

Reacciones en solución

Solvente:

- Medio de reacción
- Solvatación de compuestos (reactivos, productos e intermediarios)
- Puede ser reactivo (ej. hidrólisis, esterificación)

Macroscópico (continuo)

Punto de ebullición

Densidad

Viscosidad

Permitividad dieléctrica

Conductividad térmica

Microscópico (discontinuo)

Momento dipolar

Puente H (Donante-aceptor)

Polarizabilidad

Electrones (Donante-aceptor)

Tipos de solventes

Industria	Toneladas	E (m. desecho/m. producto)
Química a granel	$10^4 - 10^6$	< 1 - 5
Química fina	$10^3 - 10^4$	5 - 50
Farmacéuticos	$10 - 10^3$	25 - sobre 100

Solventes no convencionales

Solventes supercríticos

líquidos iónicos

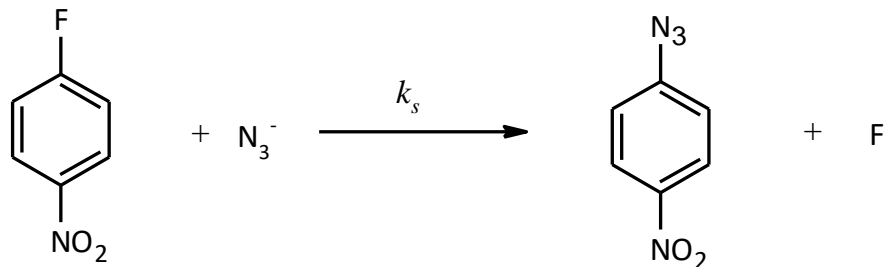
sales fundidas

mezclas eutécticas

Efecto de solventes en cinética química

Decomposition of N ₂ O ₅		
Reaction medium	log A (dm ³ mol ⁻¹ sec ⁻¹)	E _a (kJ mol ⁻¹)
Gas phase	13.6	103.3
Chloroform	13.7	102.7
Nitromethane	13.5	102.5
Pentachloroethane	14.0	104.6

Solvente como medio inerte



solvente	H ₂ O	MeOH	Me ₂ SO	HCONMe ₂	(Me ₂ N) ₃ PO
k _s /k _{H₂O}	1	1,6	1,3 10 ⁴	4,3 10 ⁴	2,0 10 ⁶

Efecto de solvente SNA

Colisiones en líquidos

THE COLLISION MECHANISM AND THE PRIMARY PHOTOCHEMICAL PROCESS IN SOLUTIONS.

BY E. RABINOWITCH AND W. C. WOOD.

Received 28th May, 1936.

(1) The Collision Number and the Collision Intervals.

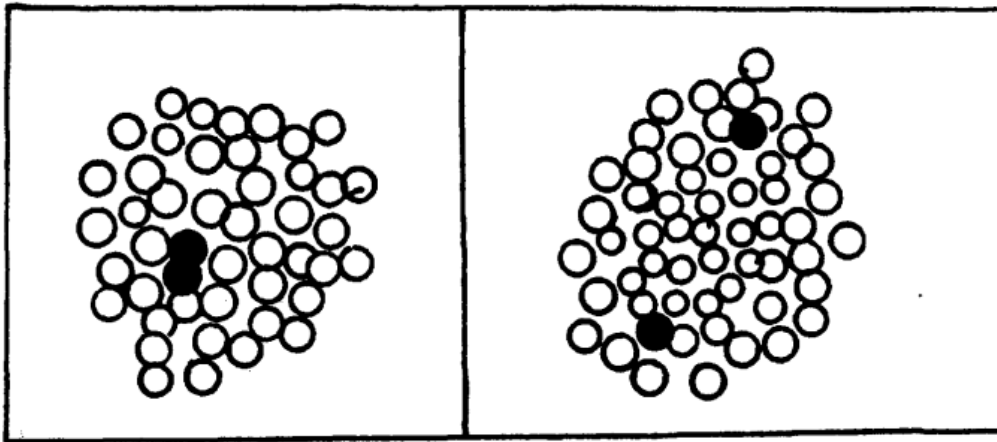


FIG. 3b.

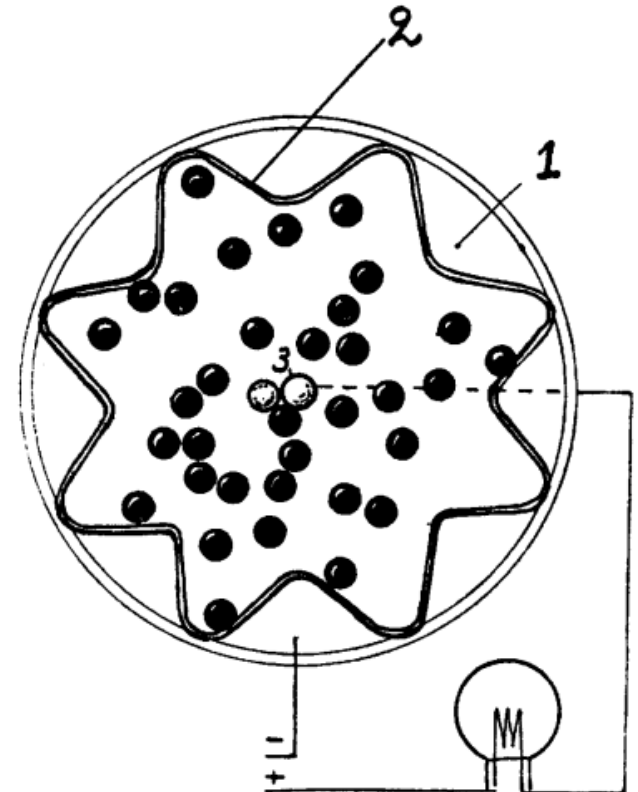
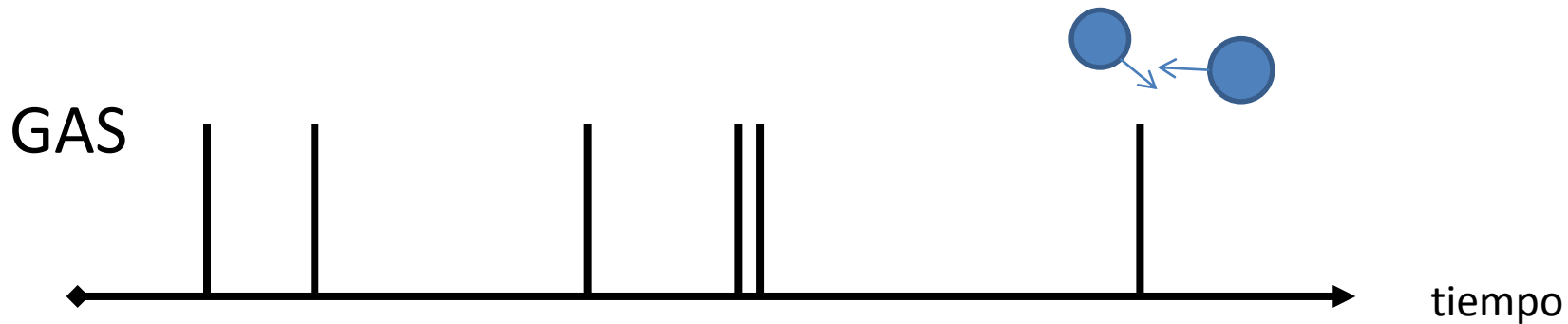
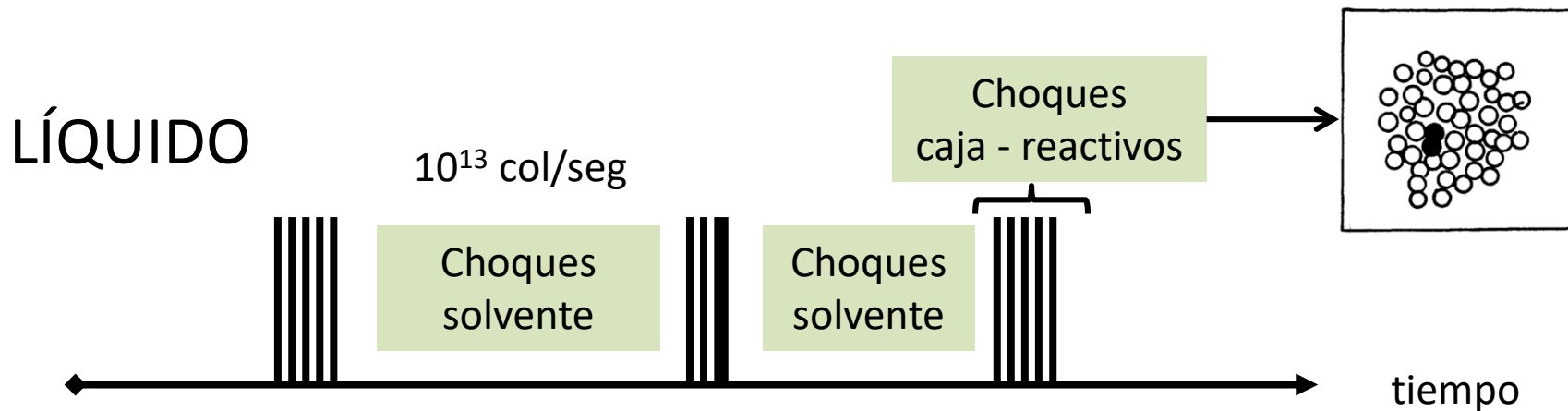


FIG. 2.

Colisiones - comparación

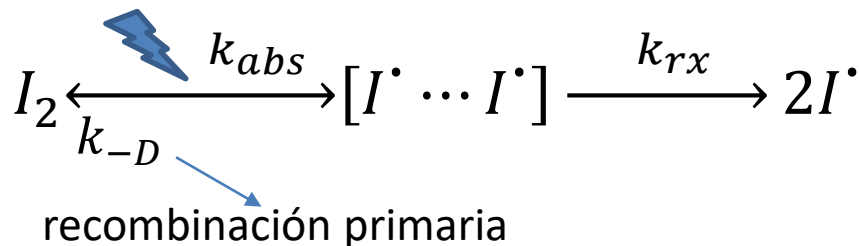


Colisiones en fase gaseosa



Colisiones en fase gaseosa, fracción de moléculas aprox 75 % v/v (si supongo HCP)

Efecto caja - recombinaciones



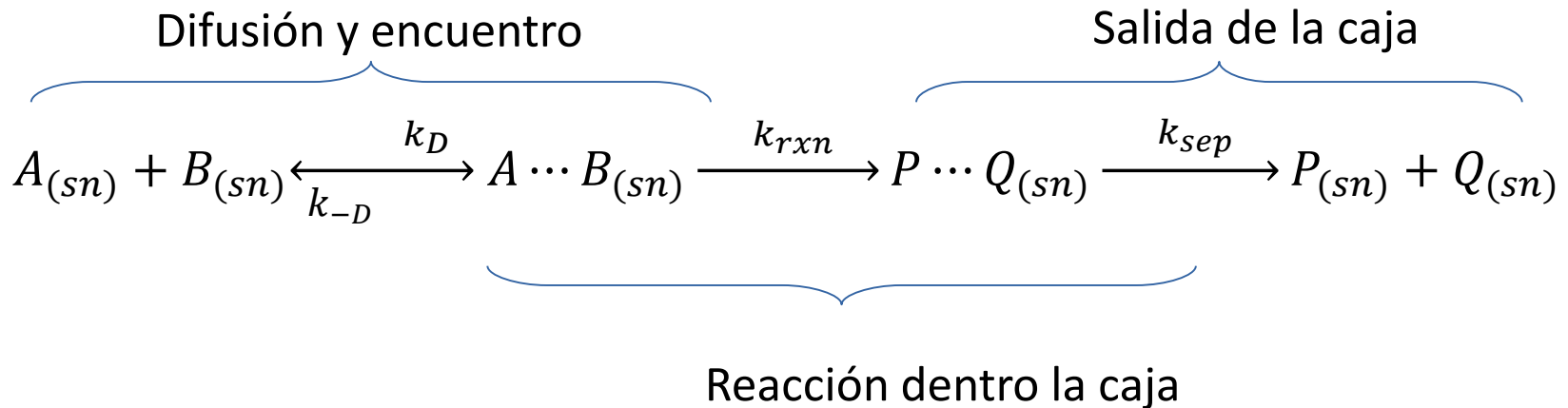
$$\frac{d[I \cdots I]}{dt} = k_{abs}[I_2] - k_{-D}[I \cdots I] - k_{rx}[I \cdots I]$$

$$\phi_{2I} = -\phi_{I_2} = \frac{k_{rx}[I \cdots I]}{k_{-D}[I \cdots I] + k_{rx}[I \cdots I]} = \frac{k_{rx}}{k_{-D} + k_{rx}}$$

Yield of decomposition of molecular iodine in a photo-induced reaction

Solvent	$-\phi_{I_2}$	$\eta_s m\rho$
Hexane	0.5	4.0
Carbon tetrachloride	0.11	9.5
Hexachlorobuta-1,3-diene	0.0042	>30

*Control cinético / difusional



$$\frac{d[A]}{dt} = -k_D [A][B] + k_{-D} [A \cdots B]$$

$$\frac{d[A \cdots B]}{dt} = k_D [A][B] - k_{-D} [A \cdots B] - k_{rxn} [A \cdots B] = 0 ; (EE)$$

$$[A \cdots B] = \frac{k_D [A][B]}{k_D + k_{rxn}}$$

Control cinético / difusional

$$\frac{d[A]}{dt} = -k_D[A][B] + k_D[A \cdots B]$$

$$\frac{d[A]}{dt} = -k_D[A][B] + k_{-D} \frac{k_D[A][B]}{k_D + k_{rxn}}$$

Control cinético

$$-\frac{d[A]}{dt} = \frac{k_D k_{rxn} [A][B]}{k_{-D}}$$

$k_{-D} \gg k_{rxn}$

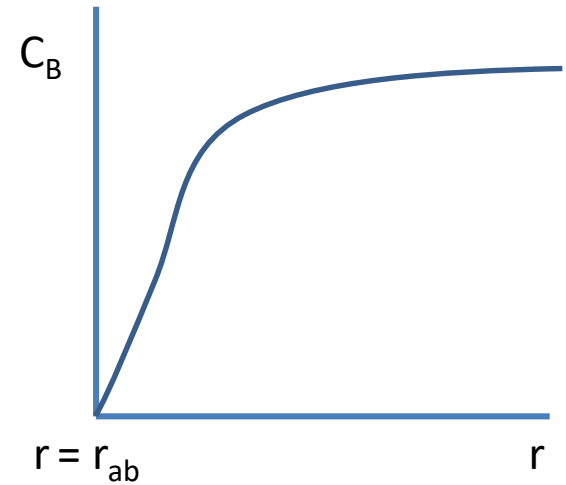
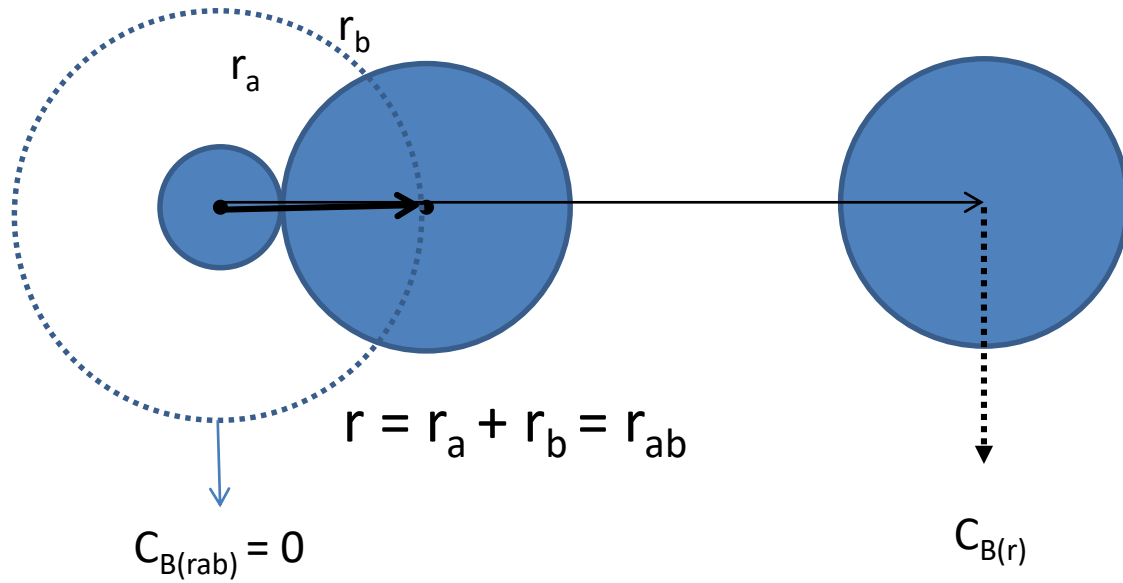
$$-\frac{d[A]}{dt} = \frac{k_D k_{rxn} [A][B]}{k_{-D} + k_{rxn}}$$

Control difusional

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

$k_{-D} \ll k_{rxn}$

Difusión (especies no cargadas) - k



$$J = -DA \frac{dC}{dr}$$

$$J_{B \rightarrow A} = D_B 4\pi r^2 \frac{dC_B}{dr}$$

$$J_{B \rightarrow A} \cdot \int_{r(r_A+r_B)}^{\infty} \frac{dr}{r^2} = 4\pi D_B \cdot \int_{C_B(r_A+r_B)}^{C_B^{\infty}} dC_B$$

$$C_{B(r_A+r_B)} = 0$$

Difusión (especies no cargadas) - k

$$J_{B \rightarrow A} = 4\pi(r_A + r_B)D_B C_B^\infty$$

Si A fuera estacionario

$$J_{B \rightarrow A} = 4\pi(r_A + r_B) (D_B + D_A) C_B^\infty$$

$$v_{reacc} = 4\pi(r_A + r_B) (D_B + D_A) C_B^\infty C_A^\infty$$

$$v_{reacc} = N_{Av} 4\pi(r_A + r_B) (D_B + D_A) C_B^\infty C_A^\infty$$

$$k_{dif} = 10^3 N_{Av} 4\pi(r_A + r_B) (D_B + D_A)$$

$$(r_A + r_B) \sim 0.5 \text{ nm}$$

$$D_B + D_A \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

$$k_{dif} \sim 4 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1} \sim 10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

*Dependencia de k con viscosidad

η

viscosidad

$$[\eta] = Pa \cdot s = N \cdot s \cdot m^{-2}$$

$$1 \text{ poise} = 0.1 Pa s$$

$$1 \text{ centipoise} = 1 cp = 1 mPa s \sim \eta_{H_2O}$$

$$D = \frac{k_B T}{6 \pi \eta r} \quad D_A + D_B = \frac{k_B T}{6 \pi \eta} \cdot \left(\frac{1}{r_A} + \frac{1}{r_B} \right) = \frac{k_B T}{6 \pi \eta} \cdot \left(\frac{(r_A + r_B)^2}{r_A r_B} \right)$$

Stokes - Einstein

$$k_{dif} = \frac{2 k_B T (r_A + r_B)^2}{3 \eta r_A r_B} \xrightarrow{r_A = r_B} \frac{8 k_B T}{3 \eta}$$

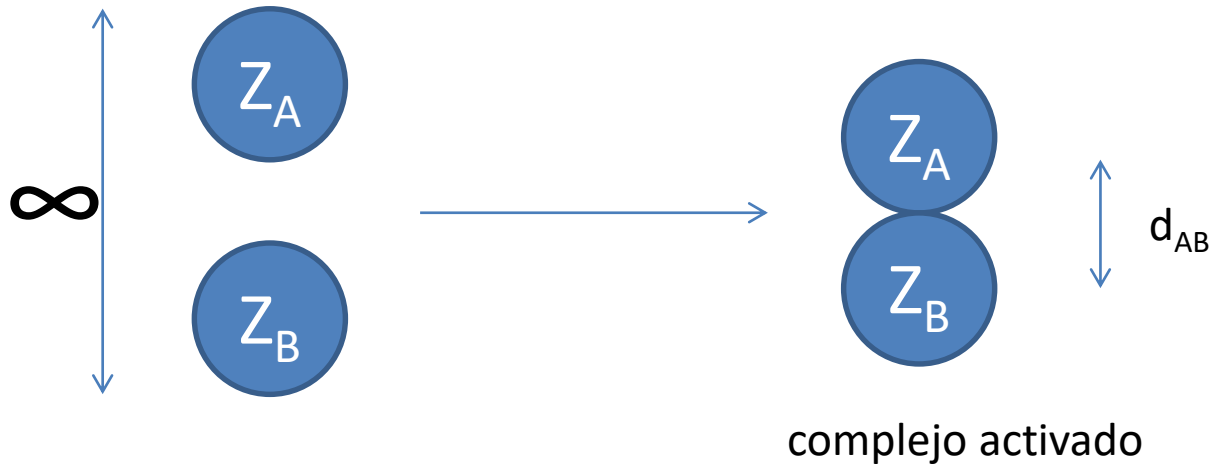
**Ojo k_{dif} no está en $dm^3 mol^{-1} s^{-1}$

Dependencia de k con viscosidad

Diffusion controlled rate constants calculated from eq. (9.24) and viscosities for some common solvents at 25 °C

Solvent	Viscosity ^a (η) (mPa sec)	k_{diff} ^b ($\text{M}^{-1}\text{sec}^{-1}$)
Carbon dioxide	0.0577 ^c	1.2×10^{11}
Diethyl ether	0.222	3.0×10^{10}
Hexane	0.294	2.2×10^{10}
Acetone	0.316	2.1×10^{10}
Toluene	0.558	1.2×10^{10}
Decane	0.861	7.7×10^9
Water	0.890	7.4×10^9
Ethanol	1.083	6.1×10^9
Propan-2-ol	2.044	3.2×10^9
Ethylene glycol	19.9 ^d	3.3×10^8
Glycerol	945	7.0×10^6

Efecto de la constante dieléctrica



$$F_{coul} = \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r^2}$$

$$dW = -\frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r^2} dr$$

$$W = -\int_{\infty}^{d_{AB}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r^2} dr$$

$$W = \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon d_{AB}}$$

Efecto de la constante dieléctrica

$$\Delta G^{\neq,0} = \Delta G^{\neq,0}_{quim} + N_{AV} \overbrace{\frac{Z_A Z_B e^2}{4\pi\epsilon_0 \epsilon d_{AB}}}^{\Delta G^{\neq,0}_{elec}}$$

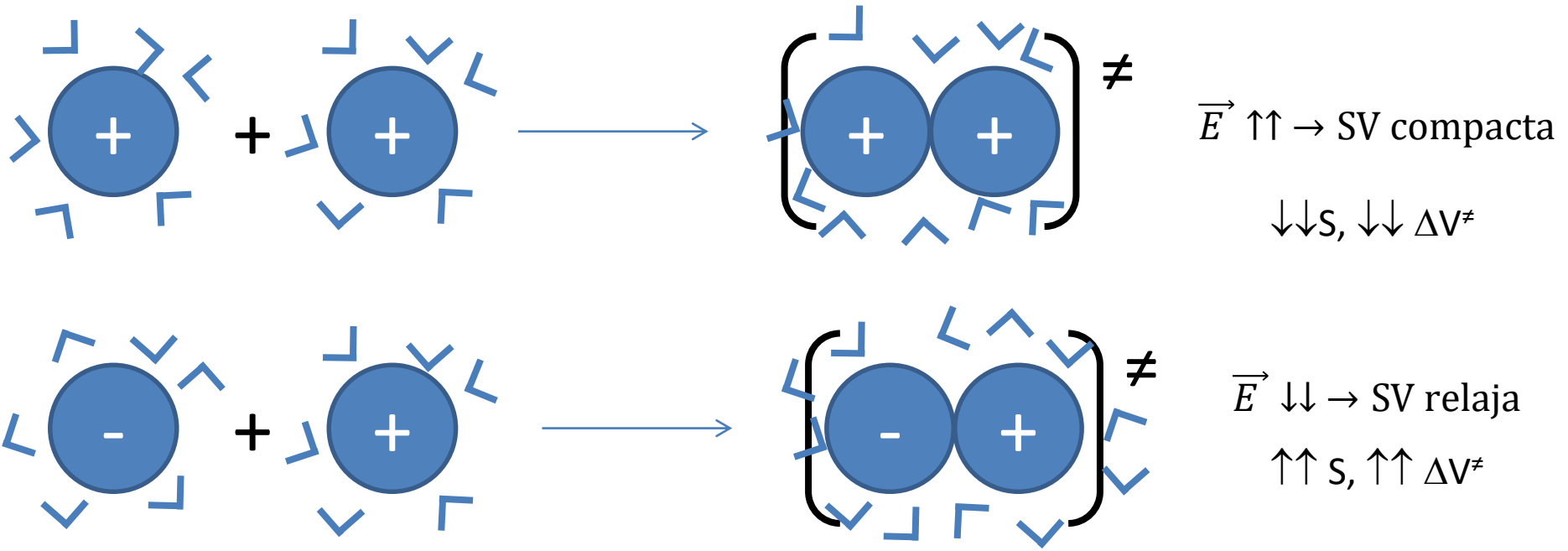
$$k_{rxn} = \frac{k_B T}{h} \cdot e^{\Delta G^{\neq,0}_{quim}/RT} \cdot e^{\Delta G^{\neq,0}_{elec}/RT}$$

$$\ln k_{rxn} = \ln k_0 - \frac{Z_A Z_B e^2}{4\pi\epsilon_0 \epsilon d_{AB}}$$

$$\left(\frac{dG}{dT} \right)_P = -S$$

$$\Delta S^{\neq,0}_{elec} = N_{AV} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 \epsilon d_{AB}} \left(\frac{d \ln \epsilon}{dT} \right)_P$$

Efecto de la constante dieléctrica



$$\epsilon_{H_2O} = 78.5$$

$$\left. \frac{d \ln \epsilon}{dT} \right)_P = -0.0046 \text{ K}^{-1}$$

$$d_{AB} \sim 200 \text{ pm}$$

$$\Delta S^{\ddagger,0}_{elec} \sim -41 \cdot Z_A Z_B \text{ J K}^{-1} \text{ mol}^{-1}$$

*Efecto de la constante dieléctrica

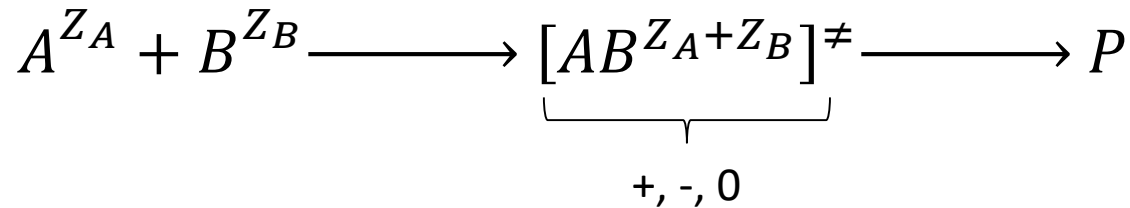
TABLE 6.4 SOME OBSERVED AND PREDICTED PRE-EXPONENTIAL FACTORS AND ENTROPIES OF ACTIVATION*

Reactants	Experimental		Estimated	
	$A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta^\ddagger S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$	$A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta^\ddagger S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{CNS}^-$	$\sim 10^{19}$	~ 126	10^{19}	126
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{OH}^-$	5×10^{17}	92	10^{17}	84
$\text{CH}_2\text{BrCOOCH}_3 + \text{S}_2\text{O}_3^{2-}$	1×10^{14}	25	10^{13}	0
$\text{CH}_2\text{ClCOO}^- + \text{OH}^-$	6×10^{10}	-50	10^{11}	-42
$\text{ClO}^- + \text{ClO}_2^-$	9×10^8	-84	10^{11}	-42
$\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{2-}$	1×10^9	-71	10^9	-84
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{Hg}^{2+}$	1×10^8	-100	10^8	-167
$\text{S}_2\text{O}_4^{2-} + \text{S}_2\text{O}_4^{2-}$	2×10^4	-167	10^5	-167
$\text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-}$	2×10^6	-126	10^5	-167

* For references to the original literature see C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, 15, 1497 (1955); D. T. Y. Chen and K. J. Laidler, *Can. J. Chem.*, 37, 599 (1959).

$$A \propto e^{\Delta S^\ddagger / R}$$

*Efecto de la fuerza iónica



Fuerza iónica (e.g. buffer)

$$K^{\neq} = \frac{\gamma_{AB}^{\neq} [AB]^{\neq}}{\gamma_A \gamma_B [A][B]}$$

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

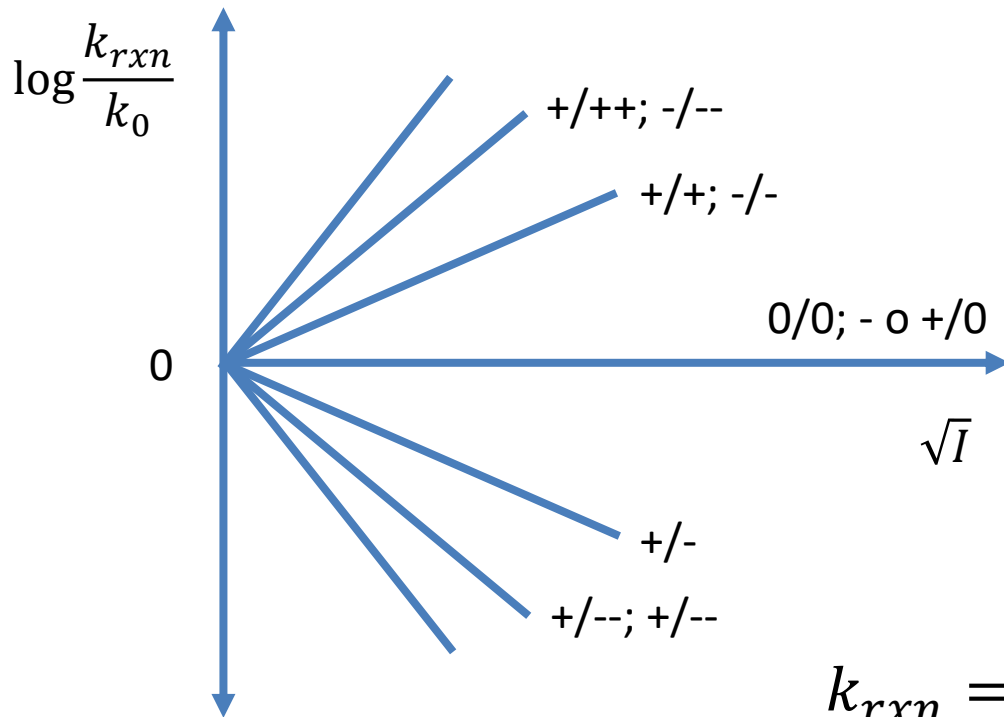
$$\log \gamma_i \sim -AZ_i^2 \sqrt{I}$$

Debye-Hückel diluida

$$k_{rxn} = \frac{k_B T}{h} K^{\neq} \frac{\gamma_{AB}^{\neq}}{\gamma_A \gamma_B} = k_{I \rightarrow 0} \frac{\gamma_{AB}^{\neq}}{\gamma_A \gamma_B}$$

Efecto de la fuerza iónica

$$\log k_{rxn} \sim \log k_0 + 2AZ_A Z_B \sqrt{I}$$



$$\log \frac{k_{rxn}}{k_0} \sim 1,018 Z_A Z_B \sqrt{I}$$

(H₂O, 298 K, I diluida)

$$k_{rxn} = \frac{k_B T}{h} K^\ddagger \frac{\gamma_{AB}^\ddagger}{\gamma_A \gamma_B} = k_{I \rightarrow 0} \frac{\gamma_{AB}^\ddagger}{\gamma_A \gamma_B}$$

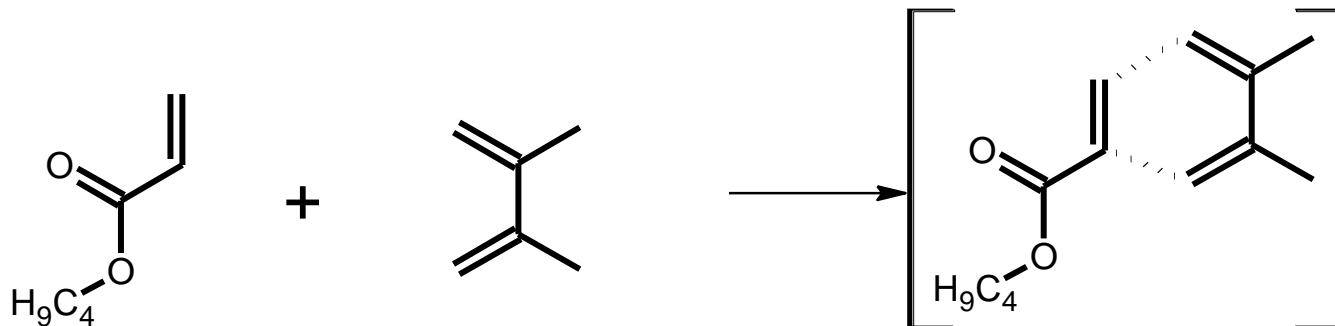
Tengo información del estado de transición

Efecto de la presión

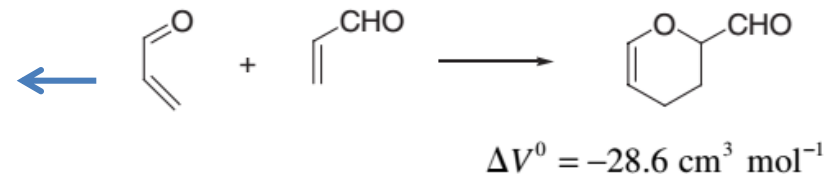
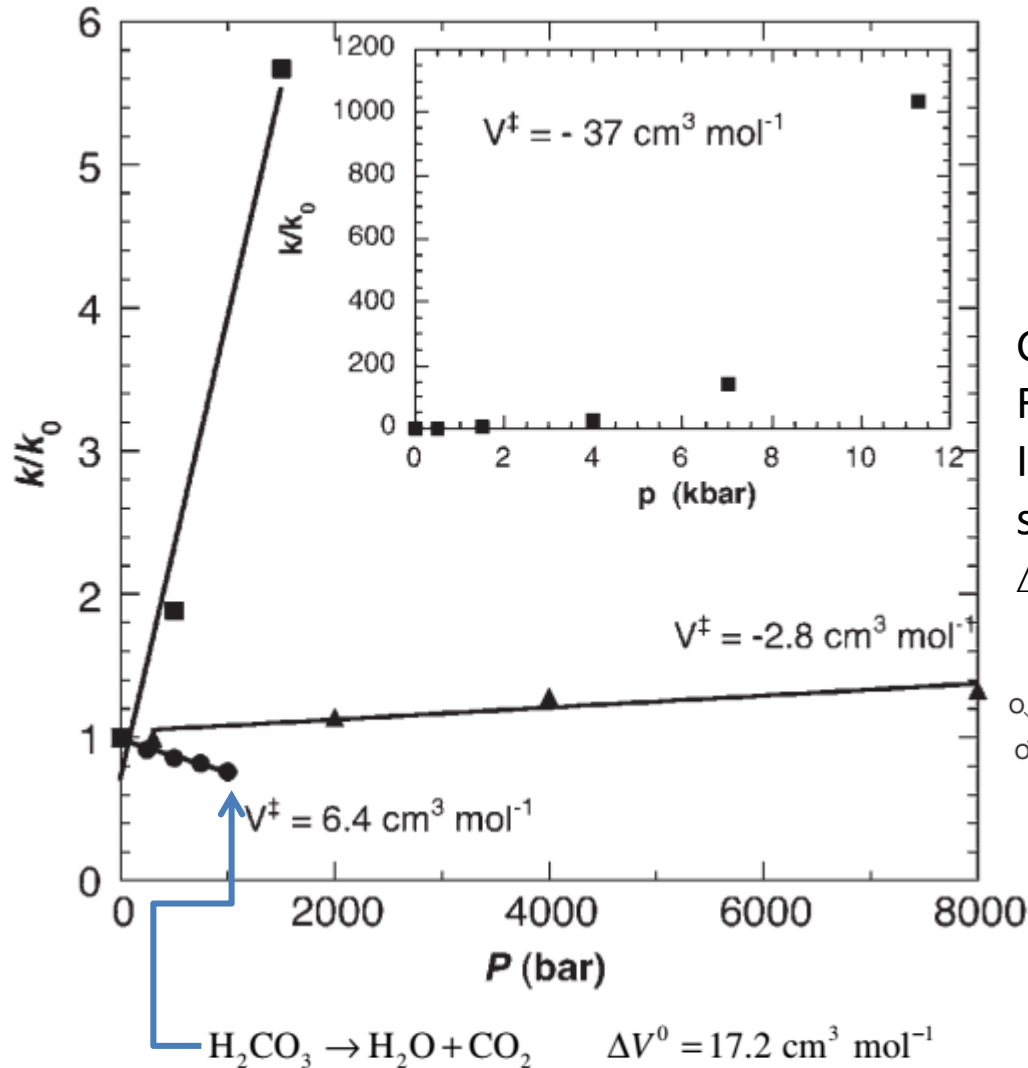
$$k_{rxn} = \frac{k_B T}{h} K^\ddagger$$

$$\ln k_{rxn} = \ln \left(\frac{k_B T}{h} \right) + \ln K^\ddagger$$

$$\ln k_{rxn} = \ln \left(\frac{k_B T}{h} \right) - \frac{\Delta G^\ddagger}{RT} \xrightarrow{\left(\frac{dG}{dP} \right)_T = V} \boxed{\left(\frac{d \ln k_{rxn}}{dP} \right)_T = - \frac{\Delta V^\ddagger}{RT}}$$



Efecto de la presión



Generalmente $\Delta V^\ddagger < \Delta V$, $\sim \pm 30 \text{ cm}^3 \text{ mol}^{-1}$
 Formación/ruptura enlace, $\pm 10 \text{ cm}^3 \text{ mol}^{-1}$
 Ionización, $-20 \text{ cm}^3 \text{ mol}^{-1}$ (contracción solvente)

ΔV^\ddagger da información del ET

