FALHAS DA TEORIA DE COLISÕES

$$k(T) = \underbrace{\pi (R_A + R_B)^2 \langle c \rangle e^{-\varepsilon_0/kT}}$$

SEÇÃO DE CHOQUE C/ BARREIRA DE ENERGIA

$$\boxed{\varepsilon = \varepsilon_t}$$

VELOCIDADE MÉDIA

$$\langle c \rangle = \left(\frac{8kT}{\pi \mu} \right)^{1/2}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

MASSA REDUZIDA

RESULTA EM VALORES DE 10 – 1000 vezes MAIOR NO CASO DE REAÇÕES COM MOLÉCULAS POLIATÔMICAS

$$A + B \xrightarrow{k_{TC}} AB$$

?

$$\varepsilon = \varepsilon_t + \boxed{\varepsilon_v + \varepsilon_{rot}}$$

CORREÇÃO :

$$k(T) = \boxed{p}\, \underset{\text{COLISÕES}}{k(T)} \qquad p < 1$$

p: FATOR ESTÉRICO $\quad p \in (0.1 - 0.001)$

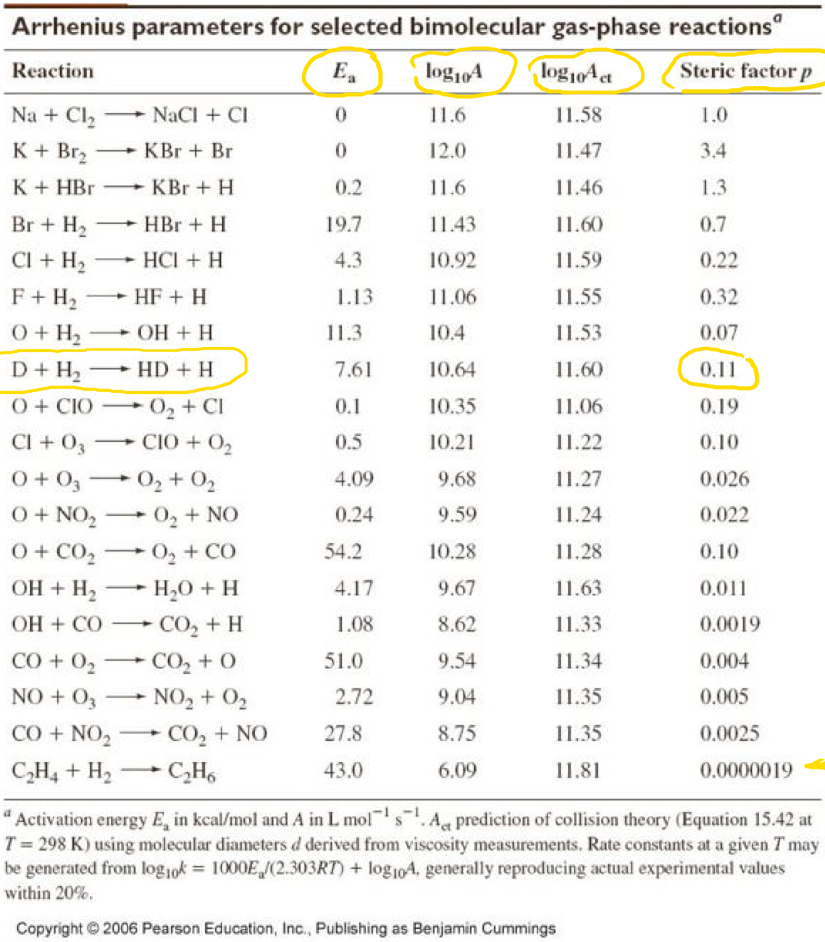
ORIENTAÇÃO MOLECULAR NA COLISÃO É FATOR DETERMINANTE.

CORREÇÃO :

$$k(T) = \boxed{p}\, \underset{\text{COLISÕES}}{k(T)} \qquad p < 1$$

p : FATOR ESTÉRICO $\quad p \in (0.1 - 0.001)$

ORIENTAÇÃO MOLECULAR NA COLISÃO É FATOR DETERMINANTE.

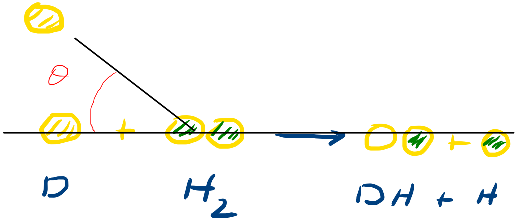


Arrhenius parameters for selected bimolecular gas-phase reactions[a]

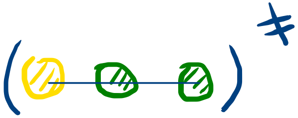
CALCULADO

Reaction	E_a	$\log_{10}A$	$\log_{10}A_{ct}$	Steric factor p
$Na + Cl_2 \longrightarrow NaCl + Cl$	0	11.6	11.58	1.0
$K + Br_2 \longrightarrow KBr + Br$	0	12.0	11.47	3.4
$K + HBr \longrightarrow KBr + H$	0.2	11.6	11.46	1.3
$Br + H_2 \longrightarrow HBr + H$	19.7	11.43	11.60	0.7
$Cl + H_2 \longrightarrow HCl + H$	4.3	10.92	11.59	0.22
$F + H_2 \longrightarrow HF + H$	1.13	11.06	11.55	0.32
$O + H_2 \longrightarrow OH + H$	11.3	10.4	11.53	0.07
$D + H_2 \longrightarrow HD + H$	7.61	10.64	11.60	0.11
$O + ClO \longrightarrow O_2 + Cl$	0.1	10.35	11.06	0.19
$Cl + O_3 \longrightarrow ClO + O_2$	0.5	10.21	11.22	0.10
$O + O_3 \longrightarrow O_2 + O_2$	4.09	9.68	11.27	0.026
$O + NO_2 \longrightarrow O_2 + NO$	0.24	9.59	11.24	0.022
$O + CO_2 \longrightarrow O_2 + CO$	54.2	10.28	11.28	0.10
$OH + H_2 \longrightarrow H_2O + H$	4.17	9.67	11.63	0.011
$OH + CO \longrightarrow CO_2 + H$	1.08	8.62	11.33	0.0019
$CO + O_2 \longrightarrow CO_2 + O$	51.0	9.54	11.34	0.004
$NO + O_3 \longrightarrow NO_2 + O_2$	2.72	9.04	11.35	0.005
$CO + NO_2 \longrightarrow CO_2 + NO$	27.8	8.75	11.35	0.0025
$C_2H_4 + H_2 \longrightarrow C_2H_6$	43.0	6.09	11.81	0.0000019

[a] Activation energy E_a in kcal/mol and A in L mol^{-1} s^{-1}. A_{ct} prediction of collision theory (Equation 15.42 at $T = 298$ K) using molecular diameters d derived from viscosity measurements. Rate constants at a given T may be generated from $\log_{10}k = 1000E_a/(2.303RT) + \log_{10}A$, generally reproducing actual experimental values within 20%.

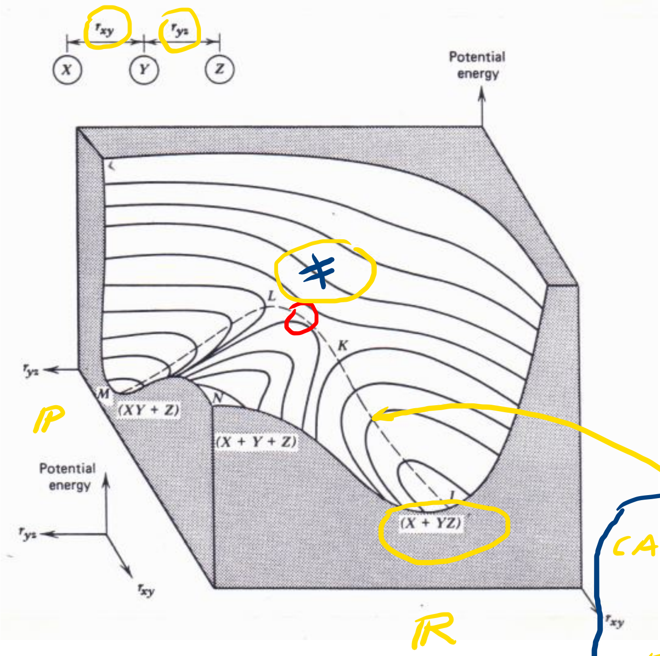


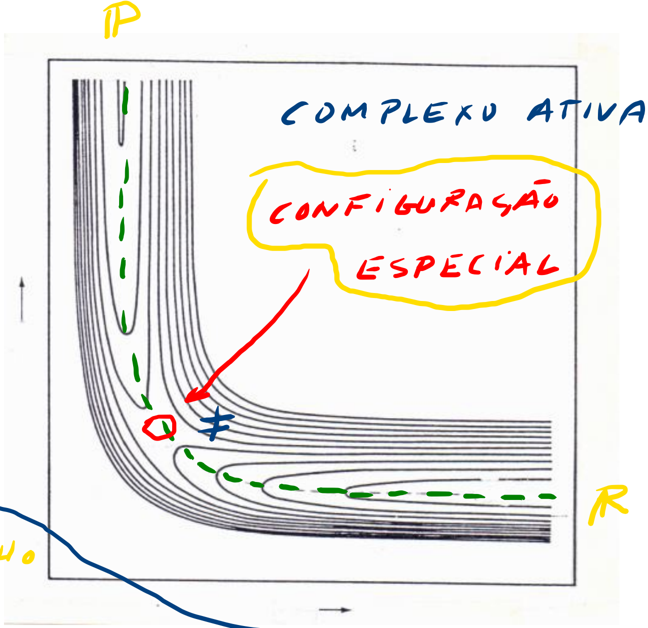
REAÇÃO HIPOTÉTICA



$$X + YZ \xrightarrow{k} XY + Z$$

PES



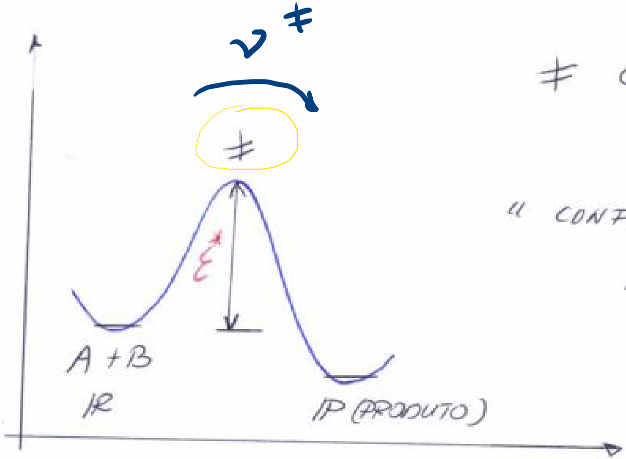


COMPLEXO ATIVADO

CONFIGURAÇÃO ESPECIAL

CAMINHO DE ENERGIA MÍNIMA SOBRE A SUPERFÍCIE

TEORIA DO COMPLEXO ATIVADO



‡ COMPLEXO ATIVADO

" CONFIGURAÇÃO MOLECULAR A⋯B QUE ESTÁ NO TOPO DA BARREIRA

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^{\ddagger} \xrightarrow{k_2} P$$

FREQ $\nu^{\ddagger}$ ii) único modo

i) ‡ em QUASI equilíbrio c/ os reagentes

$$\frac{d[P]}{dt} = k_2[AB^{\ddagger}]$$

SUPONDO UM PRÉ-EQUILÍBRIO $A + B \rightleftharpoons AB^{\ddagger}$

$$\underline{[AB^{\ddagger}]} = K_{eq} \cdot [A][B]$$

$$\frac{d[P]}{dt} = \underbrace{k_2 K_{eq}}_{k} [A][B] = \underbrace{\nu^{\ddagger} K_{eq}}_{\boxed{k}} [A][B]$$

TST

CONSTANTE DE VELOCIDADE DE REAÇÃO k

$$\boxed{k = \gamma^{\ddagger} K_{eq}} \quad (1) \; ✓$$

$$\underbrace{Q_A \text{ e } Q_B}_{\text{BEM DETERMINADO}}$$

PELA MECÂNICA ESTATÍSTICA ✓

$$\boxed{K_{eq} = \frac{Q^{\ddagger}}{Q_A Q_B} e^{-\varepsilon^{*}/kT}} \quad (2)$$

$$Q^{\ddagger} = ?$$

$Q_i \equiv$ FUNÇÃO DE PARTIÇÃO: SOMA SOBRE ESTADOS

$$Q_i = \underset{\substack{\downarrow \\ \text{TRANSLAÇÃO}}}{q_t} \cdot \underset{\substack{\downarrow \\ \text{VIBRAÇÃO}}}{q_v} \cdot \underset{\substack{\searrow \\ \text{ROTAÇÃO}}}{q_r} \quad \leftarrow$$

CÁLCULO DE $\nu^\ddagger$

$$\underline{q_v^\ddagger} = q_{v'}^\ddagger \, \underline{z_v^\ddagger} \qquad z_v^\ddagger = \left(1 - e^{-h\nu^\ddagger/kT}\right)$$

$\underline{v'}$

1 FREQ

RETIRADA

$\nu^\ddagger$

$$h\nu^\ddagger < kT \qquad \boxed{z_v^\ddagger \simeq \frac{kT}{h\nu^\ddagger}} \quad (3)$$

$$e^{-h\nu^\ddagger/kT} \simeq 1 - \frac{h\nu^\ddagger}{kT}$$

CONCLUINDO (3), (2) ⇒ (1)

$$\boxed{k(T) = \left(\frac{kT}{h}\right) \frac{Q^{\ddagger}}{Q_A Q_B}\, e^{-\varepsilon^{*}/kT}} \qquad (4) \quad ✓$$

TEORIA DO ESTADO DE TRANSIÇÃO

OBS: 298 K $\quad \frac{h}{kT} = 0.16 \text{ ps} = 1,6 \times 10^{-13} \text{ s}$

ou

$$\boxed{k(T) = \left(\frac{kT}{h}\right) K^{\ddagger}} \qquad (5)$$

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q_A Q_B} \exp\left(-\varepsilon^{*}/kT\right)$$

$$\underbrace{Q_i = q_t \cdot q_v \cdot q_r}$$

3 I

3N-6

N: ÁTOMOS

MODOS NORMAIS

IV

TABLE 4.1 PARTITION FUNCTIONS FOR DIFFERENT TYPES OF MOTION

Motion	Degrees of freedom	Partition function	Order of magnitude
Translation	3	$\frac{(2\pi m\mathrm{k}T)^{3/2}}{h^3}$ (per unit volume)	10^{31}–10^{32} m^{-3}
Rotation (linear molecule)	2	$\frac{8\pi^2 I\mathrm{k}T}{\sigma h^2}$	10–10^2
Rotation (nonlinear molecule)	3	$\frac{8\pi^2(8\pi^3 I_A I_B I_C)^{1/2}(\mathrm{k}T)^{3/2}}{\sigma h^3}$	10^2–10^3
Vibration (per normal mode)	1	$\frac{1}{1 - e^{-h\nu/\mathrm{k}T}}$	1–10
Free internal rotation	1	$\frac{(8\pi^2 I'\mathrm{k}T)^{1/2}}{h}$	1–10

INTERNO

10^7

where m = mass of molecule
I = moment of inertia for linear molecule
I_A, I_B, and I_C = moments of inertia for a nonlinear molecule about three axes at right angles to one another
I' = moment of inertia for internal rotation
ν = normal-mode vibrational frequency
k = Boltzmann constant
h = Planck constant
T = absolute temperature
σ = symmetry number[a]

It is useful to remember that the power to which h appears is equal to the number of degrees of freedom.

---

[a] As discussed in the text (Section 4.5.4), symmetry numbers are used in the calculation of equilibrium constants, but for rates an alternative procedure is recommended.

INTERPRETAÇÃO TERMODINÂMICA

$$k(T) = \left(\frac{kT}{h}\right) K^{\ddagger}$$

$$\frac{kT}{h}(298) \cong 6\times 10^{12}\ s^{-1}$$ ✓

$$K^{\ddagger} = \exp\left[-\Delta G^{\ddagger}/RT\right]$$ ✓

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$ ✓

$$\boxed{k(T) = \underbrace{\left(\frac{kT}{h}\right) e^{\Delta S^{\ddagger}/R}} \cdot e^{-\underbrace{\Delta H^{\ddagger}}_{\to\, E_0}/RT}} \qquad (6)$$ ✓

FATOR PRE-EXPONENCIAL

E FUNÇÃO DA

ENTROPIA ATIVAÇÃO → FATOR ESTÉRICO (p)

$$\Delta S^{\ddagger} = S^{\ddagger} - S_{A+B} < 0$$

ENTROPIA ESTADO TRANSIÇÃO COMPLEXO EM CONFIG. DEFINIDA

ENTROPIA DOS REAGENTES

A///B

1

A + B

2

1 - 2 = - 1 (Nº PARTÍCULAS GÁS)

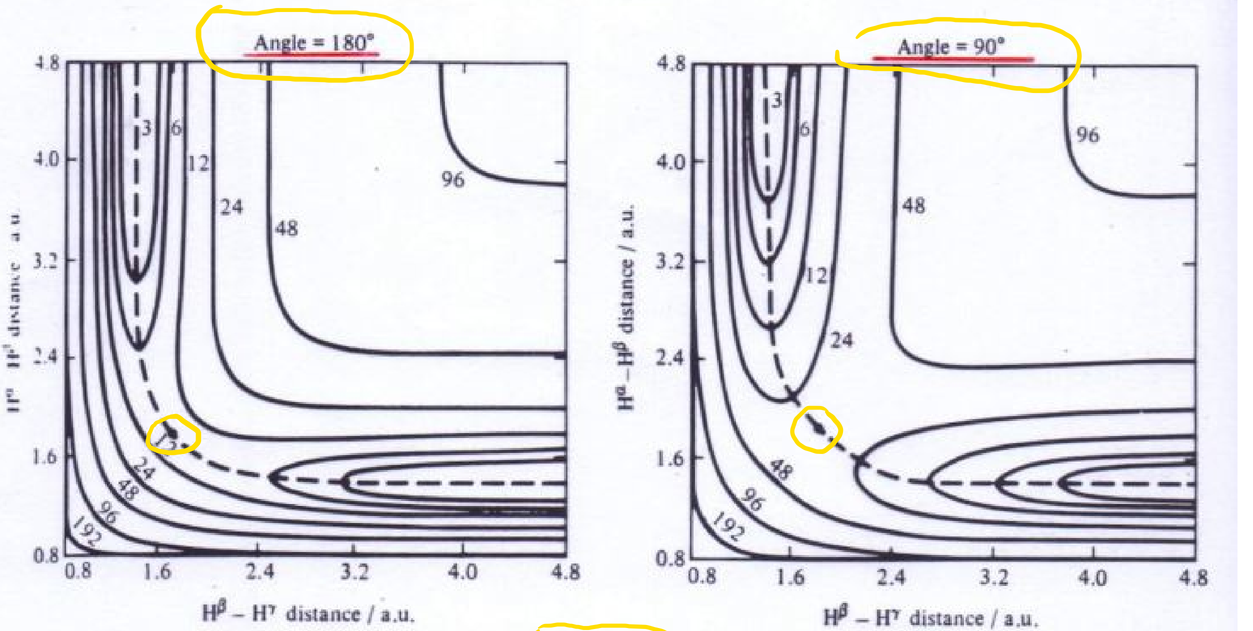


Figure 3.10 Potential-energy surfaces for the $H + H_2$ reaction, as given by Truhlar and Horowitz[15] on the basis of the ab initio calculations of Siegbahn and Liu. The numbers on the contours show the values of the energies in kcal mol^{-1} (1 kcal = 4.184 kJ); the unit for the bond distances is the atomic unit, or bohr (1 bohr = 52.92 pm).