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Dependence of the Population on the Temperature in the Boltzmann Distribution: A Simple Relation Involving the Average Energy

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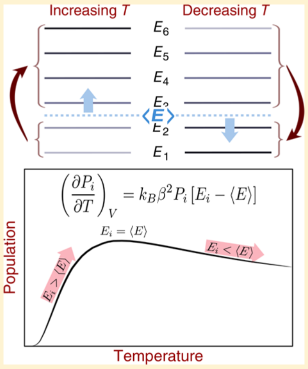
ABSTRACT: The dependence on the temperature of the population of the *i*th state, P_i, in the Boltzmann distribution is analyzed by studying its derivative with respect to the temperature, T. A simple expression is found, involving P_i, the energy of the state, E_i, and the average energy, $\langle E \rangle$. This relation is completely general (it has the same form in all the thermodynamic ensembles), and it has a relevant didactic content, given that it predicts the qualitative variation of P_i with T even in complex systems. The derivation of this relation, the discussion of its properties, and its application to simple problems is appropriate for a statistical thermodynamics course in the chemistry curriculum.



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The Boltzmann distribution plays a central role in university-level statistical thermodynamics courses. Its derivation depends on the thermodynamic ensemble considered and is, in general, attained by maximizing the number of states of the supersystem (the Ω or *W* function, see refs 1−3 for an exhaustive definition) following an approach based on the use of the Lagrange multipliers to take into account the various constraints (which depend on the specific thermodynamic ensemble). This approach is described in most textbooks on this subject (see, for instance, refs 1−4), but alternative approaches have been reported in this journal.[5−14] The reader is referred to the cited books and articles for more details. Here it is worth noting that in statistical thermodynamics in the chemistry curriculum the system under study is usually assumed to have a set of discrete (possibly infinite in number) states and the case of a continuum of states is not treated explicitly. In this paper, we apply the same assumption.

The full derivation of the Boltzmann distribution is not relevant for this paper, and we limit ourselves to report that, for the Canonical statistical ensemble, the fractional number of systems in the *i*th state, P_i, (also known as population or probability of occupation of the *i*th state) with energy E_i is given by

$$P_i = \frac{e^{-\beta E_i}}{Q} \tag{1}$$

where

$$Q = \sum_j e^{-\beta E_j} \tag{2}$$

is the Canonical partition function and

$$\beta = \frac{1}{k_B T} \qquad k_B = \text{Boltzmann constant} \tag{3}$$

The Canonical partition function is then linked to the key quantities of classical thermodynamics (internal energy, U; enthalpy, H; Helmholtz free energy, A; Gibbs free energy, G; entropy S; pressure, p; constant volume heat capacity, C_V; etc.), showing that the knowledge of Q gives access to all of them (see, for instance, refs 1−3). The same approach can be followed for the molecular partition function, q, or for the grand canonical partition function, Ξ.

In such a scheme, the state populations P_i play a central role, given that they describe the properties and the behavior of a system in a simple pictorial way. Consider, for instance, the logical sequence of arguments: if k_BT is much smaller than the energy separation between the first and second states of a system then the P_i are not affected by a small change in T, and then also the average energy $\langle E \rangle = \sum_j P_j E_j$ remains unchanged, and the constant volume heat capacity, C_V, is zero (this scheme can be used to explain why $C_V = 0$ for $T = 0$ in the Einstein model of a solid). Another example of the use of the P_i is given by the interpretation of the entropy of a system using the equation

$$S = -k_B \sum_j P_j \log P_j \tag{4}$$

Despite the importance of the state populations P_i, their dependence on T is normally discussed only for the simple two-state model, whereas a simple scheme is missing for more complex systems. In this paper, we address this aspect from a

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general point-of-view and show that the dependence of P_i on T can be described in simple terms.

■ MATHEMATICAL DERIVATION

Starting from eq 1, the derivative of P_i with respect to T at constant volume is

$$\begin{aligned}\left(\frac{\partial P_i}{\partial T}\right)_V &= -k_B\,\beta^2\left(\frac{\partial P_i}{\partial \beta}\right)_V \\ &= -k_B\,\beta^2\left[-\frac{E_i e^{-\beta E_i}}{Q} - \frac{e^{-\beta E_i}}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)_V\right] \\ &= k_B\,\beta^2 P_i\left[E_i + \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V\right]\end{aligned} \tag{5}$$

Equation 5 can be further simplified by remembering that the average energy, $\langle E\rangle$, is related to Q by

$$\langle E\rangle = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V \tag{6}$$

Using this expression, eq 5 becomes

$$\left(\frac{\partial P_i}{\partial T}\right)_V = k_B\,\beta^2 P_i[E_i - \langle E\rangle] \tag{7}$$

If the derivation is performed for the population of a molecular state (for which we use the same symbol, P_i, used for the populations of the macrostates of the canonical ensemble) with energy ε_i, one obtains formally the same equation

$$\left(\frac{\partial P_i}{\partial T}\right)_V = k_B\,\beta^2 P_i[\varepsilon_i - \langle \varepsilon\rangle] \tag{8}$$

where $\langle\varepsilon\rangle$ is the average molecular energy

$$\langle \varepsilon\rangle = -\frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V \tag{9}$$

and q is the molecular partition function. In the following, eq 7 is analyzed, but the same considerations hold also for eq 8.

Equation 7 is a useful relation. Indeed, it identifies three different situations:

- $E_i > \langle E\rangle$: $(\partial P_i/\partial T)_V$ is positive, and therefore P_i increases with T.
- $E_i = \langle E\rangle$: $(\partial P_i/\partial T)_V = 0$, so P_i is stationary with respect to T and has its maximum value.
- $E_i < \langle E\rangle$: the derivative $(\partial P_i/\partial T)_V$ is negative, and therefore P_i decreases if T increases.

It is worth noting that $\langle E\rangle$ is a growing function of T. Indeed, the derivative of $\langle E\rangle$ with respect to T at constant volume is the constant volume heat capacity, C_V, which can be shown to be always positive with simple thermodynamic arguments. In statistical thermodynamics, one can show that

$$\begin{aligned}C_V = \left(\frac{\partial \langle E\rangle}{\partial T}\right)_V &= -k_B\,\beta^2\sum_j E_j\left(\frac{\partial P_j}{\partial \beta}\right)_V \\ &= k_B\,\beta^2[\langle E^2\rangle - \langle E\rangle^2] = k_B\,\beta^2\Delta E^2 > 0\end{aligned} \tag{10}$$

where use has been made of eq 7 for $(\partial P_j/\partial\beta)_V$ and $\Delta E^2 = \langle E^2\rangle - \langle E\rangle^2$ is the variance of the energy, a measure of the dispersion of the energy around its average value.

Such dependence of $\langle E\rangle$ on T, together with the assumption that the energy of the lowest state is taken as 0 (as often done to simplify the equations; see, for instance, ref 2), describes in simple terms the behavior of a system with a set of discrete states upon heating, starting from $T = 0$ (for which $P_0 = 1$ and $P_i = 0\ \forall i \neq 0$):

- For T very close to zero ($k_BT \ll [E_1{-}E_0]$), the only state with energy lower than $\langle E\rangle$ is the lowest state and, therefore, the population of this state decreases as T increases, whereas the populations of all other states increase. In kinetic language, we can say that the increase of T promotes a fraction of the systems from the lowest state to the other states.
- Increasing T up to a certain value, one possibly has $E_1 = \langle E\rangle$: at this temperature P_1 reaches a maximum.
- For the values of T for which $E_1 < \langle E\rangle < E_2$, the populations of states 0 and 1 decrease with T, whereas the populations of the other states increase.
- A similar behavior is shown also for other states: increasing T, the population increases, it possibly reaches a maximum, and then it decreases.

It is worth noting that for systems with a finite number of states, $\langle E\rangle$ reaches a limiting value for $T \to \infty$. (All states have the same population, and the average energy is the arithmetic mean of the energies of the states.) Therefore, for all states higher in energy than this limiting value, P_i is an increasing function of T (the maximum is approached only at the limit $T \to \infty$).

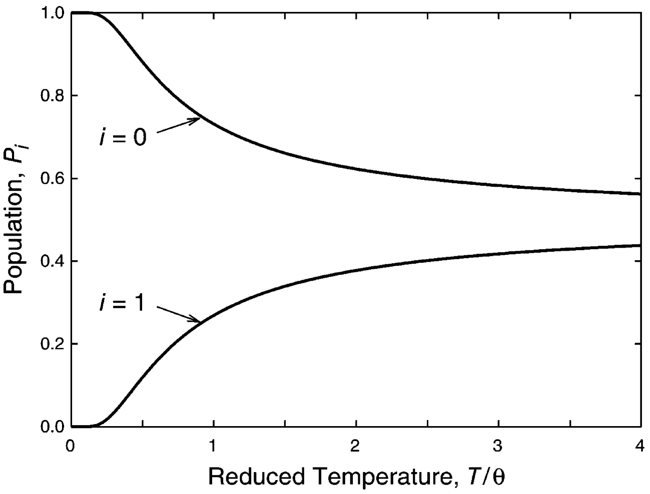

Figure 1. Populations, P_0 and P_1, for the two-state model.

The dependence of P_i on T is often presented for the two-state model, for which the two populations show a monotonic behavior (decreasing for the lowest state and increasing for the highest one, see Figure 1), as can be expected from eq 7 and from the considerations reported in the previous paragraph. (Note that the average energy is always lower than half the energy separation between the two states.) It is worth noting that for a system with three equally spaced states, the P_i are also monotonic functions of T (decreasing for the lowest state and increasing for the other two states), given that $\langle E\rangle$ is always lower than the energy of the second and third states for any finite temperature. From these examples, the students can extend such results to more complex systems, thus supposing that the population of the lowest state is a decreasing function of T, whereas for the other states it is an increasing function of T. In light of the discussion above, this interpretation is not correct and the populations of some states can exhibit a more complex behavior.

Another consideration concerns the derivative of P_i with respect to T for $T = 0$, which is equal to zero for all states. Indeed, note that for $T \to 0$, β^2 goes to ∞ as T^{-2}, whereas the term $P_i[E_i - \langle E \rangle]$ goes to 0 with an exponential decreasing (for the lowest state due to the $E_0 - \langle E \rangle$ term, for the other states due to the P_i term). This has consequences on the classical thermodynamic properties, such as the internal energy, which has a vanishing derivative with respect to T at $T = 0$.

Equation 7 provides the students with a simple interpretative model that can be used to guess the variation of the populations P_i with respect to T, even in complex systems. It expresses a general relation that can be obtained also in the grand canonical ensemble or for the molecular partition function (see eq 8). The meaning of the average energy as well as the "state" energy is obviously dependent on the specific theoretical frame, but expressions 7 and 8 remain valid.

In the next section, the ideas here developed are applied to a few didactically relevant cases.

EXAMPLES OF THE DIDACTIC USE OF EQS 7 AND 8 AND OF THEIR APPLICATION TO MODEL SYSTEMS

Relations shown in eqs 7 and 8 are, in our opinion, interesting from the didactic point of view, given that they link the variation of P_i (with respect to T) with the difference between the energy of the ith state and an "intuitive" quantity, the average energy $\langle E \rangle$, which also has a direct connection with a classical thermodynamics property, the internal energy, U.

Verification that the Constant Volume Heat Capacity is Always Positive

The derivation reported in the previous section concerning the dependence of $\langle E \rangle$ on T (see eq 10) gives us the opportunity to highlight the didactic usefulness of eq 7 with a first example. Indeed, the fact that C_V is always positive, that is, that $\langle E \rangle$ is an increasing function of T, can be presented as a trivial consequence of eq 7, given that under a small variation of T, the populations of all states with energies lower than $\langle E \rangle$ decrease while the populations of all states with energies higher than $\langle E \rangle$ increase, leading to an increase of $\langle E \rangle$. This consideration can provide a simple pictorial representation of the origin of the variation of $\langle E \rangle$ with T.

Harmonic Oscillator

This system is used as a model in the presentation of different topics of statistical thermodynamics (such as, for instance, the Einstein model of a solid and the vibration in molecules), and for this reason, it is relevant to discuss how the populations of the states change with the temperature. This aspect has been ignored in general in the standard didactic program, in our opinion, because a simple approach was missing. This system is in general studied using the molecular partition function, q, which is defined using the energy of a single system (indicated with the symbol ε_i) instead of the energies of a collection of N systems (indicated with E_i) as done in the canonical ensemble. This approach is used also in the following. The use of eq 8 allows a simple discussion of the modification of the populations with T, as shown hereafter.

For this system (an infinite number of equally spaced states with $\varepsilon_{j+1} - \varepsilon_j = \varepsilon$), the molecular partition function, q, and the average energy, $\langle \varepsilon \rangle$, are

$$q = \frac{1}{1 - e^{-\beta\varepsilon}} \tag{11}$$

$$\langle \varepsilon \rangle = \frac{\varepsilon e^{-\beta\varepsilon}}{1 - e^{-\beta\varepsilon}} \tag{12}$$

where it has been assumed that the first state has an energy equal to zero so that $\varepsilon_I = i\varepsilon$ (where $i = 0, 1, 2, ...$). In this case, $\langle \varepsilon \rangle \to \infty$ if $T \to \infty$. Therefore, from eq 8 one can say that all the states of the systems (except the lowest one) have $P_i = 0$ for $T = 0$, and then P_i increases, reaches a maximum, and then goes to zero (for $T \to \infty$ one has $P_i \to 0$ for all states). The lowest state always has an energy lower than $\langle \varepsilon \rangle$ (apart from when $T = 0$, where the two quantities are equal), so its population continuously decreases from 1 for $T = 0$ to 0 for $T \to \infty$.

For the other states, P_i reaches a maximum when $\varepsilon_i = \langle \varepsilon \rangle$, that is

$$\varepsilon_i = i\varepsilon = \frac{\varepsilon e^{-\beta\varepsilon}}{1 - e^{-\beta\varepsilon}} \tag{13}$$

After a few algebraic steps, one eventually obtains that the temperature T_i^*, for which P_i is maximum, is

$$T_i^* = \frac{\varepsilon}{k_B \log\left(\frac{1+i}{i}\right)} \tag{14}$$

At this temperature, the value of P_i is

$$P_i(T_i^*) = \frac{1}{1+i}\left(\frac{i}{1+i}\right)^i \tag{15}$$

A pictorial representation of the dependence of P_i on T for the first four states of the harmonic oscillator is shown in Figure 2 (left scale), together with the dependence of $\langle \varepsilon \rangle$ on T (right

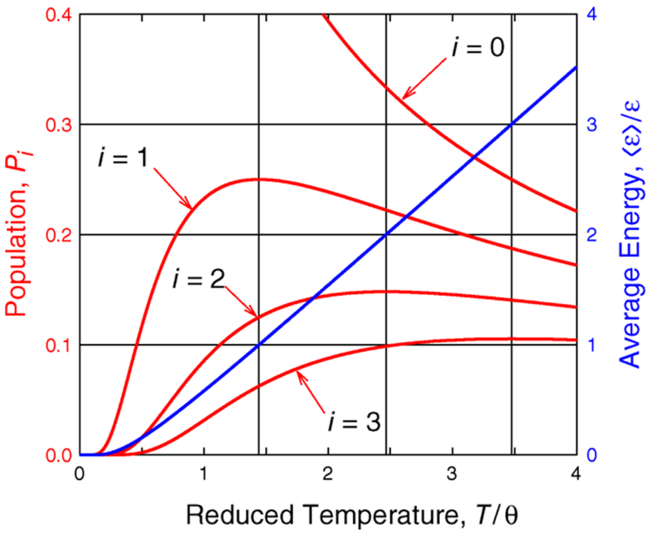

Figure 2. Populations of the first four states (red lines, left scale) and reduced average energy ($\langle \varepsilon \rangle/\varepsilon$, blue line, right scale) of the harmonic oscillator as a function of the reduced temperature T/θ. Vertical black lines are at T/θ = 1.4427, 2.4663, and 3.4761 (the values for which one of the P_i is maximum, see eq 14). The horizontal black lines are at $\langle \varepsilon \rangle/\varepsilon$ = 1, 2, and 3.

scale). In this figure, use has been made of the reduced temperature (T is expressed in units of $\theta = \varepsilon/k_B$, and the energies are expressed in units of ε). To facilitate the reading of this graphical representation, three horizontal lines (corresponding to $\langle\varepsilon\rangle/\varepsilon$ = 1, 2, and 3) and three vertical lines {corresponding to $T/\theta = [\log(2)]^{-1}$, $[\log(3/2)]^{-1}$, and $[\log(4/3)]^{-1}$} have been added. Although the population of the first state is always decreasing, the other three states present a maximum for the values of T/θ for which the average energy is equal to the energy of the state.

System of n + 1 Equally Spaced States

The model of a finite set of equally spaced states is perhaps less central in the course of statistical thermodynamics than the harmonic oscillator, nevertheless, it is used, for example, to discuss the coupling of a magnetic moment due to a spin (nuclear or electronic) with a magnetic field.

Here, we consider a model system with a finite number, n + 1, of equally spaced states (ε is the energy difference between two successive states). The energies of the states are $\varepsilon_j = i\varepsilon$, for $0 \leq i \leq n$.

In this system, the molecular partition function is

$$q = \frac{1 - e^{-\beta\varepsilon(n+1)}}{1 - e^{-\beta\varepsilon}} \tag{16}$$

and the average energy can be written in the form

$$\begin{aligned}\langle\varepsilon\rangle &= \langle\varepsilon^{\text{harm}}\rangle\left[1 - \frac{(n+1)e^{-\beta\varepsilon n}}{q}\right]\\ &= \langle\varepsilon^{\text{harm}}\rangle[1 - (n+1)P_n]\end{aligned} \tag{17}$$

where $\langle\varepsilon^{\text{harm}}\rangle$ is the average energy of the harmonic oscillator (defined in eq 12). From eq 17 one gets the following limits:

- $\lim_{T\to\infty} q = n + 1$;
- $\lim_{n\to\infty} \langle\varepsilon\rangle = \langle\varepsilon^{\text{harm}}\rangle$ (for any finite value of T, P_n goes exponentially to zero when n goes to infinity);
- $\lim_{T\to\infty} \langle\varepsilon\rangle = [(n\varepsilon)/2]$

In this case, one cannot obtain the analytic expression for the temperatures at which the P_i are maximized, but these values can be computed numerically. We have considered, for instance, the cases of 5 and 10 equally spaced levels. The dependence of the populations of the first four states and of $\langle\varepsilon\rangle/\varepsilon$ on T/θ is displayed in Figures 3 and 4. In Table 1, we report the values of T/θ for which P_i is maximum and the corresponding value of P_i (T^*/θ and P^*, respectively) for the two cases n + 1 = 5 and n + 1 = 10, as well as for the harmonic oscillator for the sake of comparison. The dependence on T of the state populations is clearly different from that observed for the harmonic oscillator. These differences can easily be understood using eq 8. Indeed, from Figures 2, 3, and 4, one clearly notes that the increase of average energy with T is less pronounced in the cases of a finite number of states than for the harmonic oscillator. For this reason, the values of T for which $\langle\varepsilon\rangle$ is equal to ε_i are higher for a finite number of states than for the harmonic oscillator. This displacement is more and more pronounced as n decreases. Moreover, with a finite number of states, the average energy tends to a limiting value when $T \to \infty$: in the present case $\lim_{T\to\infty} \langle\varepsilon\rangle/\varepsilon$ = 2.0 and 4.5 for n + 1 = 5 and 10, respectively. For this reason, P_i has a maximum for only one state for the system with n + 1 = 5 and for four states for the system with n + 1 = 10.

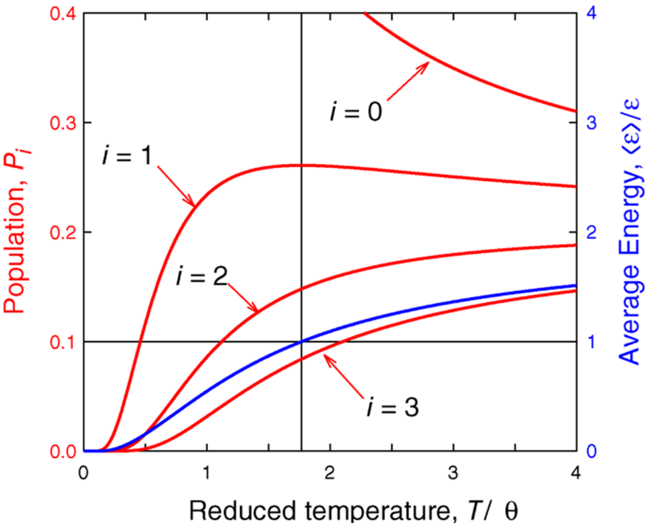

Figure 3. Populations of the first four states (red lines, left scale) and reduced average energy [$\langle\varepsilon\rangle/\varepsilon$, blue line, right scale] for a system of five equally spaced levels as a function of the reduced temperature T/θ. The vertical black line is at T/θ = 1.7665 (the value for which P_1 is maximum). The horizontal black line is at $\langle\varepsilon\rangle/\varepsilon$ = 1.

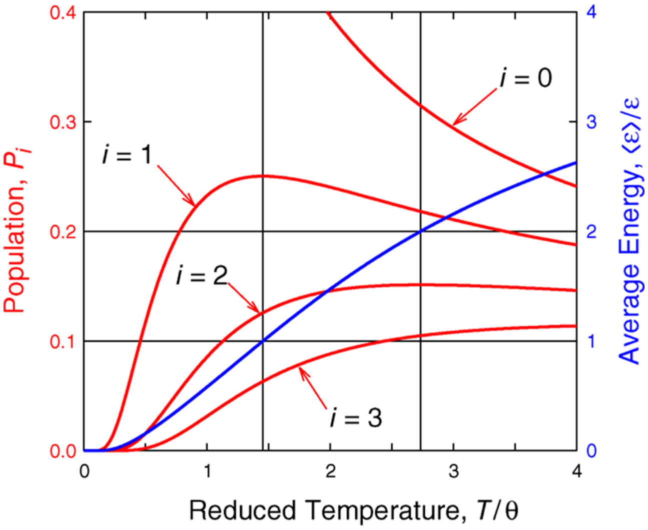

Figure 4. Populations of the first four states (red lines, left scale) and reduced average energy [$\langle\varepsilon\rangle/\varepsilon$, blue line, right scale] for a system of ten equally spaced levels as a function of the reduced temperature T/θ. The vertical black lines are at T/θ = 1.4534 and 2.7345 (the values for which P_1 and P_2 are maximum, respectively). The horizontal black lines are at $\langle\varepsilon\rangle/\varepsilon$ = 1 and 2.

Maxwell–Boltzmann Distribution of Speed

Let us consider the Maxwell–Boltzmann distribution of speed, v,

$$f(v) = \sqrt{\left(\frac{m\beta}{2\pi}\right)^3}\, 4\pi v^2 e^{(-\beta m v^2/2)} \tag{18}$$

This equation is usually commented upon by using a pictorial representation in which $f(v)$ is shown as a function of v at various temperatures, highlighting that the curves have a maximum for $v = (2/\beta m)^{1/2}$. By increasing T, the maximum appears therefore at higher values of v: it is lower and the curve is broader. From the comparison of the curves at two different temperatures, T_1 and T_2, one notes that for some speeds, $f(v)$ is

Table 1. Values of T/θ (T^*/θ) for which the Population Reaches a Maximum (P^*) for the Lowest States of the Systems with 5 and 10 Equally Spaced Levels and for the Harmonic Oscillator

i	5 states[a]		10 states[a]		harmonic oscillator	
	T^*/θ	P^*	T^*/θ	P^*	T^*/θ	P^*
1	1.7665	0.2608	1.4534	0.2503	1.4427	0.2500
2			2.7345	0.1513	2.4663	0.1481
3			5.1834	0.1151	3.4761	0.1055
4			16.3976	0.1015	4.4814	0.0819
5					5.4848	0.0670
6					6.4872	0.0567
7					7.4889	0.0491
8					8.4902	0.0433
9					9.4912	0.0387

[a] When the values are not reported, the population shows a monotonic increase as a function of T (without a maximum).

lower at T_1 than at T_2 and that for other speeds the contrary happens. How can this be explained? To face this point, let us consider a simple didactical problem.

Consider an infinitesimal change in the temperature from T to $T + \delta T$. For which speeds will $f(v)$ decrease, and for which will it increase? This problem can be solved by setting the derivative of $f(v)$ with respect to T equal to zero, eventually obtaining after some algebraic steps, that for v lower than $(3/\beta m)^{1/2}$, $f(v)$ decreases, while for higher values, $f(v)$ increases. The quantity $(3/\beta m)^{1/2}$ is also known as the root-mean-squared speed.

On the other hand, this result can be trivially obtained using eq 8 (one can easily verify that this equation is valid also for a continuous distribution of the energies if the concept of the "population" of a state with a given energy is changed to that of "density of particles" with that energy). Note that in this problem, $f(v)$ plays the role of the populations in the case of discrete states. The translational average energy is $\langle\varepsilon\rangle = [3/(2\beta)]$, while the kinetic energy of a particle is $\varepsilon = mv^2/2$. The equality $\varepsilon = \langle\varepsilon\rangle$, which following eq 8 equals to zero the derivative of the density of particles with respect to the temperature, is valid for $v = (3/\beta m)^{1/2}$. This derivation also clarifies why the root-mean-squared speed is the required quantity: it is the speed for which the kinetic energy is equal to the average energy and it is another important value to be discussed along with the most probable speed, $v_p = (2/\beta m)^{1/2}$, and the mean speed, $v = (8/\pi\beta m)^{1/2}$.

Dependence on *T* of the Rotational Structure of the Vibrational Spectrum of Diatomic Molecules

Another important subject in the chemistry curriculum is considered: the rotational structure of the vibrational spectrum of diatomic molecules. In the classroom, the problem is usually discussed by showing a graphical representation in which the intensities of the bands in the P- and R-branches are reported for a given temperature. In such a problem, after a set of approximations (see ref 15, chapter III for a complete discussion), the band intensities are proportional to the population of the rotational level with quantum number J in the starting state, which, in turn, is proportional to $(2J + 1)$ $e^{-\beta J(J+1)hcB}$ (where B is the rotational constant and c the speed of light).

Also in this case, in our opinion, it is relevant to discuss how the rotational structure of the spectrum changes upon a modification of the temperature, with particular attention to the bands that are expected to be less intense after a small modification of the temperature and to those that, on the contrary, will be more intense. The discussion can be simplified (gaining in the conceptual comprehension of the problem), if the rotational level can be considered dense with respect to the thermal energy β^{-1} so that J can be considered as a continuous variable. As in the case of the Maxwell−Boltzmann distribution of the speed, one can proceed by setting the derivative of the population with respect to T equal to zero, but the same result can be obtained trivially from eq 8 by setting the energy of the J level, $J(J + 1)hcB$, equal to the average energy for a rigid rotator, which, with the approximations here considered, is $\langle\varepsilon\rangle = \beta^{-1}$, thus obtaining

$$J(J+1) = \frac{1}{\beta hcB} \tag{19}$$

This equation can be further simplified for large J, obtaining

$$J = \sqrt{\frac{1}{\beta hcB}} \tag{20}$$

Therefore for J lower than $(\beta hcB)^{-1/2}$, the band intensity will reduce and the opposite will happen for higher J. A simulation of the spectrum of two diatomic molecules at three different temperatures is reported at page 126 of Herzberg's book (ref 15): the reported spectra can be intuitively discussed using the logic here reported. Other more complex examples in which the populations of the rotational states are discussed can be found in literature, for instance ref 16 (see Figure 2).

Dependence on *T* of the Isomer Concentrations for an Isomeric Equilibrium

Consider a molecule with two isomers A and B that are in equilibrium

$$A \rightleftarrows B$$

This problem is treated in most textbooks of statistical thermodynamics. The full set of states of the molecule can be divided in two subsets, those indicated with the index i_A (i_B) describing isomer A (B), so that

$$\sum_{i_A} P_{i_A} + \sum_{i_B} P_{i_B} = 1 \tag{21}$$

The numbers of isomers A and B, N_A and N_B, are

$$N_A = N \sum_{i_A} P_{i_A} \qquad N_B = N \sum_{i_B} P_{i_B} \tag{22}$$

Now consider the derivative of N_A with respect to T at constant V,

$$\left(\frac{\partial N_A}{\partial T}\right)_V = N \sum_{i_A} \left(\frac{\partial P_{i_A}}{\partial T}\right)_V = N k_B \beta^2 \sum_{i_A} P_{i_A}[\varepsilon_{i_A} - \langle\varepsilon\rangle]$$
$$= k_B \beta^2 N_A[\langle\varepsilon_A\rangle - \langle\varepsilon\rangle] \tag{23}$$

where use has been made of eq 8 and $\langle\varepsilon_A\rangle$ is the average energy of the A isomer

$$\langle\varepsilon_A\rangle = \frac{N}{N_A} \sum_{i_A} P_{i_A}\varepsilon_{i_A} \tag{24}$$

By noticing that

$$\langle \varepsilon \rangle = \frac{N_A\langle \varepsilon_A \rangle + N_B\langle \varepsilon_B \rangle}{N_A + N_B} \tag{25}$$

($\langle \varepsilon_B \rangle$ is defined analogously to $\langle \varepsilon_A \rangle$), one eventually has

$$\left(\frac{\partial N_A}{\partial T}\right)_V = \frac{N_A N_B}{N} k_B \beta^2 [\langle \varepsilon_A \rangle - \langle \varepsilon_B \rangle] \tag{26}$$

This equation can be used to qualitatively discuss the variation of N_A and N_B as a function of temperature. It is worth noticing that in this approach the energies of the two isomers are measured from a common zero.

Suppose that A has the lowest ground-state energy (the reaction A → B is endothermic): at low T, the average energy $\langle \varepsilon_A \rangle$ is lower than $\langle \varepsilon_B \rangle$ and the derivative in eq 26 is negative, thus N_A is a decreasing function of T. By increasing T, both $\langle \varepsilon_A \rangle$ and $\langle \varepsilon_B \rangle$ increase and, in general, the energy inequality $\langle \varepsilon_A \rangle < \langle \varepsilon_B \rangle$ remains valid (note that the translational contribution to the average energy is the same for the two isomers, therefore only the internal degrees of freedom have a differential effect). In this situation, N_A continuously decreases as T increases. Obviously, the contrary happens for N_B. However, one can imagine that for some particular cases, $\langle \varepsilon_A \rangle$ can grow upon heating faster than $\langle \varepsilon_B \rangle$, so that for a given T^*, one eventually has $\langle \varepsilon_A \rangle = \langle \varepsilon_B \rangle$ and for higher temperatures, $\langle \varepsilon_A \rangle > \langle \varepsilon_B \rangle$. In such a situation, N_A will show a minimum (N_B a maximum) for $T = T^*$. This behavior, even if not common, has been found in studies concerning the relative stability of fullerene isomers as a function of T.[17−19] When more than two isomers are considered in the equilibrium, a generalization of eq 26 must be used

$$\left(\frac{\partial N_A}{\partial T}\right)_V = \frac{N_A}{N} k_B \beta^2 \sum_{I \neq A} N_I [\langle \varepsilon_A \rangle - \langle \varepsilon_I \rangle] \tag{27}$$

At the end of this section, it is worth noticing that the dependence of P_i on T in all the systems considered here can be fully accounted for (both qualitatively and quantitatively) by the strategy developed in the Mathematical Derivation. The didactic effectiveness of eqs 7 and 8, in particular, is borne out by the simplification it brings to the analysis of the qualitative behavior of P_i, as well as by the possibility to have a simple model accounting for the complex behavior of the system under study.

■ CONCLUSION

We have presented the derivation of a simple equation relating the energy difference $E_i - \langle E \rangle$ (the energy of a given state i minus the average energy) to the derivative of the population of the ith state (P_i) with respect to the temperature. Such a relation, in the authors' opinion, has a relevant didactic content, as has been shown by the examples discussed here. The dependence of P_i on T can be simple (monotonic increase or decrease) or more complex (a first part in which P_i increases with T and a second part where P_i decreases with T). This behavior may appear counterintuitive for the students if the dependence of P_i on T is discussed only for simple models (such as the two-state model). We suggest including this derivation and some simple applications in the statistical thermodynamics courses just after the derivation of the equation that relates $\langle E \rangle$ to the partition function.

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Notes

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