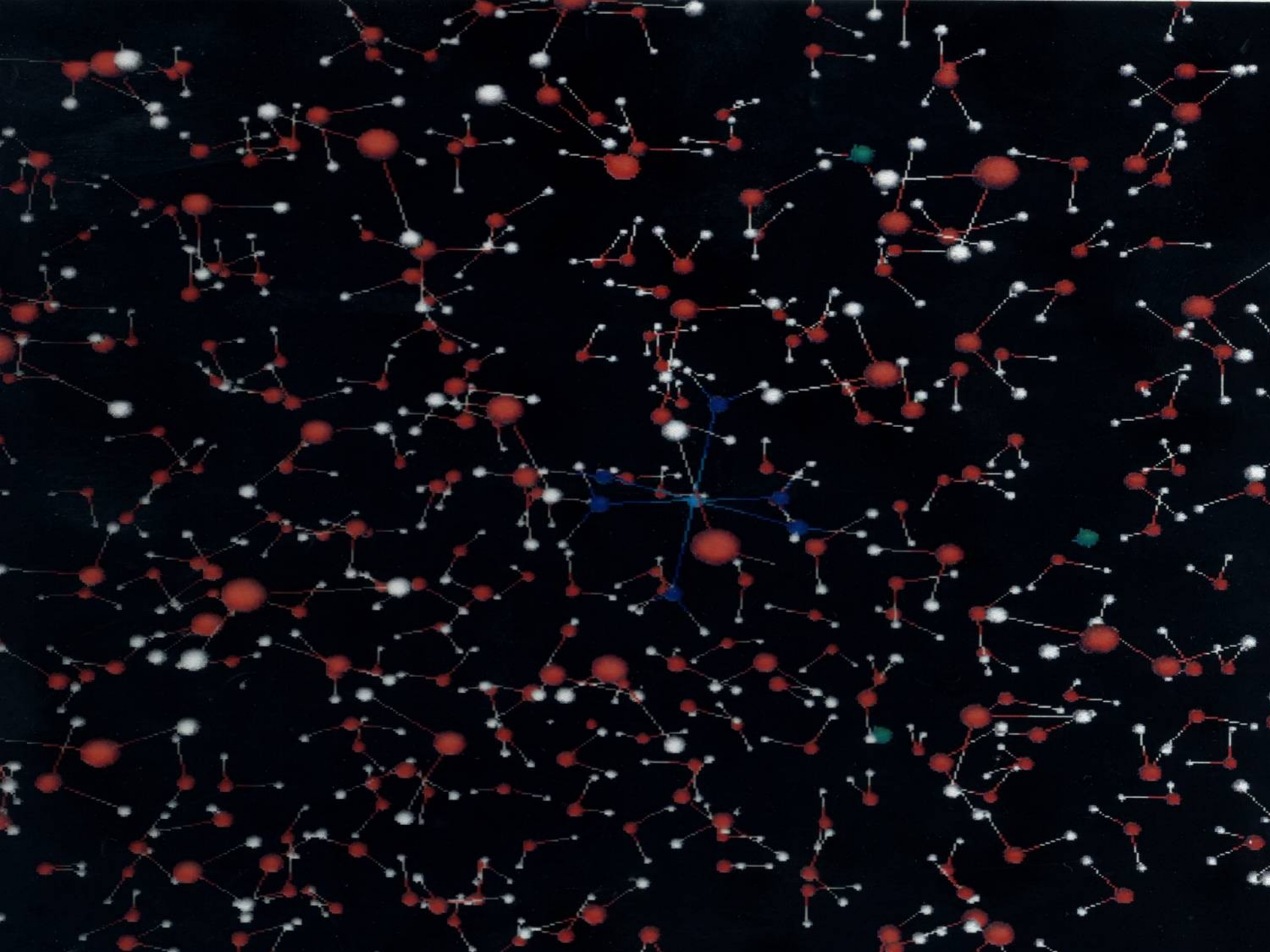
TEMA 6: TERMODINÁMICA ESTADÍSTICA

6.1 Microestados y Configuraciones. Ley de distribución de Boltzmann
6.2 Funciones de partición.
6.3 Funciones de partición moleculares traslacional, rotacional y vibracional
6.4 Equilibrio químico

Bibliografía: *Basic Chemical Thermodynamics* 5ª Ed.
(E. Brian Smith, Imperial College Press, 2005)

- **Mecánica Estadística** es la herramienta teórica con la cual se estudian las propiedades de sistemas macroscópicos, constituidos de muchos átomos o moléculas, y se relacionan con la constitución macroscópica del sistema.

- Una rama de la Mecánica Estadística es la **Termodinámica Estadística** que se ocupa en calcular las funciones termodinámicas de un sistema de una composición dada cuando las fuerzas de interacción entre las moléculas o átomos constituyentes del sistema son conocidas o se presumen cómo son.



Para calcular las propiedades termodinámicas debe deducirse en qué forma se distribuyen las moléculas entre distintos niveles de energía

$$U = \sum_{estados,i} n_i \varepsilon_i$$

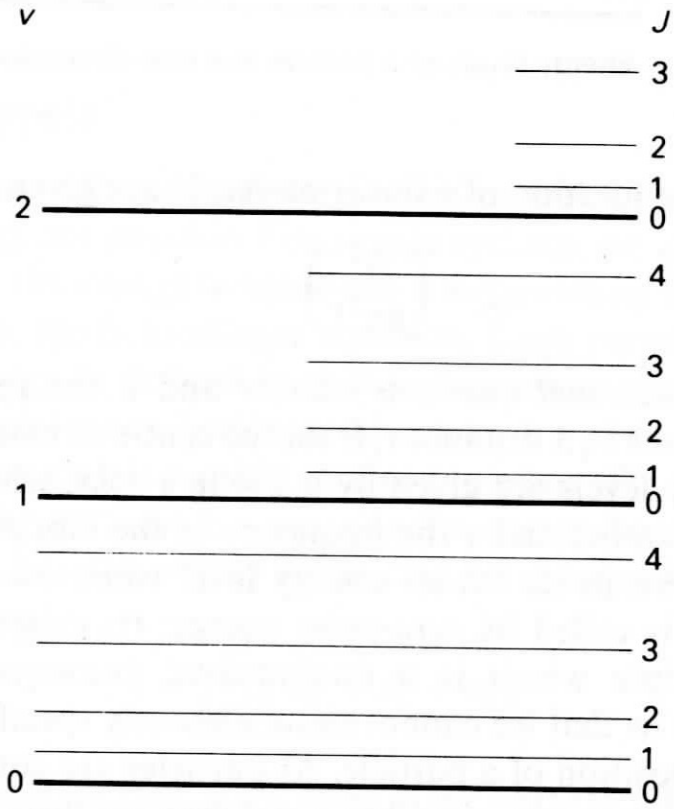
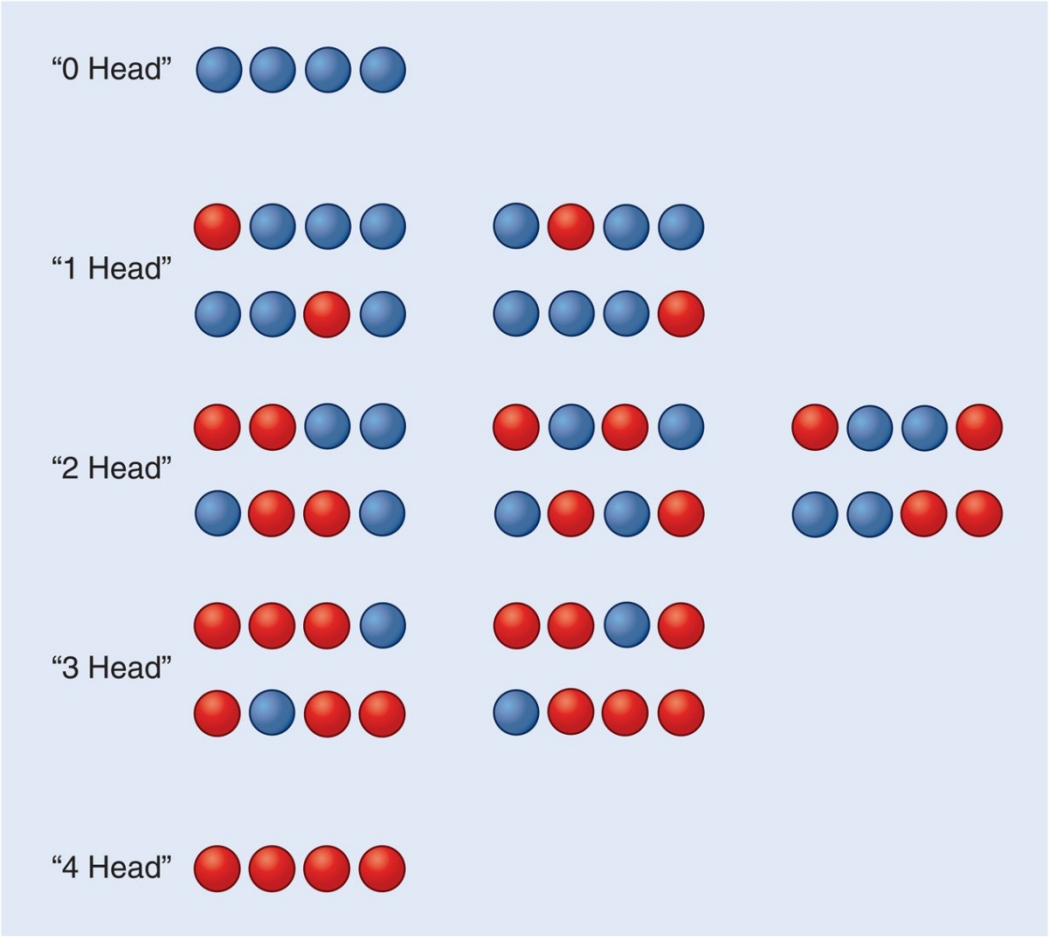


Fig. 9.2. Vibrational and rotational energy levels. *v* and *J* are the vibrational and rotational quantum numbers.

Configuraciones y permutaciones posibles de lanzar una moneda al aire 4 veces



La configuración más probable para un lanzamiento es

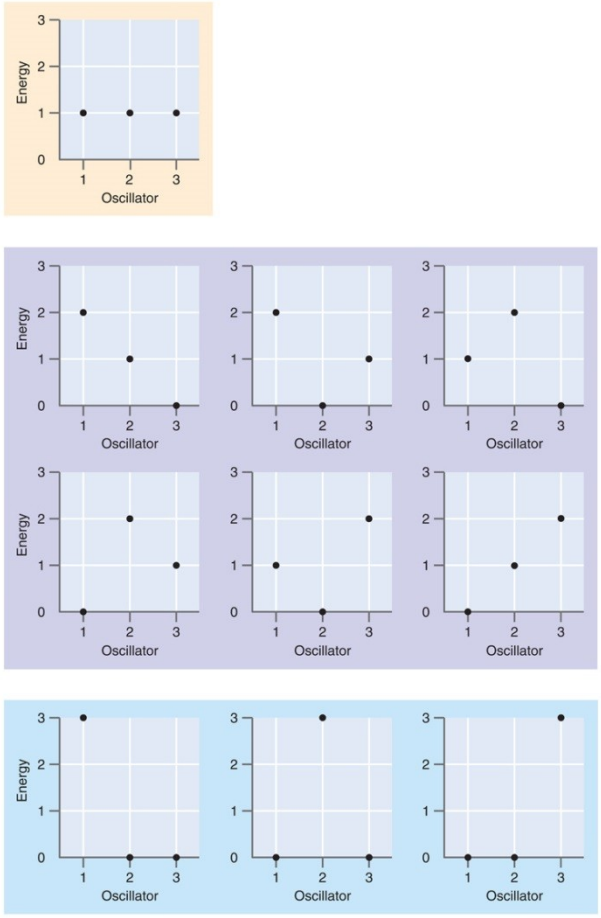
aquélla con el mayor número de permutaciones asociadas

Formas de distribuir 3 moléculas entre 4 niveles de energía de forma que la energía total sea 3

$W_{III} = 1$

$W_{II} = 6$

$W_{I} = 3$



Microestado: forma en la que puede construirse el estado total del sistema a partir de sus elementos constituyentes

Número de microestados asociados a una distribución: $W = \frac{N!}{n_1!\, n_2! \ldots}$

Ley de distribución de Boltzmann

$$\frac{n_i}{n_o} = \frac{g_i}{g_o} e^{-(\varepsilon_i - \varepsilon_o)/kT}$$

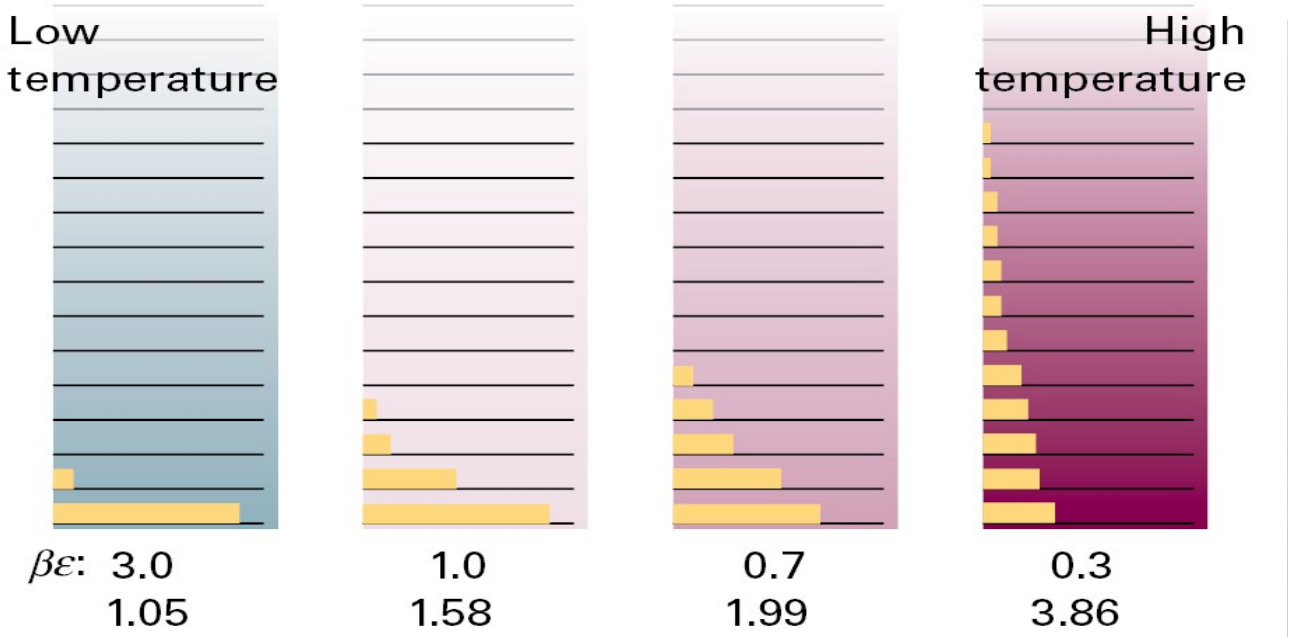


Figure 15B.4 The populations of the energy levels of the system shown in Fig.15B.1 at different temperatures, and the corresponding values of the partition function as calculated from eqn 15B.2b. Note that $\beta = 1/kT$.

Función de partición molecular

$$q = \sum_i e^{-\varepsilon_i/kT} = \sum_i g_i e^{-\varepsilon_i/kT}$$

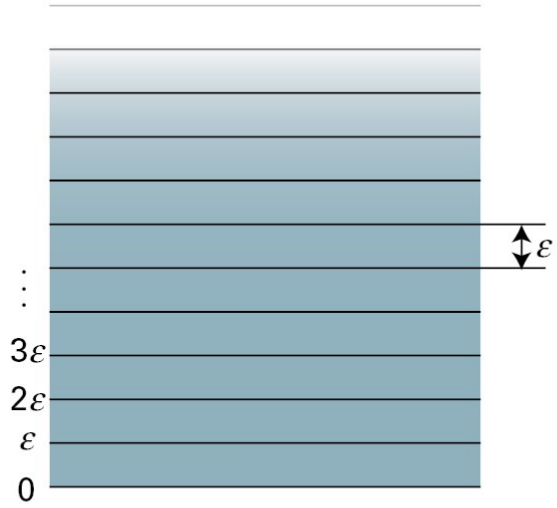


Figure 15B.1 The equally-spaced infinite array of energy levels used in the calculation of the partition function. A harmonic oscillator has the same spectrum of levels.

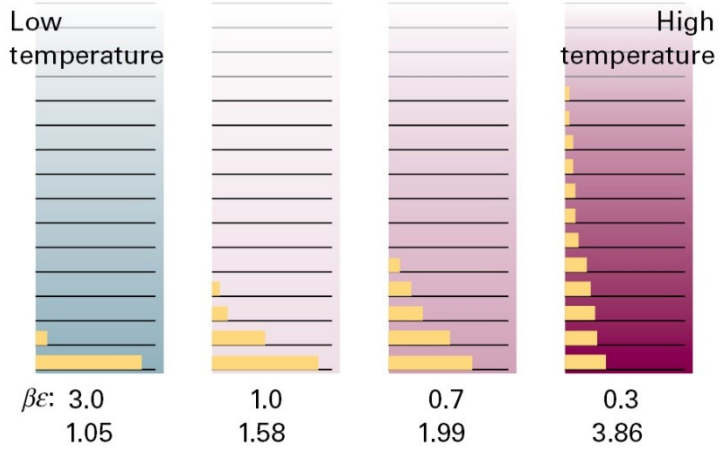


Figure 15B.4 The populations of the energy levels of the system shown in Fig.15B.1 at different temperatures, and the corresponding values of the partition function as calculated from eqn 15B.2b. Note that $\beta = 1/kT$.

Table 9.3 Molar thermodynamic functions in terms of the molecular partition function, z

Solids	Perfect gases
$U = RT^2\left(\frac{\partial \ln z}{\partial T}\right)_V$	$U = RT^2\left(\frac{\partial \ln z}{\partial T}\right)_V$
$S = R\ln z + RT\left(\frac{\partial \ln z}{\partial T}\right)_V$	$S = R\ln z + RT\left(\frac{\partial \ln z}{\partial T}\right)_V - R\ln N_A + R$
$A = U - TS = -RT\ln z$	$A = -RT\ln z + RT\ln N_A - RT$
$P = -\left(\frac{\partial A}{\partial V}\right)_T = RT\left(\frac{\partial \ln z}{\partial V}\right)_T$	$P = RT\left(\frac{\partial \ln z}{\partial V}\right)_T = RT$
$H = U + PV$	$H = RT\left[T\left(\frac{\partial \ln z}{\partial T}\right)_V + V\left(\frac{\partial \ln z}{\partial V}\right)_T\right]$
$= RT\left[T\left(\frac{\partial \ln z}{\partial T}\right)_V + V\left(\frac{\partial \ln z}{\partial V}\right)_T\right]$	$= RT\left[T\left(\frac{\partial \ln z}{\partial V}\right)_V + 1\right]$
$G = H - TS$	$G = -RT\left[\ln z - V\left(\frac{\partial \ln z}{\partial V}\right)_T - \ln N_A + 1\right]$
$= -RT\left[\ln z - V\left(\frac{\partial \ln z}{\partial V}\right)_T\right]$	$= -RT\ln\left(\frac{z}{N_A}\right)$
$C_V = \left(\frac{\partial U}{\partial T}\right)_V = RT\left[2\left(\frac{\partial \ln z}{\partial T}\right)_V + T\left(\frac{\partial^2 \ln z}{\partial T^2}\right)_V\right]$	$C_V = RT\left[2\left(\frac{\partial \ln z}{\partial T}\right)_V + T\left(\frac{\partial^2 \ln z}{\partial T^2}\right)_V\right]$
$\mu_i = -RT\ln(z_i e^{-Y/RT})$	$\mu_i = -RT\ln\left(\frac{z_i}{N_i}\right)$

Función de partición canónica

$$Q = q^N$$

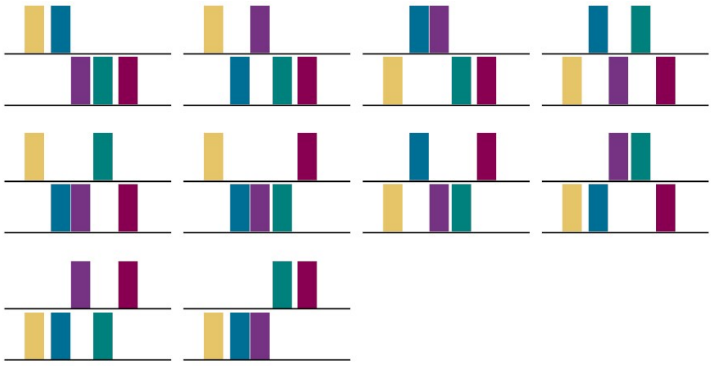


Figure 15A.1 Whereas a configuration {5,0,0,…} can be achieved in only one way, a configuration {3,2,0,…} can be achieved in the ten different ways shown here, where the tinted blocks represent different molecules.

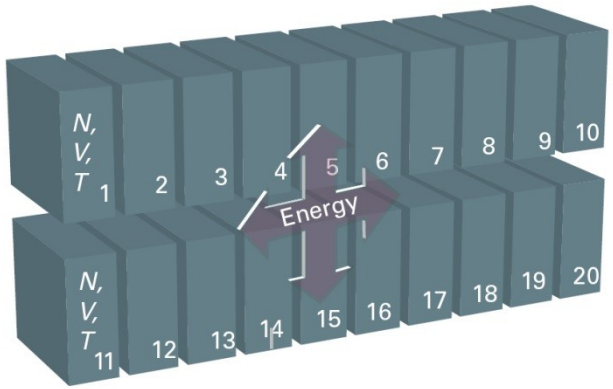
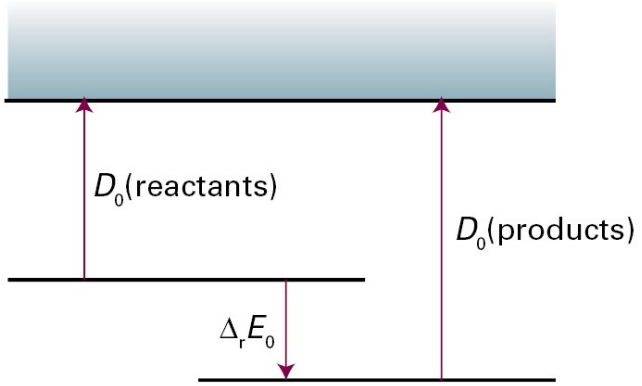


Figure 15D.1 A representation of the canonical ensemble, in this case for $\tilde{N} = 20$. The individual replications of the actual system all have the same composition and volume. They are all in mutual thermal contact, and so all have the same temperature. Energy may be transferred between them as heat, and so they do not all have the same energy. The total $\tilde{E}$ of all 20 replications is a constant because the ensemble is isolated overall.

Equilibrio Químico

$$A \rightleftharpoons B$$



$$K = \frac{n_B}{n_A} = \frac{q_B}{q_A} e^{-\Delta\varepsilon_o / kT}$$

$$= \pi r^2$$

Figure 15F.1 The definition of $\Delta_r E_0$ for the calculation of equilibrium constants.

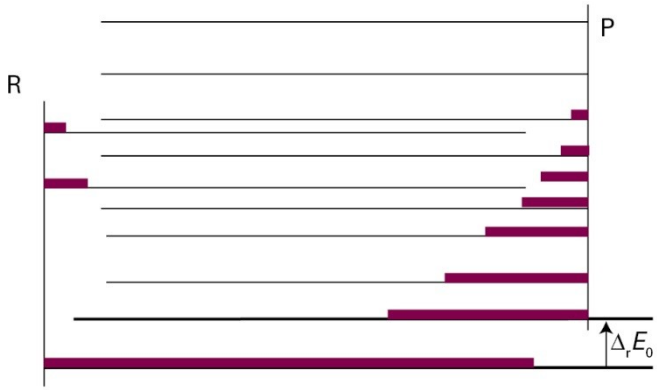


Figure 15F.3 It is important to take into account the densities of states of the molecules. Even though P might lie above R in energy (that is, $\Delta_r E_0$ is positive), P might have so many states that its total population dominates in the mixture. In classical thermodynamic terms, we have to take entropies into account as well as enthalpies when considering equilibria.

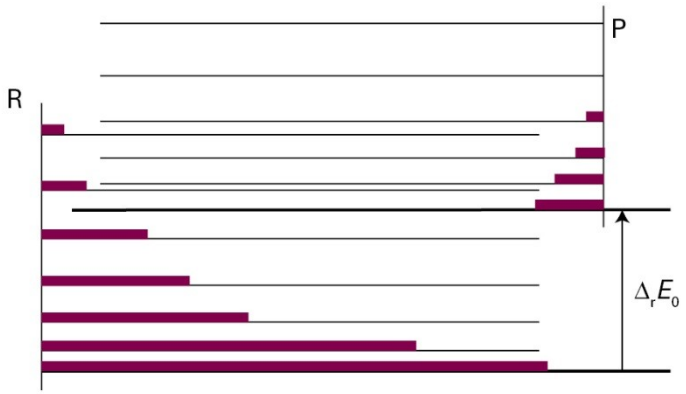


Figure 15F.2 The array of R(eactants) and P(roducts) energy levels. At equilibrium all are accessible (to differing extents, depending on the temperature), and the equilibrium composition of the system reflects the overall Boltzmann distribution of populations. As $\Delta_r E_0$ increases, R becomes dominant.

$$R \rightleftharpoons P$$

R tiene un solo estado accesible, $q_R = 1$
P tiene un conjunto de estados separados por ε, $q_P = \frac{kT}{\varepsilon} e^{-\Delta \varepsilon / kT}$

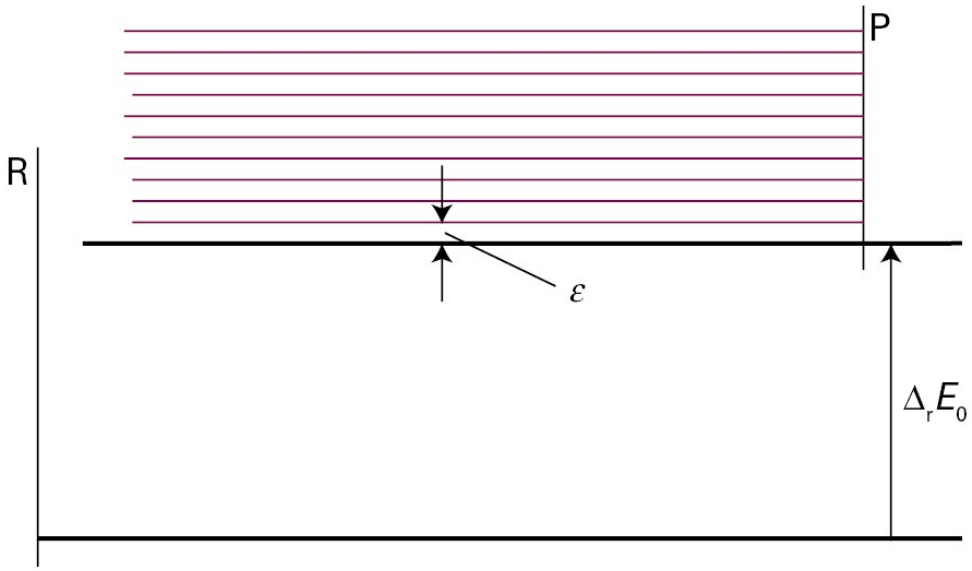


Figure 15F.4 The model used in the text for exploring the effects of energy separations and densities of states on equilibria. The products P can dominate provided $\Delta_r E_0$ is not too large and P has an appreciable density of states.