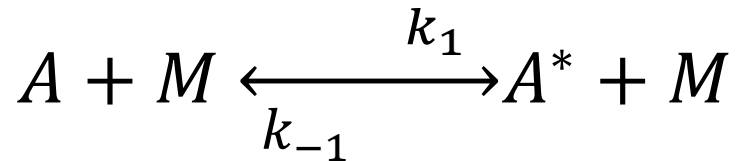
para valores típicos de  $A_{\infty} \sim 10^{13} \text{ s}^{-1}$  y  $E_0/kT \sim 40$

<b>s</b>	1	5	10
$k_2 / \text{s}^{-1}$	$10^{13}$	$10^9$	$10^{6.5}$

tiempo de vida de una molécula energizada aumenta cuando tengo más formas de almacenar/distribuir E



# Teoría Rice-Ramsperger-Kassel (RRK)



$$\frac{d[A^\ddagger]}{dt} = 0 = k_2[A^*] - k^\ddagger[A^\ddagger]; \text{ (EE)}$$

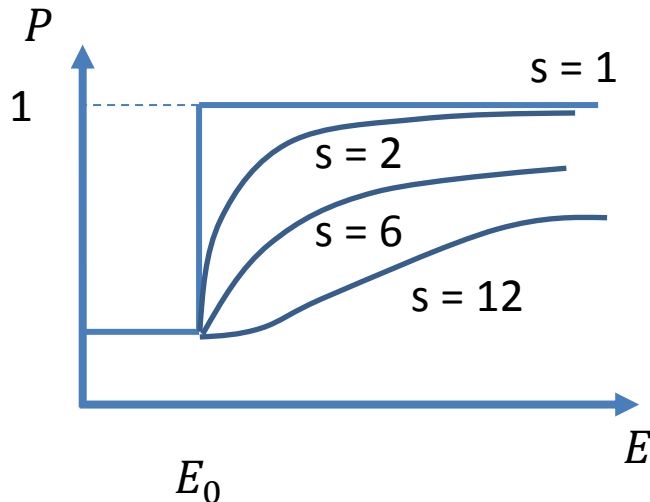
$$k_2 = \frac{k^\ddagger[A^\ddagger]}{[A^*]}$$

Energía “fluye” entre distintos modo vibracionales (anarmonicidad)

# Tratamiento clásico RRK

Calcula la probabilidad de un sistemas de  $s$  osciladores clásicos con  $E_{\text{total}}$  tenga una  $E \geq E_0$  en un solo oscilador

$$P(E > E_0, \text{ en un solo } s) = \left( \frac{E - E_0}{E} \right)^{s-1}$$



$$\frac{[A^\ddagger]}{[A^*]} = \left( \frac{E - E_0}{E} \right)^{s-1}$$

proporción de moléculas energizadas en modo crítico

# Tratamiento clásico RRK

$$k_2 = \frac{k_{\neq} [A^{\neq}]}{[A^*]} = k_{\neq} \left( \frac{E - E_0}{E} \right)^{s-1}$$

una vez que concentró  $E \geq E_0$  en modo reactivo (o enlace crítico)  $\rightarrow$  reacción inmediata

$$k_{\neq} = \nu_{\neq} \longrightarrow \sim \text{frecuencia vibracional}$$

$$k_2 = \nu_{\neq} \left( \frac{E - E_0}{E} \right)^{s-1}$$

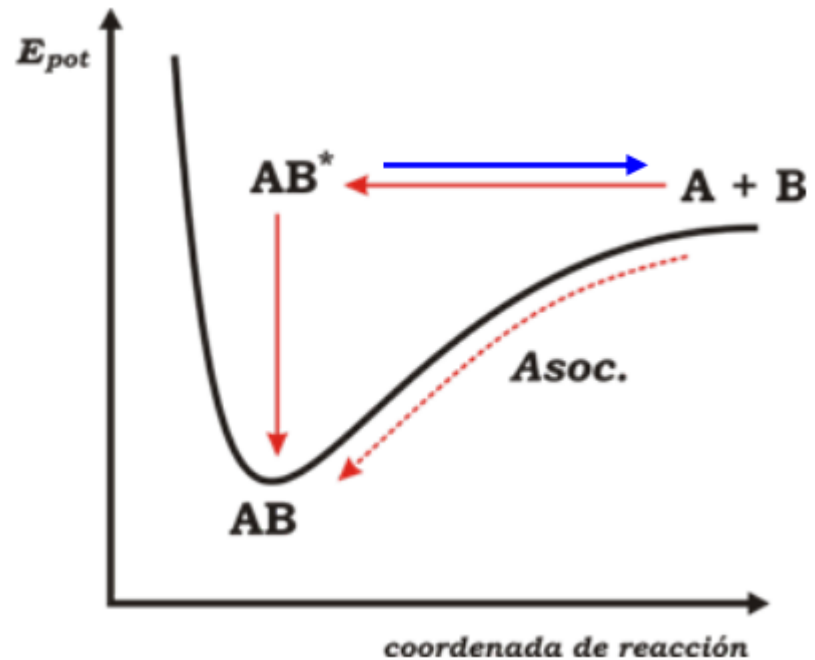
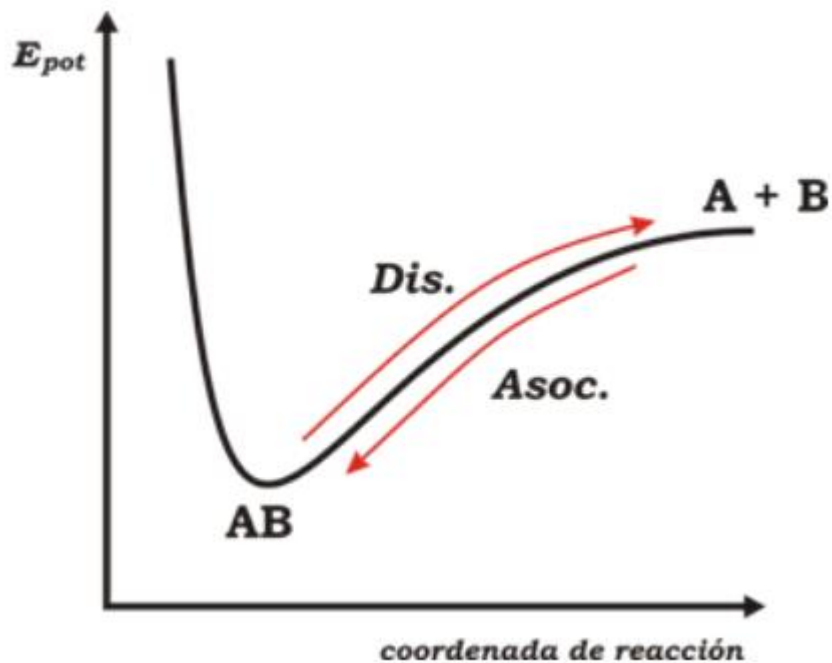
$$k_1 = Z_1 \frac{1}{(s-1)!} \left( \frac{E^*}{k_B T} \right)^{s-1} e^{-E^*/k_B T}$$

$$k_{-1} = Z_{-1} = Z_1$$

# Resumiendo...

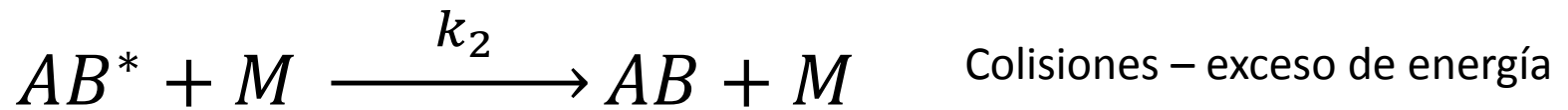
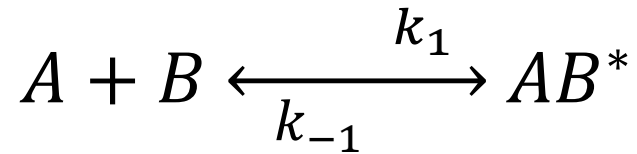
- Mecanismo de Lindemann-Christiansen descripción más simple (antes de TST!)
- Simplicidad implica no tener en cuenta estructura molecular.
- Hinshelwood toma en cuenta modos internos, corrige  $k_1$ .
- RRK considera todas las moléculas que tienen  $E \geq E_0$  y que contribuyen a  $k_2$ .

# Reacciones de asociación



No hay barrera de activación

# Reacciones de asociación



$$\frac{d[AB^*]}{dt} = 0 = k_1[A][B] - (k_{-1} + k_2[M])[AB^*]; \text{ (EE)}$$

$$[AB^*] = \frac{k_1[A][B]}{k_{-1} + k_2[M]}$$

# Reacciones de asociación

$$\frac{d[AB]}{dt} = v_{reacc} = k_2[AB^*][M]$$

$$v_{reacc} = \frac{k_1 k_2 [M]}{k_{-1} + k_2 [M]} [A][B]$$

$\uparrow\uparrow [M]$

$k_{obs}$

$\downarrow\downarrow [M]$

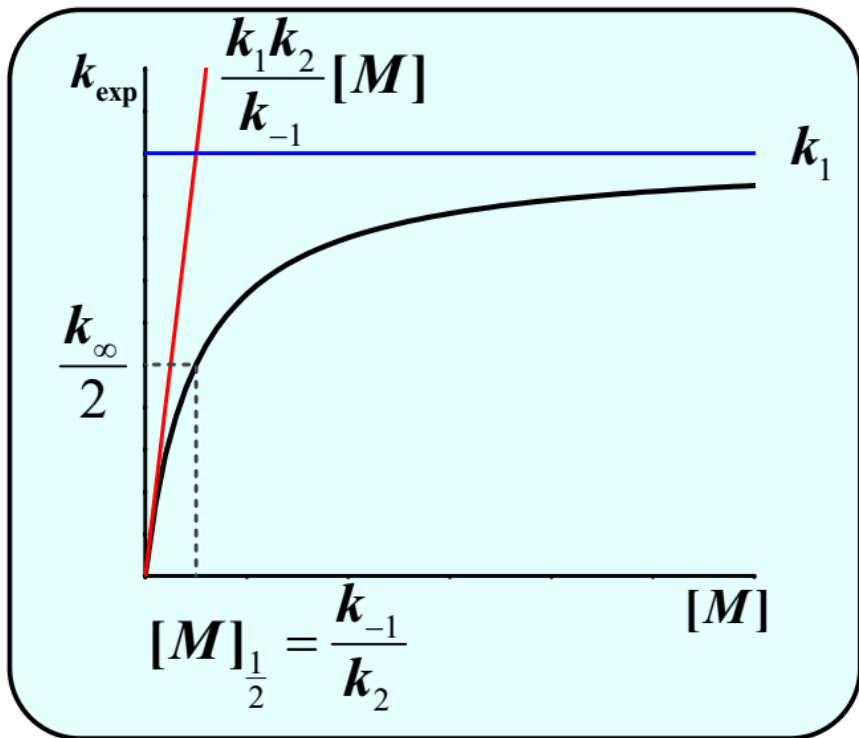
$$v_{reacc} = k_1 [A][B]$$

limita formación  $AB^*$

$$v_{reacc} = \frac{k_1 k_2 [M]}{k_{-1}} [A][B]$$

limita desactivar  $AB^*$

# Reacciones de asociación



$$k_{exp} = \frac{k_1 k_2 [M]}{k_{-1} + k_2 [M]}$$

$$v_{reacc, \uparrow [M]} = k_1 [A][B]$$

orden 2

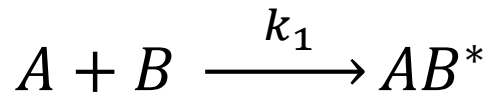
$$k_{exp} = k_{\infty} = k_1$$

$$v_{reacc, \downarrow [M]} = \frac{k_1 k_2 [M]}{k_{-1}} [A][B]$$

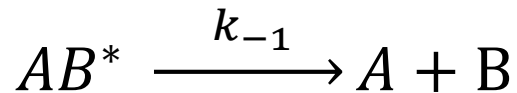
orden 3



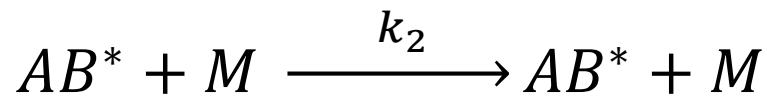
# Reacciones de asociación



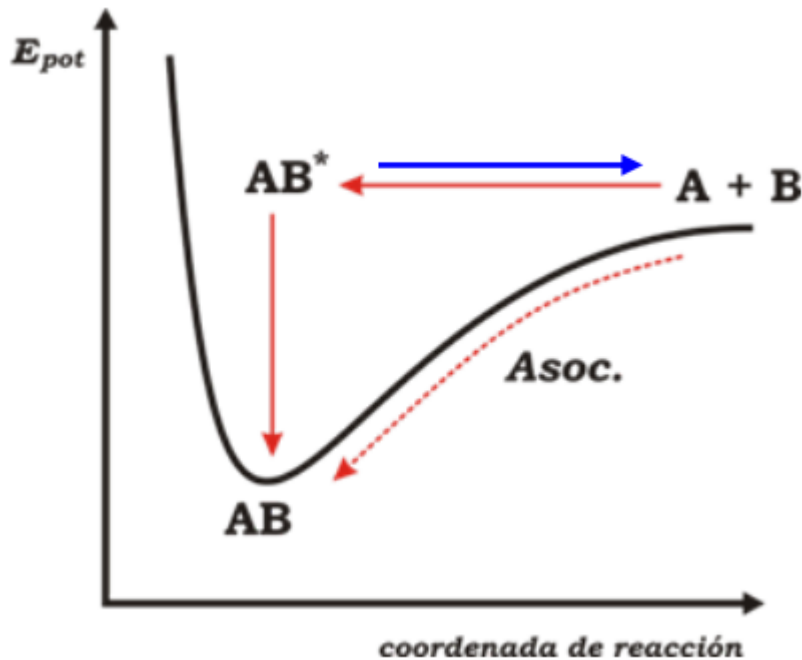
$$k_1 \sim Z_1 \sim 10^{11} M^{-1} s^{-1}$$



$$k_{-1} \sim \nu_{vibr} \sim 10^{14} - 10^{13} s^{-1}$$



$$k_2 \sim Z_{AB^*-M} \sim 10^{11} M^{-1} s^{-1}$$



**Table 5.4** Data for radical recombination reactions at 300 K

Reaction	Lifetime of adduct/s	Pressure/ Pa for $k_{-1} = k_3[M]$
$I + I \rightarrow I_2$	$10^{-12} - 10^{-13}$	Not attained
$CH_3 + H \rightarrow CH_4$	$10^{-10}$	$\approx 10^5$
$CH_3 + CH_3 \rightarrow C_2H_6$	$2 \times 10^{-8}$	$\approx 10^3$

$$\tau_{AB^*} = \frac{1}{k_{-1}}$$