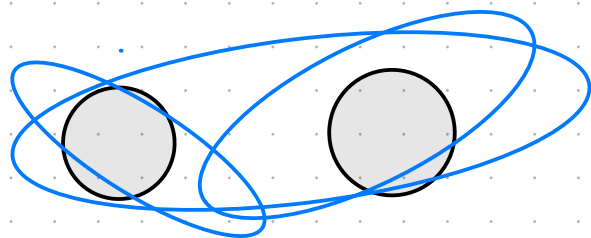


Gas diatómico

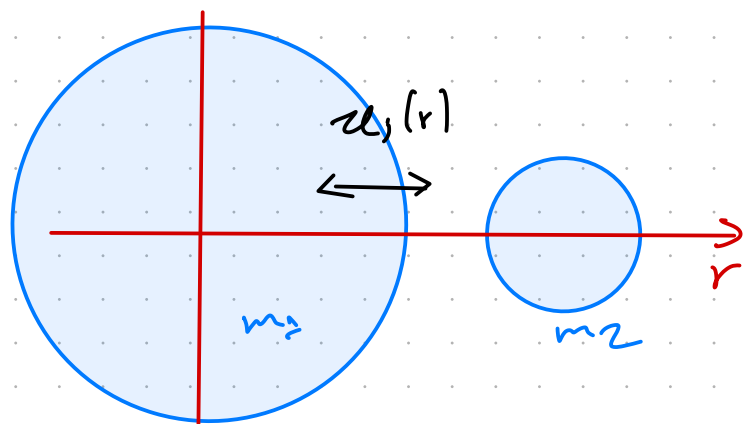


Núcleos lentos  
Electrones rápidos

Los  $e^-$  se mueven en el campo producido por los núcleos

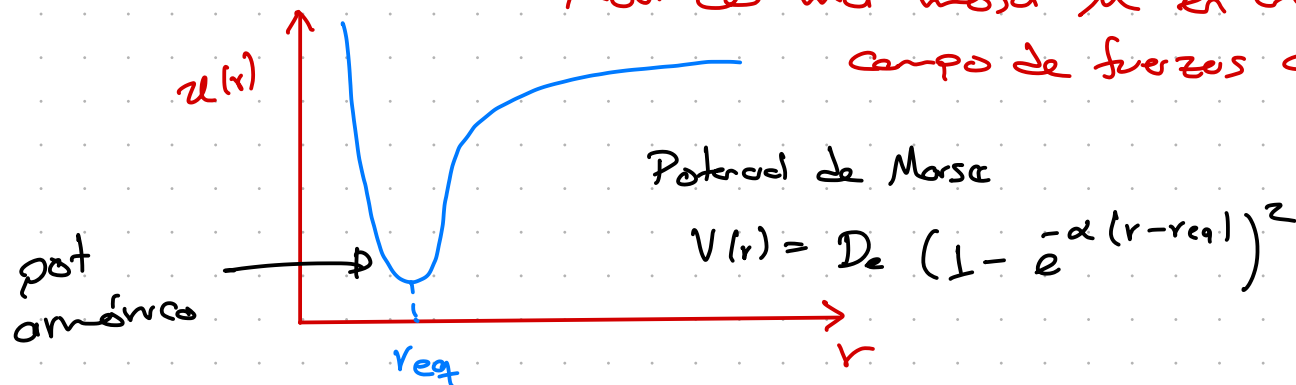
Los eigenvalores de energía son  $\epsilon_j(r)$

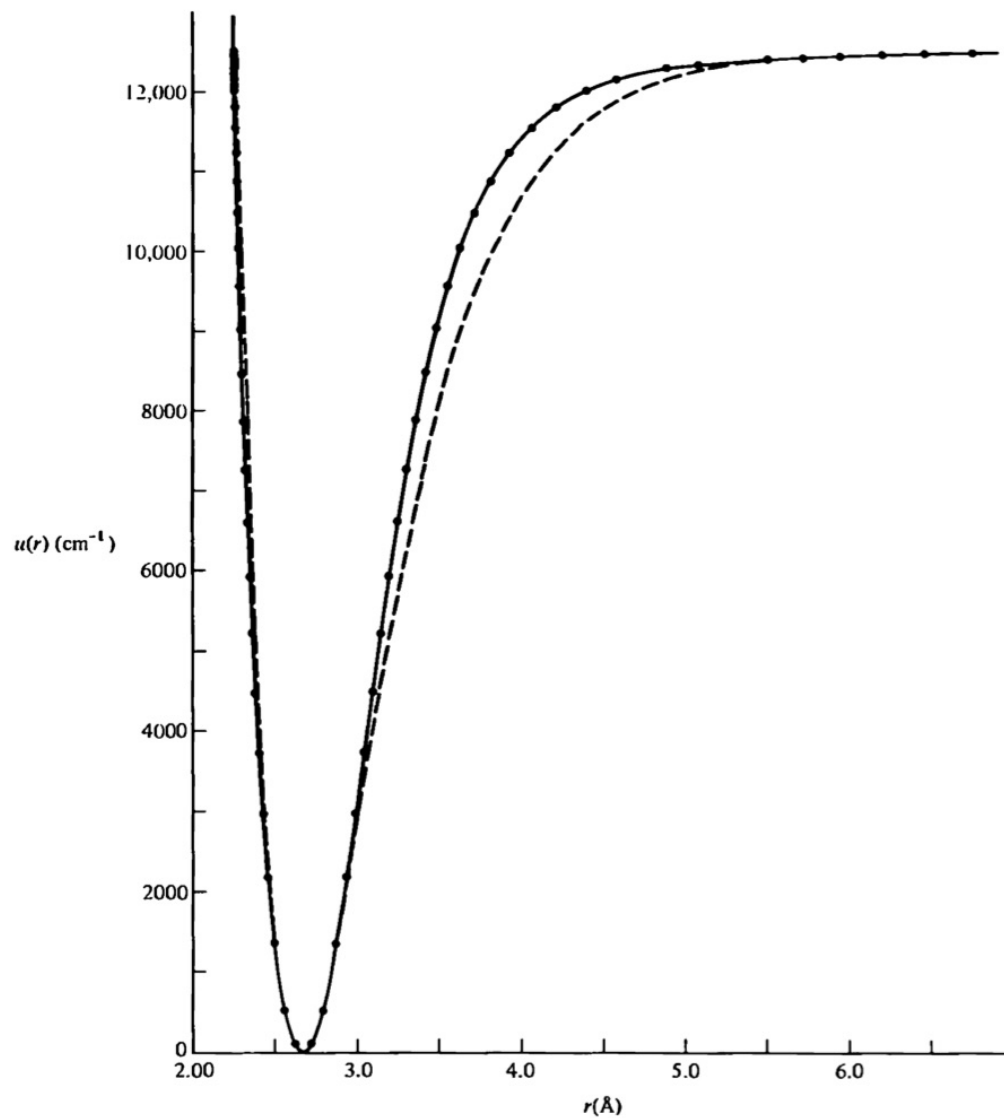
Los núcleos se mueven en el campo producido por las  $e^-$



El cálculo de  $\epsilon_j$  no es sencillo  
Potenciales empíricos

Mov. de una masa  $\mu$  en un campo de fuerzas central





**Figure 6-1.** The internuclear potential energy curve for the ground state of  $\text{I}_2$  as computed from ultraviolet spectroscopy. The dashed curve is the Morse curve. (From R. D. Verma, *J. Chem. Phys.*, **32**, 738, 1960.)

Molécula  $\left\{ \begin{array}{l} \text{traslación} \\ \text{conformacional} \\ \text{intermolecular} \end{array} \right. \left\{ \begin{array}{l} \text{rotación} \\ \text{vibración} \end{array} \right.$

Hamiltoniano

$$H = H_{\text{tras}} + H_{\text{int}}$$

$$\epsilon = \epsilon_{\text{tras}} + \epsilon_{\text{int}}$$

Función de partición

$$q = q_{\text{tras}} q_{\text{int}}$$

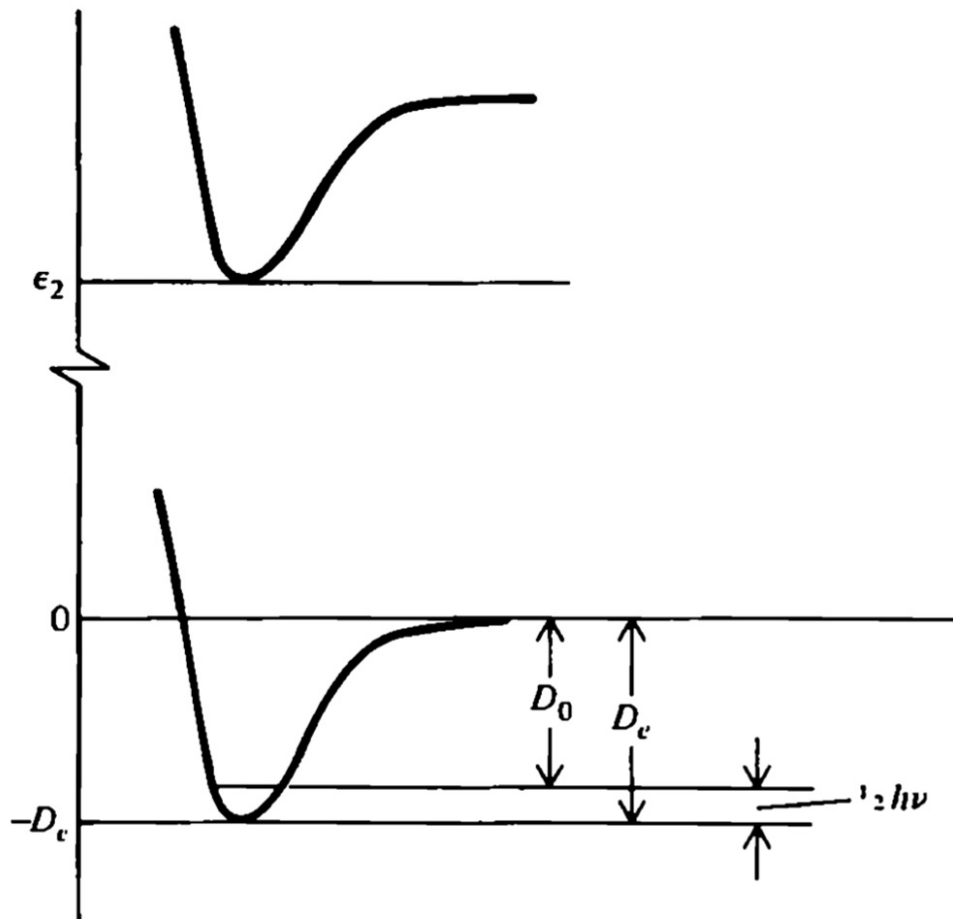
$$q_{\text{tras}} = \left( \frac{2\pi(m_1+m_2)k_B T}{h^2} \right)^{3/2} V$$

$$Q = \frac{q_{\text{tras}}^N q_{\text{int}}^N}{N!}$$

$$q_{\text{int}} = q_{\text{rot}} q_{\text{vib}}$$

Aproximación rotor rígido-oscilador armónico

# Función de partición electrónica



El cero de energía está medido con respecto al estado electrónico más bajo  $-D_e$

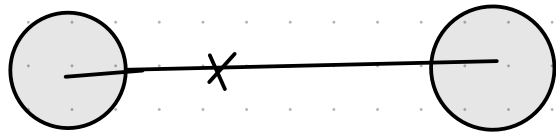
Función de partición

$$q_{elec} = \omega_{e1} e^{-D_e/k_B T} + \omega_{e2} e^{-E/k_B T} + \dots$$

Se define  $D_0 = D_e - \frac{h\nu}{2}$

Se puede medir con espectroscopia y calorimetría

## Rotor rígido



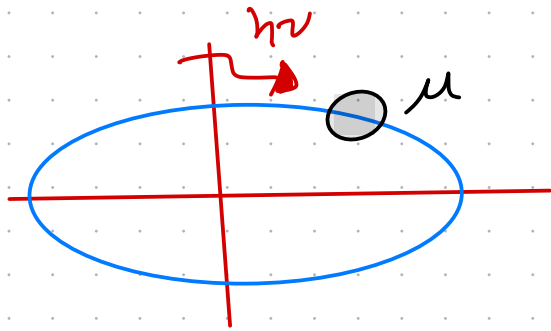
$$\epsilon_j = \frac{\hbar^2}{2I} j(j+1) \quad j = 0, 1, 2, \dots$$

$$I = \mu r_{eq}^2$$

momento de inercia

degeneración  $2j+1$

Para que ocurra una transición rotacional  $j \rightarrow j+1$



$$h\nu = \epsilon_{j+1} - \epsilon_j$$

$$= \frac{\hbar^2}{2I} \left[ (j+1)(j+2) - j(j+1) \right]$$

$$= \frac{\hbar^2}{2I} 2(j+1) = \frac{\hbar^2}{I} (j+1) = \frac{h^2}{4\pi^2 I} (j+1)$$

$$\nu = \frac{h}{4\pi^2} \left( \frac{1}{\mu r_{eq}^2} \right) (j+1) \quad \text{frecuencia de absorción/emisión}$$

$$\nu = \frac{h}{4\pi^2} \left( \frac{1}{\mu r_{eq}^2} \right) (j+1)$$

Longitud de onda

$$\lambda = \frac{c}{\nu} \quad \text{Microondas}$$

Número de onda

$$\bar{\omega} = \frac{1}{\lambda} = \frac{\nu}{c}$$

$$\bar{\omega} = \frac{h}{4\pi^2 c} \left( \frac{1}{\mu r_{eq}^2} \right)$$

$$[\bar{\omega}] = \text{cm}^{-1}$$

Se define la constante rotacional  $\bar{B}$  como

$$\bar{B} = \frac{h}{8\pi^2 I c}$$

Energía

$$E_j = \frac{h^2 j(j+1)}{8\pi^2 I} = \bar{B} j(j+1)$$

$$\frac{E_j}{hc} = \frac{\bar{B} j(j+1)}{hc} = \epsilon^*$$

Frecuencia

$$\nu = 2h \bar{B} (j+1)$$



# Función de partición rotacional

$$q_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-\beta \bar{B} j(j+1)}$$

$$\frac{1}{k} \bar{B} = \Theta_r \quad \text{temp rotacional}$$

Table 6-1. Molecular constants for several diatomic molecules\*

molecule	electronic state	$\bar{\omega}$ (cm <sup>-1</sup> )	$\Theta_v$ (°K)	$\bar{B}$ (cm <sup>-1</sup> )	$\Theta_r$ (°K)	$k \times 10^{-5}$ (dynes/cm)	$D_0$ (kcal/mole)
H <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4320	6215	59.3	85.3	5.5	103.2
D <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3054	4394	29.9	42.7	5.5	104.6
Cl <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	561	808	0.244	0.351	3.2	57.1
Br <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	322	463	0.0809	0.116	2.4	45.4
I <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	214	308	0.0373	0.0537	1.7	35.6
O <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	1568	2256	1.437	2.07	11.6	118.0
N <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2345	3374	2.001	2.88	22.6	225.1
CO	<sup>1</sup> Σ <sup>+</sup>	2157	3103	1.925	2.77	18.7	255.8
NO	<sup>2</sup> Π <sub>1/2</sub>	1890	2719	1.695	2.45	15.7	150.0
HCl	<sup>1</sup> Σ <sup>+</sup>	2938	4227	10.44	15.02	4.9	102.2
HBr	<sup>1</sup> Σ <sup>+</sup>	2640	3787	8.36	12.02	3.9	82.4
HI	<sup>1</sup> Σ <sup>+</sup>	2270	3266	6.46	9.06	3.0	70.5
Na <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	159	229	0.154	0.221	0.17	17.3
K <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	92.3	133	0.0561	0.081	0.10	15.8

limite a altas temperaturas si  $\Theta_r \leq T$

$$\begin{aligned} q_{\text{rot}} &= \int_0^{\infty} (2j+1) e^{-\Theta_r j(j+1)/T} dj \\ &= \int_0^{\infty} e^{-\Theta_r j(j+1)/T} d(j^2+j) = T \frac{e^{-\Theta_r j(j+1)/T}}{\Theta_r} \Big|_0^{\infty} \\ &= \frac{T}{\Theta_r} \\ &= \frac{k_B T}{B} \\ &= \frac{8\pi^2 I k_B T}{h^2} \end{aligned}$$

$$q_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-\Theta_r j(j+1)/T}$$

A bajas temperaturas

$$q_{\text{rot}} = 1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + 7e^{-12\Theta_r/T}$$

Válido si  $\Theta_r \gg 0.7T$

$$q_{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-\Theta_r j(j+1)/T}$$

\* Temperaturas intermedias

Serie de Maclourin

$$\sum_{n=a}^b f(n) = \int_a^b f(n) dn + \frac{1}{2} \{f(b) + f(a)\} + \sum_{j=1}^{\infty} (-1)^j \frac{B_j}{(2j)!} \{f^{(2j-1)}(a) - f^{(2j-1)}(b)\}$$

Números de Bernoulli  $B_1 = -1/6$ ,  $B_2 = 1/30$ ,  $B_4 = -1/42$

Sea la función  $f(n) = (2n+1) e^{-\Theta_r n(n+1)/T}$

$$q_{rot} = \frac{I}{\Theta_r} + \frac{1}{2} \{f(\infty) + f(0)\} + \sum_{j=1}^{\infty} (-1)^j \frac{B_j}{(2j)!} \{f^{(2j-1)}(a) - f^{(2j-1)}(b)\}$$

$$q_{\text{rot}} = \frac{I}{\Theta_v} + \frac{1}{2} \{f(\infty) + f(0)\} + \sum_{j=1}^{\infty} (-1)^j \frac{B_j}{(2j)!} \left\{ f^{(2j)}(a) - f^{(2j)}(b) \right\}$$

$$f(n) = (z^{n+1}) e^{-\Theta_v n(n+1)/T}$$

$$\frac{df}{dn} = z e^{-\Theta_v n(n+1)/T} - (z^{n+1}) e^{-\Theta_v n(n+1)/T} \frac{\Theta_v (2n+1)}{T}$$

$$\frac{df}{dn}(\infty) = 0 \quad \frac{df}{dn}(0) = z - \frac{\Theta_v}{T}$$

$$q_{\text{rot}} = \frac{I}{\Theta_v} + \frac{1}{2} \{0 + z\} - \frac{1/6}{2} \{f'(0) + f'(\infty)\} + \dots$$

$$= \frac{I}{\Theta_v} + \frac{1}{2} - \frac{1}{12} \left\{ z - \frac{\Theta_v}{T} + 0 \right\} + \dots$$

$$= \frac{I}{\Theta_v} + \frac{1}{3} + \frac{\Theta_v}{12T} + \dots$$

# Temperatures in termedras

$$q_{\text{rot}} = \frac{T}{\Theta_r} \left\{ 1 + \frac{1}{3} \left( \frac{\Theta_r}{T} \right) + \frac{1}{15} \left( \frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_r}{T} \right)^3 + \dots \right\}$$

temp a ltes

okl poa temperaturas ambiente  $T > \Theta_r$

## Energia

$$E = N k_B T^2 \frac{\partial \ln q_{\text{rot}}}{\partial T} = N k_B T^2 \left[ \ln T - \ln \Theta_r + \ln \left\{ \dots \right\} \right]$$
$$= N k_B T + \dots$$

## Capacidad calorifica

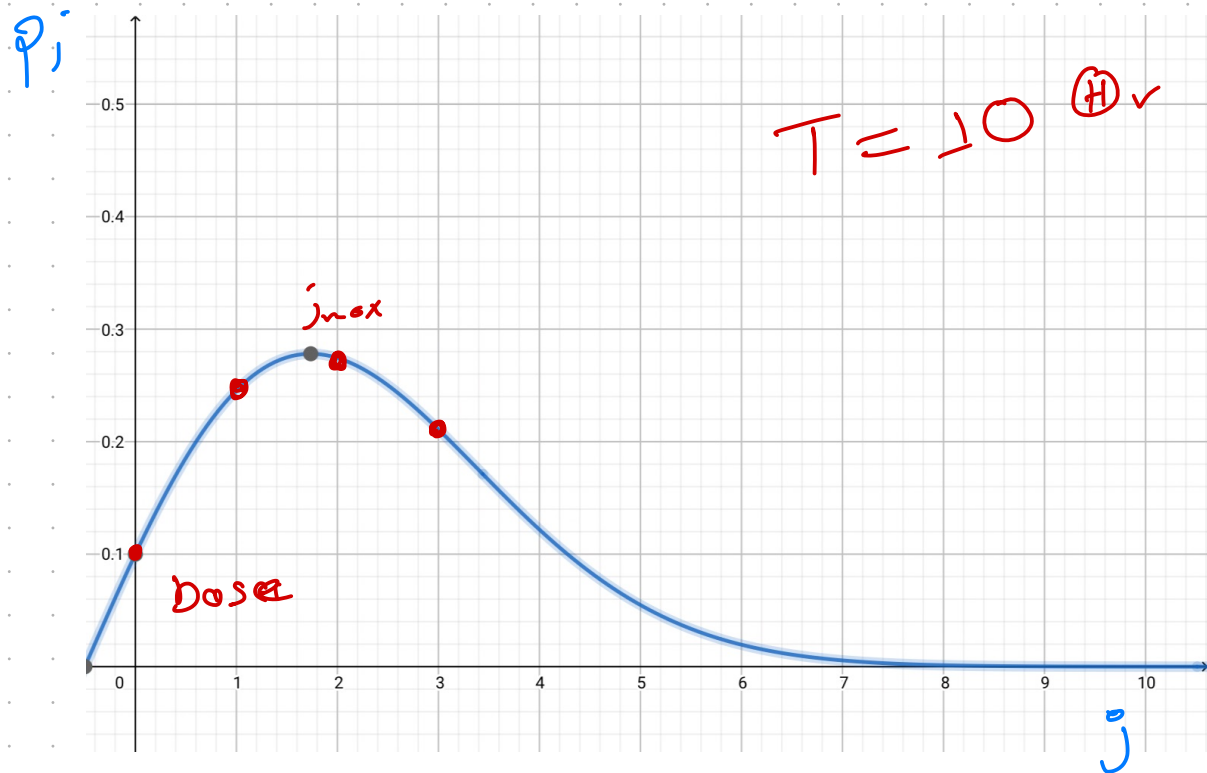
$$C_V = N k_B + \dots$$

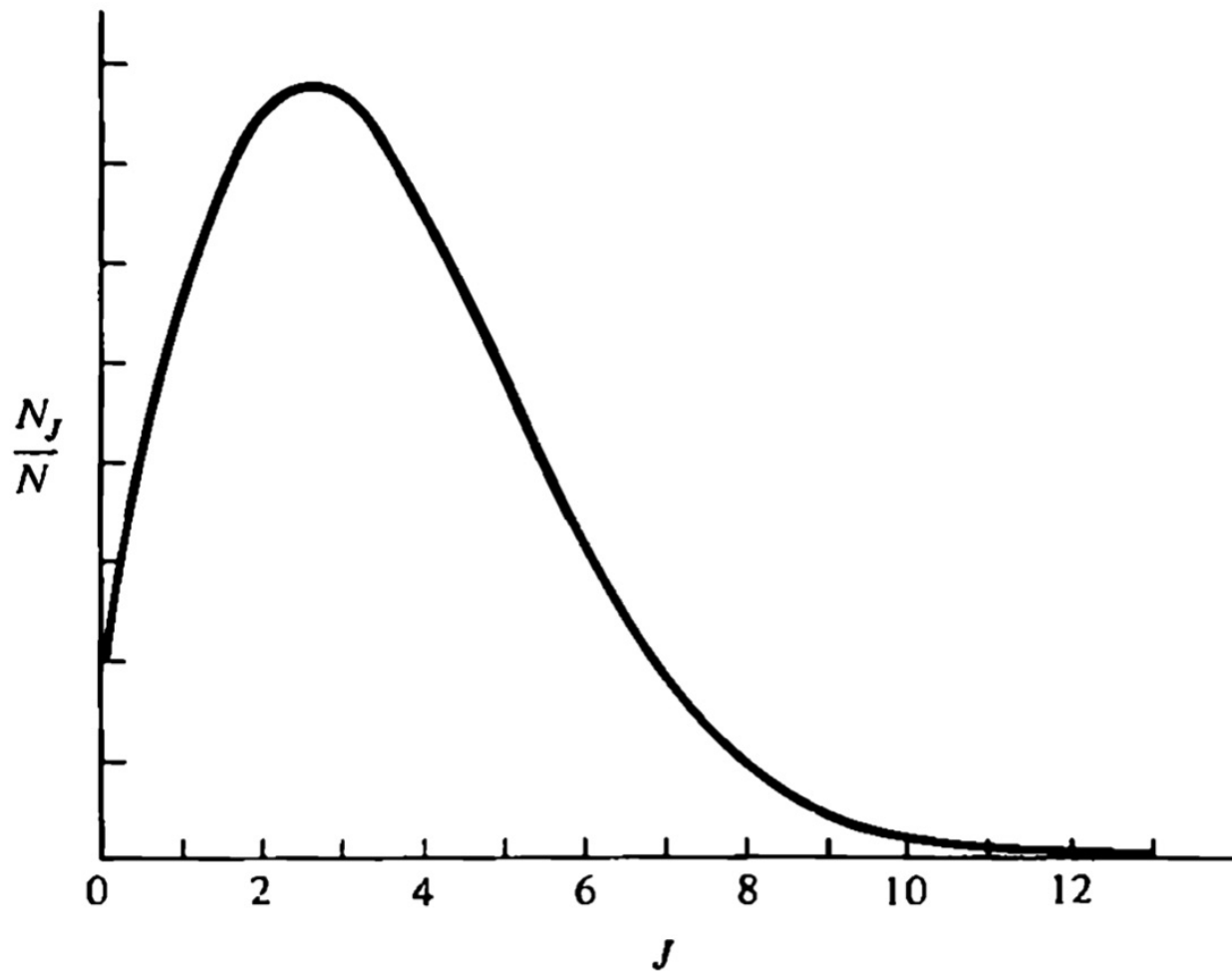
Fración de moléculas en un estado excitado

$$P_j = \frac{(2j+1) e^{-\Theta_r j(j+1)/T}}{q_{rot}}$$

Altas temperaturas

$$P_j = \frac{(2j+1) e^{-\Theta_r j(j+1)/T}}{T / \Theta_r}$$





**Figure 6-5. The population of the rotational levels of hydrogen chloride at 300°K.**



Para obtener el máximo de la distribución

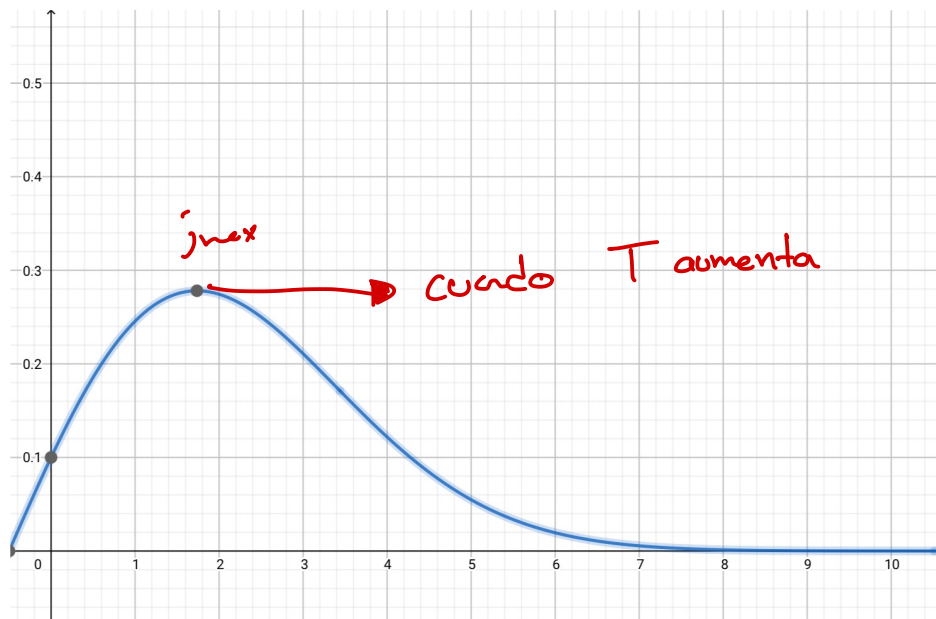
$$P_j = \frac{(z_{j+1}) e^{-\Theta_r j(j+1)/T}}{T / \Theta_r}$$

$$\frac{dP_j}{dj} = \frac{z e^{-\Theta_r j(j+1)/T}}{T / \Theta_r} - \frac{(z_{j+1})^2 e^{-\Theta_r j(j+1)/T}}{T / \Theta_r} \frac{\Theta_r}{T} = 0$$

$$(z_{j+1})^2 = \frac{zT}{\Theta_r}$$

$$j = \frac{\sqrt{\frac{zT}{\Theta_r}} - 1}{z}$$

$$\rightarrow j_{\max} \approx \sqrt{\frac{T}{2\Theta_r}} \approx \sqrt{\frac{k_B T}{2\bar{B}}}$$



¿Qué significa que  $j \rightarrow 0$ ?

## Oscilador armónico

Pot. intermolecula alrededor de  $r_{eq}$

$$u(r) = u(r_{eq}) + \cancel{\left. \frac{du}{dr} \right|_{r_{eq}}} (r-r_{eq}) + \frac{1}{2} \left. \frac{d^2u}{dr^2} \right|_{r_{eq}} (r-r_{eq})^2 + \dots$$
$$= u(r_{eq}) + \frac{1}{2} k (r-r_{eq})^2 + \dots$$

↑  
cte elástica

Espectro de energías

$$E_n = (n + 1/2) h\nu \quad n = 0, 1, 2, \dots$$

$$\nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}$$

no hay degeneración

Para que ocorra uma transição vibracional

$$\begin{aligned} h\nu &= E_{n+1} - E_n \\ &= \frac{h}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \underbrace{(n+3/2 - n - 1/2)}_1 \end{aligned}$$

$$k \sim 10^{-5} \frac{\text{dm}}{\text{cm}} \left( \frac{10^{-9} \text{N}}{1 \text{dm}} \right) \left( \frac{100 \text{cm}}{2\pi} \right) = 10^{-8} \text{N/m}$$

## Función de partición vibracional

$$\begin{aligned}q_{\text{vib}} &= \sum e^{-\beta E_n} & E_n &= h\nu \left(n + \frac{1}{2}\right) \\ &= e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu n} \\ &= \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}\end{aligned}$$

## Energía

$$\begin{aligned}E_{\text{vib}} &= N k_B T^2 \frac{\partial}{\partial T} \ln q_{\text{vib}} \\ &= N k_B T^2 \frac{\partial}{\partial T} \left[ -\frac{h\nu}{2k_B T} - \ln(1 - e^{-h\nu/k_B T}) \right] \\ &= N k_B T^2 \left[ \frac{h\nu}{2k_B T^2} - \frac{e^{-h\nu/k_B T} \left( + \frac{h\nu}{k_B T^2} \right)}{1 - e^{-h\nu/k_B T}} \right]\end{aligned}$$

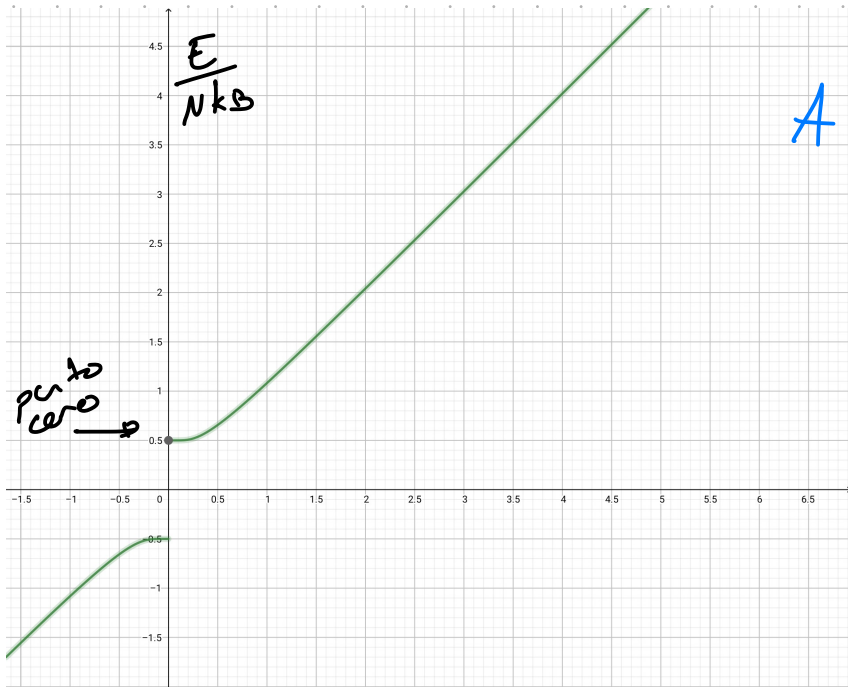
$$= \frac{N h \nu}{2} + \frac{N h \nu e^{-h\nu/k_B T}}{1 + e^{-h\nu/k_B T}}$$

$$E_{vib} = \frac{N k_B \Theta}{2} + \frac{N k_B \Theta}{e^{\Theta/T} - 1}$$

con  $\Theta = \frac{h\nu}{k_B}$

Temperatura  
vibracional

$$\frac{E_{vib}}{N k_B} = \frac{\Theta}{2} + \frac{\Theta}{e^{\Theta/T} - 1}$$



A altas temperaturas

$$E_v \rightarrow N k_B \left( \frac{\Theta}{2} + \frac{\Theta}{\Theta/T} \right)$$

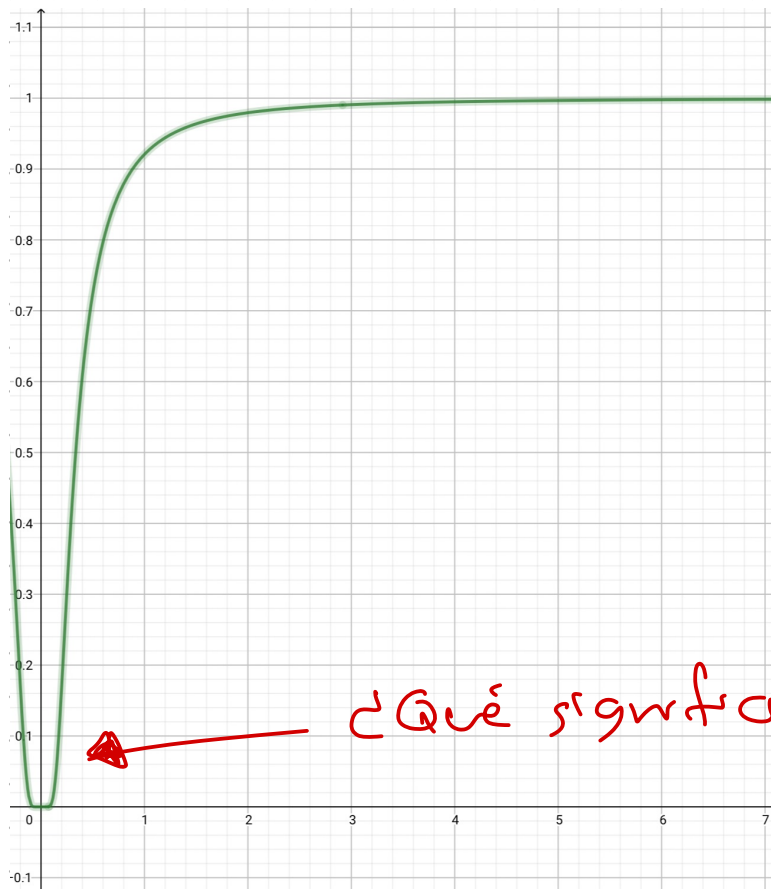
$$\rightarrow N k_B T$$

Capacidad calorífica

$$C_V = \frac{\partial \bar{E}_{vib}}{\partial T} = + \frac{N k_B \Theta}{(e^{\Theta/T} - 1)^2} \frac{e^{\Theta/T} \Theta}{T^2} = N k_B \left(\frac{\Theta}{T}\right)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T} - 1)^2}$$

A altas temperaturas

$$C_V \rightarrow N k_B \left(\frac{\Theta}{T}\right)^2 \frac{1 + \Theta/T}{(\Theta/T)^2} \rightarrow N k_B$$

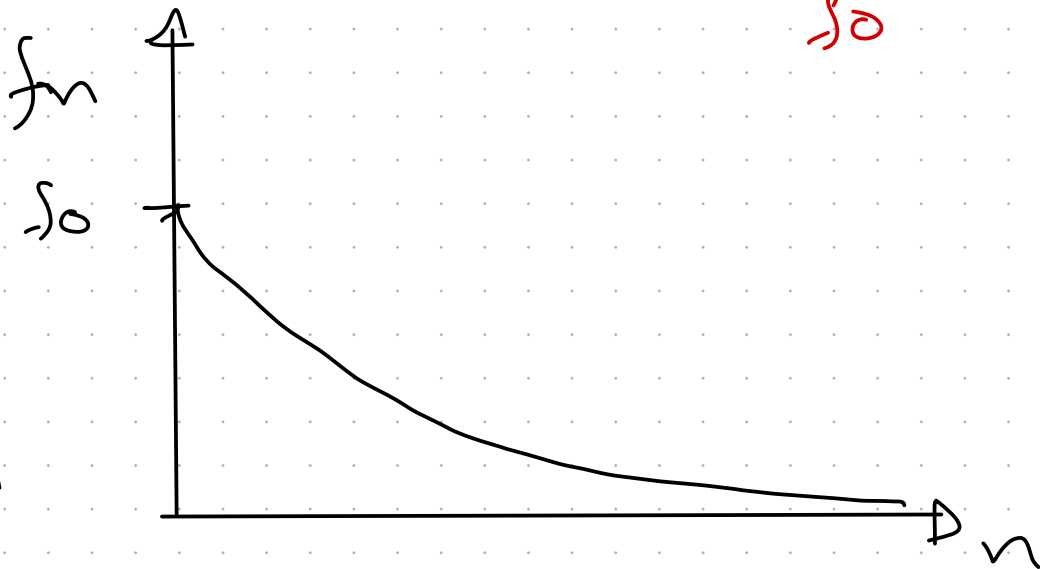


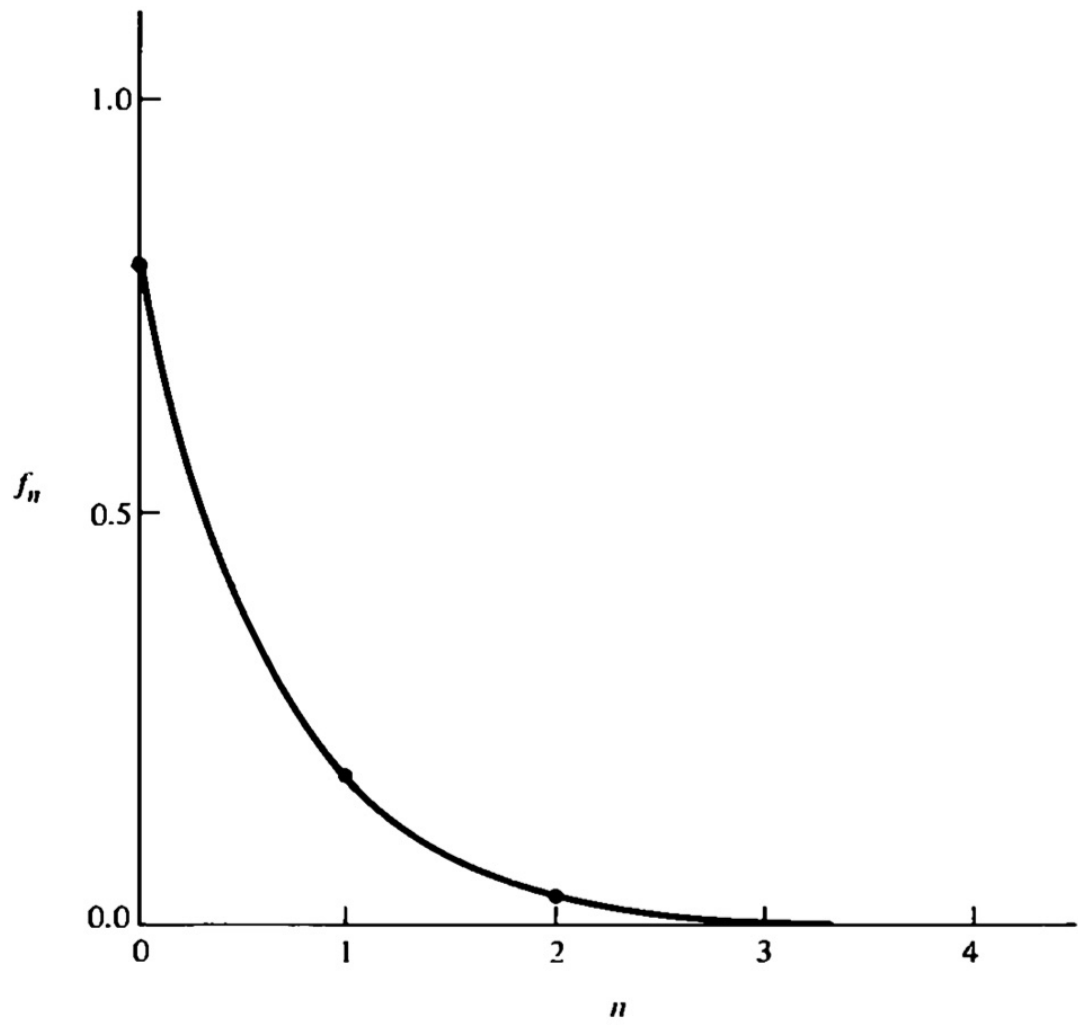
Fracción de moléculas en un estado excitado

$$f_n = \frac{e^{-\beta h \nu (n+1/2)}}{q_{vb}}$$

$$= \frac{e^{-\beta h \nu (n+1/2)}}{e^{-\beta h \nu / 2}} (1 - e^{-\beta h \nu})$$

$$= e^{-\beta h \nu n} \underbrace{(1 - e^{-\beta h \nu})}_{f_0}$$

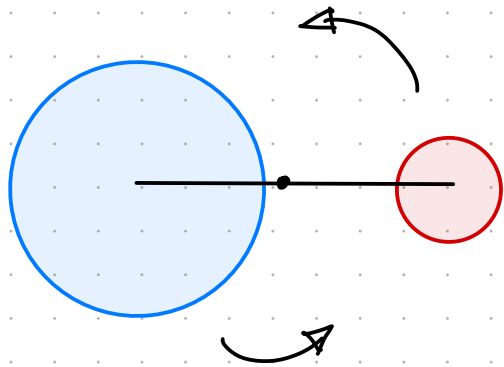




**Figure 6-4.** The population of the vibrational levels of  $\text{Br}_2$  at  $300^\circ\text{K}$ .

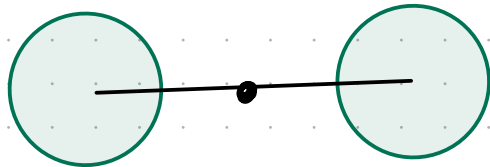


Simetría en a rotación



$$I_{\text{rot}} = \frac{I}{M_r} \left\{ 1 + \frac{1}{3} \left( \frac{M_r}{T} \right) + \frac{1}{15} \left( \frac{M_r}{T} \right)^2 + \frac{4}{315} \left( \frac{M_r}{T} \right)^3 + \dots \right\}$$

¿Qué pasa si los dos átomos son iguales



$$I_{\text{rot}} = \frac{I}{2M_r} \left\{ 1 + \frac{1}{3} \left( \frac{M_r}{T} \right) + \frac{1}{15} \left( \frac{M_r}{T} \right)^2 + \frac{4}{315} \left( \frac{M_r}{T} \right)^3 + \dots \right\}$$

↑ número de simetría

En general

$$Q_{\text{rot}} = \frac{I}{\sigma \Theta_v} \left\{ 1 + \frac{1}{3} \frac{\Theta_v}{T} + \frac{1}{15} \left( \frac{\Theta_v}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_v}{T} \right)^3 + \dots \right\}$$

Energia

$$E = N k_B T^2 \frac{\partial}{\partial T} \left\{ \ln T - \ln(\sigma \Theta_v) + \ln \left( 1 + \frac{1}{3} \frac{\Theta_v}{T} + \dots \right) \right\}$$

$$= N k_B T^2 \left\{ \frac{1}{T} + \frac{-\frac{\Theta_v}{3T^2} - \frac{2\Theta_v^2}{15T^3} - \frac{4 \times 3}{315} \frac{\Theta_v^3}{T^4} - \dots}{1 + \frac{1}{3} \frac{\Theta_v}{T} + \frac{1}{15} \left( \frac{\Theta_v}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_v}{T} \right)^3 + \dots} \right\}$$

$$\approx N k_B T^2 \left\{ \frac{1}{T} - \left( \frac{\Theta_v}{3T^2} + \frac{2\Theta_v^2}{15T^3} + \frac{12}{315} \frac{\Theta_v^3}{T^4} \right) \left( 1 - \frac{1}{3} \frac{\Theta_v}{T} - \frac{1}{15} \left( \frac{\Theta_v}{T} \right)^2 - \dots \right) \right\}$$

$$\sum N k_B T^2 \left\{ \frac{1}{T} - \left( \frac{\Theta_v}{3T^2} + \frac{2\Theta_v^2}{15T^3} + \frac{12}{315} \frac{\Theta_v^3}{T^4} - \frac{1}{9} \frac{\Theta_v^2}{T^3} - \frac{1}{45} \frac{\Theta_v^3}{T^4} + \dots \right) \right\}$$

$$\sum N k_B T \left\{ 1 - \frac{\Theta_v}{3T} - \frac{1}{45} \frac{\Theta_v^2}{T^2} + \dots \right\}$$

Capacidad calórica

$$C_v = \frac{\partial E}{\partial T} = N k_B + \frac{1}{45} \left( \frac{\Theta_v}{T} \right)^2 + \dots$$

Función de partición molecular

$$q = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \frac{8\pi^2 I k_B T}{\sigma h^2} \omega_i e^{-D_e/k_B T}$$

$\sigma = 1$  heteronuclear

$\sigma = 2$  homonuclear

Energía

$$E = N k_B T^2 \frac{\partial}{\partial T} \left[ A + \frac{3}{2} \ln T - \frac{h\nu}{2k_B T} - \ln(1 - e^{-h\nu/k_B T}) + B + \ln T + \frac{D_e}{k_B T} \right]$$

$$= N k_B T^2 \left[ \frac{3}{2T} + \frac{h\nu}{2k_B T^2} + \frac{e^{-h\nu/k_B T} \frac{h\nu}{k_B T^2}}{1 - e^{-h\nu/k_B T}} + \frac{1}{T} + \frac{D_e}{k_B T^2} \right]$$

$$E = \frac{5}{2} N k_B T + \frac{N h \nu}{2} + \frac{N h \nu}{e^{h \nu / k_B T} - 1} + \frac{D_e}{k_B T}$$

Ec de estado

$$p = N k_B T \left( \frac{\partial \ln q}{\partial V} \right) = \frac{N k_B T}{V}$$

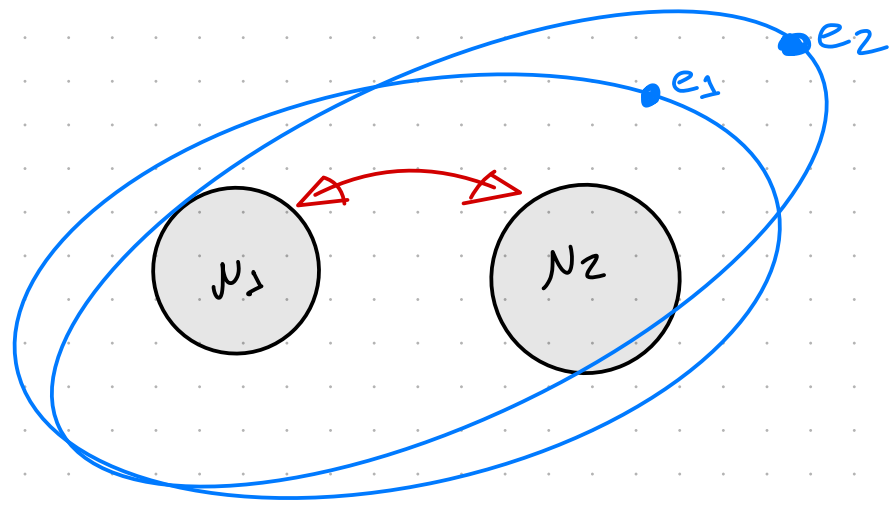
$$\frac{E}{NkT} = \frac{5}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \frac{D_e}{kT}$$

$$\frac{C_V}{Nk} = \frac{5}{2} + \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

$$\begin{aligned} \frac{S}{Nk} = \ln \left[ \frac{2\pi(m_1 + m_2)kT}{h^2} \right]^{3/2} \frac{Ve^{5/2}}{N} + \ln \frac{8\pi^2 I k T e}{\sigma h^2} \\ + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln(1 - e^{-h\nu/kT}) + \ln \omega_{e1} \end{aligned}$$

$$pV = NkT$$

$$\begin{aligned} \frac{\mu^0(T)}{kT} = -\ln \left[ \frac{2\pi(m_1 + m_2)kT}{h^2} \right]^{3/2} kT - \ln \frac{8\pi^2 I k T}{\sigma h^2} + \frac{h\nu}{2kT} \\ + \ln(1 - e^{-h\nu/kT}) - \frac{D_e}{kT} - \ln \omega_{e1} \end{aligned}$$



$$\psi(N_1, N_2, e_1, e_2)$$

$$\rightarrow \psi'(N_2, N_1, e_1, e_2)$$

Fermiones

$$\psi' = -\psi \quad \left. \vphantom{\psi'} \right\} \text{Spin}$$

Para conservar la simetría de la función de onda

\* El momento angular de la molécula se acopla con el espín

$$g(\text{rotacional} + \text{nuclear}) \neq g_{\text{rot}} g_{\text{nuc}}$$

Espin entero

$$g_{\text{rot, nucl}}(\tau) = (I+1)(zI+1) \sum_{j \text{ par}} (zj+1) e^{-\Theta_v j(j+1)/\tau} \\ + I(zI+1) \sum_{j \text{ impar}} (zj+1) e^{-\Theta_v j(j+1)/\tau}$$

Espin semientero

$$g_{\text{rot, nucl}}(\tau) = I(zI+1) \sum_{j \text{ par}} (zj+1) e^{-\Theta_v j(j+1)/\tau}$$

$$(I+1)(zI+1) \sum_{j \text{ impar}} (zj+1) e^{-\Theta_v j(j+1)/\tau}$$

Para  $\Theta_v \ll \tau$

$$\sum_{j \text{ par}} \approx \sum_{j \text{ impar}} \approx \frac{1}{2} \sum_{\text{todo } j} \approx \frac{1}{2} \int_0^{\infty} (zj+1) e^{-\Theta_v j(j+1)/\tau} dj \approx \frac{I}{2\Theta_v}$$

Ademas  $I(zI+1) + (I+1)(zI+1) = (2I+1)^2$

$\frac{\Theta_v}{\tau} \ll 0.2$

Entonces  $g_{\text{rot, nucl}} = \frac{(zI+1)^2 \tau}{2\Theta_v} \rightarrow g_{\text{rot}} = \frac{I}{2\Theta_v} \quad g_{\text{nc}} = (zI+1)^2$



¿Qué pasa si  $\frac{\Theta_r}{T}$  no es tan pequeño?

Caso del Hidrógeno (espín  $1/2$ )

$$q_{\text{rot, nuc}} = \sum_{j \text{ par}} (2j+1) e^{-\Theta_r j(j+1)/T} + 3 \sum_{j \text{ impar}} (2j+1) e^{-\Theta_r j(j+1)/T}$$

*estados para*                      *orto*

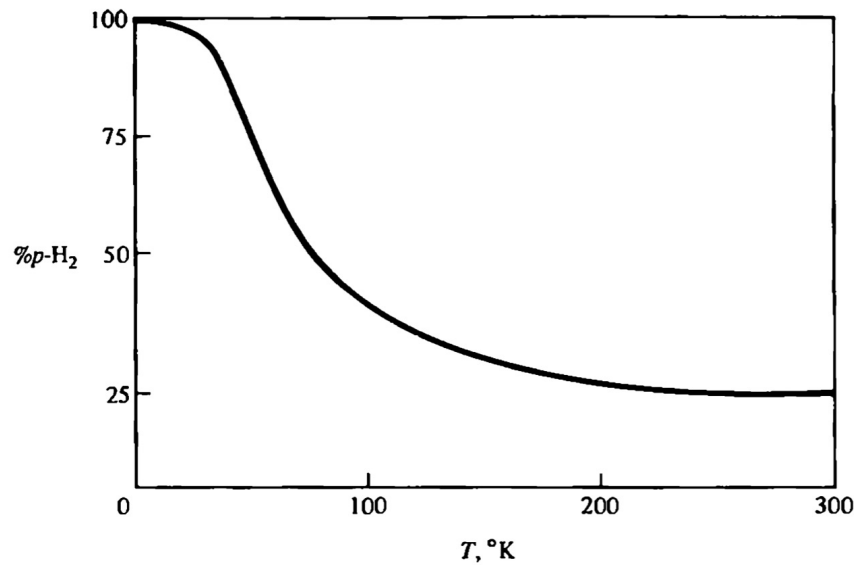


Figure 6-8. The percentage of para-hydrogen in an equilibrium mixture as a function of temperature.