

Chapter 15.

Statistical Thermodynamics:

The Concepts

Quantum Mechanics: Detailed arrangement, motion and energy of atoms and/or electrons.

Thermodynamics: The average behavior [*Equilibrium = Reversible*]

Statistical Thermodynamics = Statistical Physics:

Thermodynamics expressed

in terms of molecular properties.

15A. Boltzmann Distribution (Molecular Energy Levels)

Energy levels: $\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots$ [Fixed at the Given Volume]

Number of molecules: n_1, n_2, n_3, \dots [Independent Molecules]

Configuration of the systems: the specification of the set of
populations n_1, n_2, \dots

e.g. i) $n_1 = N, n_2 = 0, n_3 = 0 \dots \Rightarrow$ only in one way

ii) $n_1 = N - 2, n_2 = 2, n_3 = 0 \dots \Rightarrow$ more likely to occur

↓
 $\frac{1}{2}N(N-1)$ different ways of forming it

A general configuration $\{n_1, n_2, \dots\}$ can be achieved in W different ways, called its weight, where

$$W(n_1, n_2, \dots) = \frac{N!}{n_1! n_2! n_3! \dots}$$

Question: Is there, in fact, a **configuration** with so great a weight that it so overwhelms all the rest **in importance**

that there is **negligible error** in supposing that the system will always be found in it, and that the system will display properties characteristic of that configuration to the **virtual exclusion** of all others?

W Different Ways

For $\{1, 1, 1, \dots\} \Rightarrow W = N!$: the maximum value = for IQ 50

The feature missing from the discussion so far is the fact that many configurations conflict with the specified **total energy** of the system. For instance, the configurations such as $\{N, 0, 0, \dots\}$, $\{N-2, 2, 0, \dots\}$ and $\{1, 1, 1, \dots\}$, among numerous others, may be inadmissible because they cannot be achieved with the specified total energy.

Total energy criterion: $\sum_i n_i \varepsilon_i = E$ *No Free Lunch*

E = the total energy of the system

Another constraint: the total number of molecules present in the system is fixed.

Total number criterion: $\sum_i n_i = N$

The maximum value of W can be found by varying the n_i and looking for the values for which $dW = 0$.

$$W = f(n_i)$$

$$d(\ln W) = \sum_i \frac{\partial \ln W}{\partial n_i} dn_i$$

W different ways

E, N : constant

$$\sum_i \varepsilon_i dn_i = 0$$

Total energy criterion

$$\sum_i dn_i = 0$$

Total number criterion

Method of undetermined multipliers:

Lagrangian (undetermined multipliers)

A constraint should be multiplied by **some constant** and then added to the main variation equation.

$$\begin{aligned} d(\ln W) &= \sum_i \left(\frac{\partial \ln W}{\partial n_i} \right) dn_i + \alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i \\ &= \sum_i \left\{ \frac{\partial \ln W}{\partial n_i} + \alpha - \beta \varepsilon_i \right\} dn_i \end{aligned}$$

All the dn_i are now treated as independent. Hence the only way of satisfying $d \ln W = 0$ is to require that, for each i ,

$$\left(\frac{\partial \ln W}{\partial n_i} \right) + \alpha - \beta \varepsilon_i = 0$$

for the n_i taking their most probable values n_i^* .

Stirling's Approximation

For large x , $\ln x! \approx x \ln x - x$

$$\begin{aligned}\ln W &= \ln \left(\frac{N!}{n_1! n_2! n_3! \dots} \right) \\ &= \ln N! - \ln(n_1! n_2! n_3! \dots) \\ &= \ln N! - \sum_j \ln n_j! \cong (N \ln N - N) - \sum_j (n_j \ln n_j! - n_j) \\ &= N \ln N - \sum_j n_j \ln n_j \quad \left(\because N = \sum_j n_j \right)\end{aligned}$$

Differentiation with respect to n_i gives

$$\left(\frac{\partial \ln W}{\partial n_i} \right) = \frac{\partial (N \ln N)}{\partial n_i} - \sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i}$$

$$\begin{aligned}
\frac{\partial(N \ln N)}{\partial n_i} &= \left(\frac{\partial N}{\partial n_i} \right) \ln N + N \left(\frac{\partial \ln N}{\partial n_i} \right) \\
&= \left(\frac{\partial N}{\partial n_i} \right) \ln N + N \frac{1}{N} \frac{\partial N}{\partial n_i} \\
&= \left(\frac{\partial N}{\partial n_i} \right) \ln N + \frac{\partial N}{\partial n_i} = \ln N + 1 \\
&(\because N = n_1 + n_2 + n_3 + \dots)
\end{aligned}$$

$$\begin{aligned}
\sum_j \frac{\partial(n_j \ln n_j)}{\partial n_i} &= \sum_j \left\{ \left(\frac{\partial n_j}{\partial n_i} \right) \ln n_j + n_j \left(\frac{\partial \ln n_j}{\partial n_i} \right) \right\} \\
&= \sum_j \left(\frac{\partial n_j}{\partial n_i} \right) (\ln n_j + 1) \\
&= \ln n_i + 1
\end{aligned}$$

for $i \neq j$

$$\frac{\partial n_j}{\partial n_i} = 0$$

for $i = j$

$$\frac{\partial n_j}{\partial n_i} = \frac{\partial n_j}{\partial n_j} = 1$$

$$\therefore \frac{\partial \ln W}{\partial n_i} = -(\ln n_i + 1) + (\ln N + 1) = -\ln\left(\frac{n_i}{N}\right)$$

$$\therefore -\ln\left(\frac{n_i}{N}\right) + \alpha - \beta\varepsilon_i = 0$$

$$\frac{n_i^*}{N} = e^{\alpha - \beta\varepsilon_i}$$

The final step is to find the values of α and β .

$$N = \sum_i n_i^* = N e^{\alpha} \sum_i e^{-\beta\varepsilon_i}$$

$$\therefore e^{\alpha} = \frac{1}{\sum_i e^{-\beta\varepsilon_i}}$$

Hence we arrive at the form of **Boltzmann distribution:**

$$\frac{n_i^*}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}}$$

(15A.6a)

15A.1(b). The Molecular Partition Function

Molecular partition function: $q \equiv \sum_i \exp(-\beta\varepsilon_i)$ *Definition*

If the energy e_j arises from g_j different states (that is, the energy level is g_j -fold degenerate), there are g_j terms in sum all with the value $\exp(-\beta\varepsilon_j)$.

$$q = \sum_j g_j \exp(-\beta\varepsilon_j)$$

$$\frac{n_i^*}{N} = \frac{e^{-\beta\varepsilon_i}}{q}$$

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$$E = \sum_i n_i \varepsilon_i = \sum_i n_i^* \varepsilon_i$$

$$E = \frac{N}{q} \sum_i \varepsilon_i \exp(-\beta\varepsilon_i)$$

$$\frac{d}{d\beta} \exp(-\beta\varepsilon_i) = -\varepsilon_i \exp(-\beta\varepsilon_i)$$

$$\begin{aligned} \therefore E &= \frac{N}{q} \sum_i \left(-\frac{d}{d\beta} \exp(-\beta\varepsilon_i) \right) = -\frac{N}{q} \frac{d}{d\beta} \sum_i \exp(-\beta\varepsilon_i) \\ &= -\left(\frac{N}{q} \right) \left(\frac{dq}{d\beta} \right) \end{aligned}$$

$$U = U(0) + E$$

*Fixed Volume
Independent Molecules*

$$\underline{U - U(0)} = -\left(\frac{N}{q} \right) \left(\frac{\partial q}{\partial \beta} \right)_V = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V = \sum_i n_i^* \varepsilon_i \quad (15C.3)$$

This equation confirms that we need to know only the **molecular partition function** in order to calculate the internal energy.

[Entropy later
in Chap. 15]

15B. An Interpretation of Molecular Partition Function

$$\beta = \frac{1}{kT}$$

$$q = \sum_i e^{-\beta\varepsilon_i} \rightarrow 0 \quad T \rightarrow 0 \text{ K} \quad \text{except one term } (\varepsilon_1 \equiv 0)$$

$$\therefore \text{ at } \underline{T = 0 \text{ K}}, \quad q = 1 \quad (\text{or } q = g_0)$$

At the other extreme, consider the case when T is so large that for every term in the sum

$$\varepsilon_i / kT \rightarrow 0$$

Since $e^{-x} = 1$ when $x = 0$, every term in the sum then contributes to the value 1.

In general, as $\underline{T \rightarrow \infty, q \rightarrow \infty.}$

Partition function gives an **indication** of the number of states that are **thermally accessible** to the system at the given temperature.

At absolute zero, only the ground state is available, and $q = 1$.

At the highest temperatures, **virtually all the states are thermally accessible**, and so q approaches infinity.

Example:

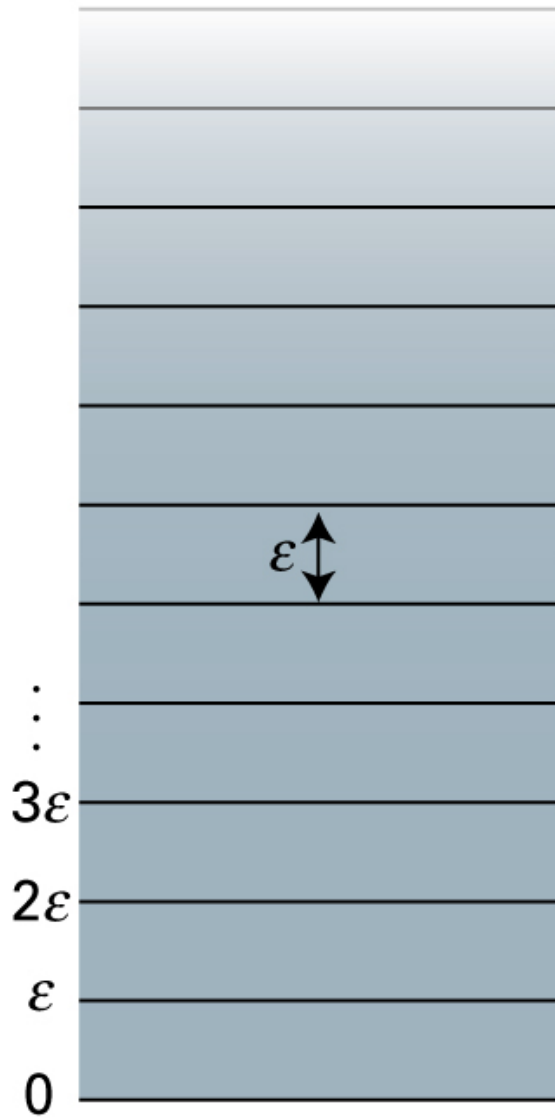


Fig. 15B.1 Harmonic Oscillator

The array of molecular energy levels used to calculate the molecular partition function.

Partition Function for a Harmonic Oscillator

$$\begin{aligned} q &= 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + \dots \\ &= 1 + e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 + \dots \\ &= (1 - e^{-\beta\varepsilon})^{-1} \end{aligned} \quad \left| \quad (1-x)^{-1} = 1 + x + x^2 + \dots$$

The proportion (P_j) of molecules in the state with energy e_j

$$P_j = \frac{n_j^*}{N} = (1 - e^{-\beta\varepsilon})^{-1} e^{-\beta\varepsilon_j}$$

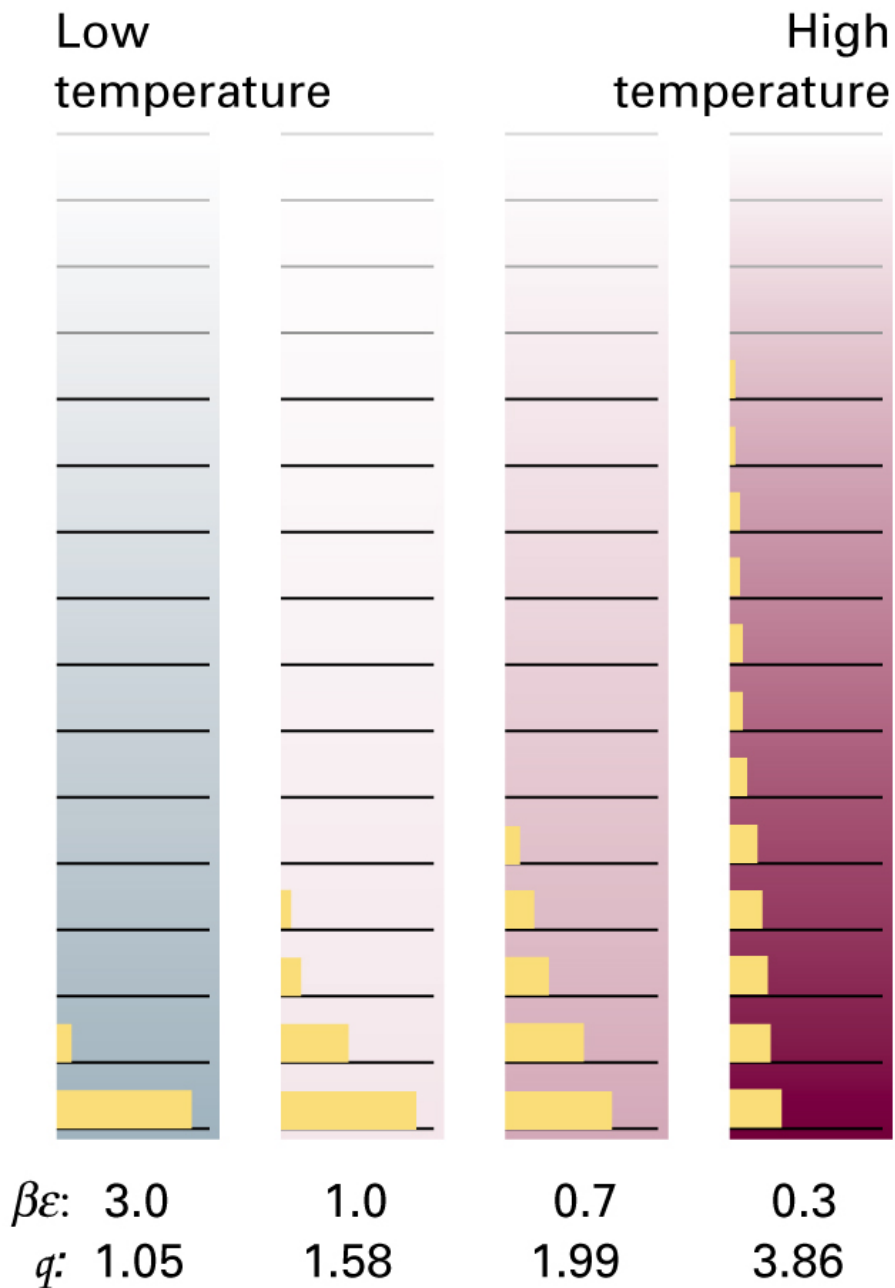


Figure 15B.4 Harmonic Oscillator
Populations of molecular states at various temperatures.

15B.2. Molecular Partition Function

Non-interacting molecules (such as a perfect gas)

An internal structure

Translational, Rotational, Vibrational, and Electronic Modes

$$\varepsilon_j = \varepsilon^{\text{translation}} + \varepsilon^{\text{rotation}} + \varepsilon^{\text{vibration}} + \varepsilon^{\text{electronic}}$$

$$q = \sum_{\text{States}} \exp(-\beta\varepsilon^t - \beta\varepsilon^r - \beta\varepsilon^v - \beta\varepsilon^e)$$

(trans, rot, vib, elec)

$$= \sum_{\text{trans.}} \exp(-\beta\varepsilon^t) \sum_{\text{rot.}} \exp(-\beta\varepsilon^r) \sum_{\text{vib.}} \exp(-\beta\varepsilon^v) \sum_{\text{elec.}} \exp(-\beta\varepsilon^e)$$

$$= q^t q^r q^v q^e$$

15B.2(a). The Translational Partition Function

Consider a perfect monatomic gas in a container of volume V (length X , width Y , depth Z).

The partition function for any one of the molecules

$$q = \sum_j \exp(-\beta \varepsilon_j)$$

ε_j : the energy at j state

j : the quantum number labelling the state

$$\varepsilon_j = \varepsilon_{j(x)} + \varepsilon_{j(y)} + \varepsilon_{j(z)}$$

$j =$ meaning n_x , n_y , and n_z quantum numbers for x -, y -, and z -directions, respectively

$$\begin{aligned}
q &= \sum_{\text{All } j} \exp(-\beta \varepsilon_{j(X)} - \beta \varepsilon_{j(Y)} - \beta \varepsilon_{j(Z)}) \\
&= \left\{ \sum_{j(X)} \exp(-\beta \varepsilon_{j(X)}) \right\} \left\{ \sum_{j(Y)} \exp(-\beta \varepsilon_{j(Y)}) \right\} \left\{ \sum_{j(Z)} \exp(-\beta \varepsilon_{j(Z)}) \right\} \\
&= q_X q_Y q_Z
\end{aligned}$$

$$\varepsilon_{j(X)} = j^2 \left(\frac{h^2}{8mX^2} \right) \quad j = 1, 2, 3, \dots$$

$$\therefore q_X = \sum_{j=1}^{\infty} \exp\left(-\frac{j^2 h^2 \beta}{8mX^2}\right)$$

15C.2(a). The Internal Energy

The translational energy levels are very close, so the sum can be replaced by an integral:

[Justific. 15B.1]

$$q_X = \int_1^\infty \exp\left(-\frac{j^2 h^2 \beta}{8mX^2}\right) dj \cong \int_0^\infty \exp\left(-\frac{j^2 h^2 \beta}{8mX^2}\right) dj$$

$$\text{Let } x^2 = \frac{j^2 h^2 \beta}{8mX^2}, \quad dj = \left(\frac{8mX^2}{h^2 \beta}\right)^{\frac{1}{2}} dx$$

$$q_X = \left(\frac{8mX^2}{h^2 \beta}\right)^{\frac{1}{2}} \int_0^\infty \exp(-x^2) dx = \left(\frac{8mX^2}{h^2 \beta}\right)^{\frac{1}{2}} \frac{\pi^{\frac{1}{2}}}{2}$$

$$\therefore q = \left(\frac{2\pi mX^2}{h^2 \beta}\right)^{\frac{1}{2}} \left(\frac{2\pi mY^2}{h^2 \beta}\right)^{\frac{1}{2}} \left(\frac{2\pi mZ^2}{h^2 \beta}\right)^{\frac{1}{2}} = \left(\frac{2\pi m}{h^2 \beta}\right)^{\frac{3}{2}} V$$

**Translational Partition Function
(Ideal Gas)**

How to calculate the internal energy of the gas

$$U - U(0) = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V$$

$$= - \left(\frac{N}{q} \right) \left(\frac{\partial q}{\partial \beta} \right)_V$$

$$\left(\frac{\partial q}{\partial \beta} \right)_V = \frac{\partial}{\partial \beta} \left\{ \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}} V \right\} = \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V \left(-\frac{3}{2} \beta^{-\frac{5}{2}} \right)$$

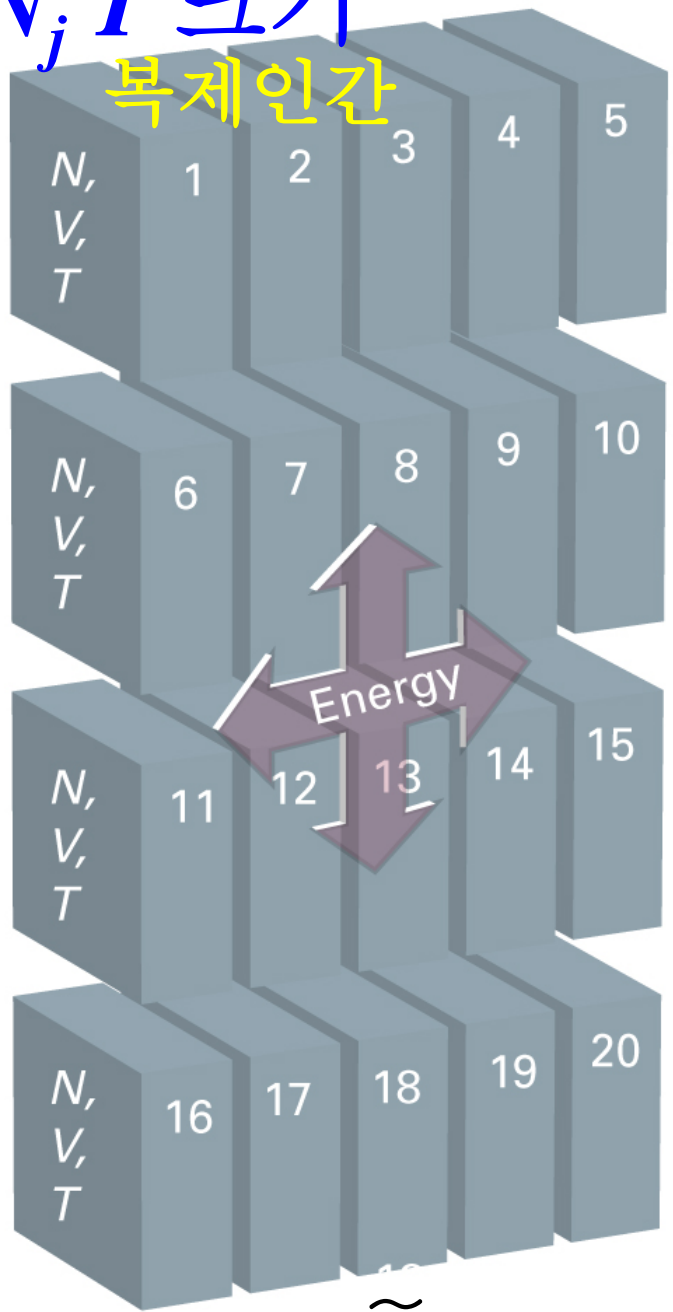
$$\therefore U - U(0) = - \left(\frac{N}{q} \right) \left(\frac{\partial q}{\partial \beta} \right)_V = - \frac{N \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V \left(-\frac{3}{2} \beta^{-\frac{5}{2}} \right)}{\left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V \left(\beta^{-\frac{3}{2}} \right)} = \frac{3N}{2\beta}$$

Given $\beta = \frac{1}{kT}$,

$$U - U(0) = \frac{3}{2} NkT = \frac{3}{2} RT \Rightarrow \text{the same result as from the equipartition value}$$

$N_j T$ 크기

복제인간



$$\tilde{N} = \infty$$

15D. Canonical Ensemble

- Imaginary collection of replications.
- Common temperature.
- **Interacting** molecules ($\sum N_j \quad V \quad T$).
- **Thermal contact among the members.**
- **Most members of ensemble have similar energies.**

Fig. 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 energy (\tilde{E}) of all 20 replications is constant because the ensemble is isolated overall.

Refinements: Ensembles and Reservoir

- In order to set up the ensemble, we take a system of specified volume, composition, and temperature, and think of it as being reproduced \tilde{N} times.
- We can think of this ensemble as consisting of approximately identical closed systems (members) in thermal contact with each other.
- This thermal contact ensures that they are all at the same temperature, but allows them to exchange energy with each other. The total energy of the ensemble \tilde{E} , however, is constant.
- This imaginary collection of replications is called the canonical ensemble.

복제인간

Microcanonical ensembles correspond to isolated systems which exchange neither energy nor mass with one another and which therefore keep the total number of particles N and the total energy E as constants.

Canonical ensembles correspond to closed isothermal systems which exchange energy but not mass with one another and which therefore keep N and temperature T as constants.

Grand canonical ensembles correspond to open isothermal systems which exchange energy and mass with one another and which therefore keep T and the chemical potential μ as constant.

Microcanonical: N, V, \mathbf{E} common

Canonical: N, V, \mathbf{T} common

Grand canonical: $\mathbf{\mu}, V, T$ common

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Dominating Configurations

\tilde{E} Total ensemble energy ∞ since $\tilde{N} \rightarrow \infty$

No Free Lunch

$\frac{\tilde{E}}{\tilde{N}}$ Average energy of any member

\tilde{n}_i Number of members of the ensemble being
in a state i with energy E_i

\tilde{W} Weight of each configuration

$\tilde{N} \rightarrow \infty$:

At **thermodynamic limit**, the most probable configuration is overwhelmingly the most probable.

p. 631

$$\tilde{W}(\tilde{n}_1, \tilde{n}_2, \dots) = \frac{\tilde{N}!}{\tilde{n}_1! \tilde{n}_2! \dots}$$

$$\frac{\tilde{n}_i}{\tilde{N}} = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}$$

Canonical Distribution = *Dependent*
[*Interacting*]

(Boltzmann Distribution = *Independent*)

Canonical partition function Q is more general than

molecular partition function q because

Q does not assume that the molecules are independent.

→ Properties of condensed phases and real gases.

[Fig. 15D.2 and Fig. 15D.3]

(p. 632)

15D.2. Thermodynamics from Canonical Partition Ftn (textbook)

The Canonical partition function

$$Q = \sum_i \exp(-\beta E_i) \quad \text{Canonical partition function} \quad [g_i\text{-fold degenerate}]$$

$$\tilde{P}_i = \frac{\tilde{n}_i^*}{\tilde{N}} = \frac{1}{Q} \exp(-\beta E_i) \quad \text{Proportion of members that are in the state } i \text{ with energy } E_i \text{ in an ensemble}$$

The mean energy of a member

$$U - U(0) = \sum_i \tilde{P}_i E_i = \frac{1}{Q} \sum_i E_i \exp(-\beta E_i)$$

$$U - U(0) = -\left(\frac{1}{Q}\right) \left(\frac{\partial Q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V \quad (15D.5)$$

Molecular Partition Function

$$\sum_i n_i \varepsilon_i = E$$

$$U - U(0) = -N \left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

$$S = k_B \ln W \quad (15A.1)$$

$$(15E.7)$$

Derivation for S from q [molecular pt]

<http://bp.snu.ac.kr> (white board)

15E.2. Entropy

$$S(T) = \frac{U(T) - U(0)}{T} + k \ln Q$$

(15E.8c)

$$F = -kT \ln Q$$

15D.3. Canonical Partition Ftn for **Independent (Same) Molecules**

The total energy of a collection of N independent molecules is the sum of the energies of the molecules. Therefore, we can write the total energy of a state $ijkl\dots$ of the system as:

$$E_{ijkl\dots} = \varepsilon_i^{(1)} + \varepsilon_j^{(2)} + \varepsilon_k^{(3)} + \dots + \varepsilon_l^{(N)}$$

$ijkl\dots$ = every possible state
오만 가지
infinite

where $\varepsilon_i^{(1)}$ is the energy of molecule 1 in the member of ensemble happening to be in the state i with energy ε_i .

Canonical partition function

$$Q = \sum_{ijkl\dots}^{\infty} e^{-\beta(\varepsilon_i^{(1)} + \varepsilon_j^{(2)} + \varepsilon_k^{(3)} + \dots + \varepsilon_l^{(N)})}$$

$$N = 10^{28} \text{ atoms}$$

$$\tilde{N} = \text{복제인간 수} = \infty$$

The sum over the states of the system can be produced by letting each molecule enter all its own individual states.

Therefore, instead of summing over the states $ijkl\dots$ of the system, we can sum over all the individual states of i of molecule 1, all the states i of molecule 2, and so on:

$$Q = \left(\sum_i^{\infty} e^{-\beta\varepsilon_i^{(1)}} \right) \left(\sum_i e^{-\beta\varepsilon_i^{(2)}} \right) \cdots \left(\sum_i e^{-\beta\varepsilon_i^{(N)}} \right) \quad i = i\text{-th energy level}$$

Since all the molecules may have the same energy states,

$$Q = \left(\sum_i^{\infty} e^{-\beta\varepsilon_i} \right) \left(\sum_i e^{-\beta\varepsilon_i} \right) \cdots \left(\sum_i e^{-\beta\varepsilon_i} \right) = \left(\sum_i e^{-\beta\varepsilon_i} \right)^N$$

$$Q = q^N \quad (15D.6)$$

If all the molecules are the same and free to move, we cannot distinguish one from another.

<u>molecules</u>	<u>state</u>		<u>molecules</u>	<u>state</u>
1	<i>a</i>	indistinguishable	1	<i>b</i>
2	<i>b</i>		2	<i>c</i>
3	<i>c</i>		3	<i>a</i>

For indistinguishable independent molecules,

$$Q = \frac{q^N}{N!}$$

(15D.7)

Gibbs paradox

15D.3. *Indistinguishable and Independent Molecules:*

Identical molecules in an ideal gas are free to move, and no way of keeping track of the identity.

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15E.2(b)

Translational Entropy of a Monatomic Ideal Gas

Since they are not interacting, the molecular partition function can be used to find U and S .

The canonical partition function will be retained if we deal with interacting atoms.

Since the only degree of freedom for the atoms is translational, the molecular partition function is

$$q = \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}} V$$

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$$U - U(0) = - \left(\frac{N}{q} \right) \left(\frac{\partial q}{\partial \beta} \right)_V = \frac{3}{2} nRT \quad \text{*n mole*}$$

$$\therefore S = \frac{U - U(0)}{T} + nR(\ln q - \ln N + 1)$$

$$= \frac{3}{2}nR + nR \left\{ \ln \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V - \ln N + 1 \right\}$$

$$= nR \left\{ \ln e^{\frac{3}{2}} + \ln \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V - \ln N + \ln e \right\}$$

$$= nR \ln \left(e^{\frac{5}{2}} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V / N \right)$$

$$Q = \frac{q^N}{N!}$$

Indistinguishable &
Independent

(15E.10a)


Sackur-Tetrode equation for the entropy of a monatomic perfect gas

$$S = nR \ln \left\{ e^{\frac{5}{2}} \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \left(\frac{kT}{p} \right) \right\} \quad \left| \quad V = \frac{nRT}{p} \right.$$

When a perfect gas expands isothermally from V_i to V_f ,

$$\begin{aligned} \Delta S &= S_f - S_i = nR \ln aV_f - nR \ln aV_i \\ &= nR \ln \frac{V_f}{V_i} \quad \leftarrow \text{the same result as thermodynamic argument} \end{aligned} \quad (3A.1)$$

Gibbs Paradox

$$Q = \frac{q^N}{N!}$$


Indistinguishable &
Independent

15E. Statistical Thermodynamics: Applications

q = Noninteracting (independent)

How to calculate the partition function?

Here, Q = Indistinguishable & independent molecules

$$Q = \frac{q^N}{N!}$$

$$q = \sum_j \exp(-\beta \epsilon_j), \quad \beta = \frac{1}{kT}$$

Q = for Interacting Molecules

How to calculate the thermodynamic functions?

$$U - U(0) = - \left(\frac{1}{Q} \right) \left(\frac{\partial Q}{\partial \beta} \right)_V = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_V \quad (15F.1a)$$

$$S = \frac{U - U(0)}{T} + k \ln Q \quad (15F.1b)$$

The Helmholtz function, A

$$A = U - TS$$

$$A(0) = U(0) \quad \text{at } T = 0$$

$$\therefore \underline{A - A(0)} = U - U(0) - TS$$

$$= U - U(0) - T \left\{ \frac{U - U(0)}{T} + k \ln Q \right\}$$

$$= \underline{-kT \ln Q}$$

(15F.2)

The pressure

$$p = - \left(\frac{\partial A}{\partial V} \right)_T = kT \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

(15F.3)
[reversible]

The enthalpy, H

$$H = U + pV$$

$$H(0) = U(0) \quad \text{at } T = 0 \text{ K}$$

$$\therefore H - H(0) = U - U(0) + pV$$

$$= U - U(0) + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$= - \left(\frac{\partial \ln Q}{\partial \beta} \right)_V + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

(15F.4)

The Gibbs function, G

$$G = H - TS = U + pV - TS, \quad G(0) = U(0) \quad \text{at } T = 0 \text{ K}$$

$$G - G(0) = U - U(0) + pV - TS$$

$$= U - U(0) + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T - \left(\frac{U - U(0)}{T} + k \ln Q \right) T$$

$$= \cancel{U - U(0)} + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T - \cancel{(U - U(0))} - kT \ln Q$$

$$= -kT \ln Q + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (15F.6)$$

In the case of a perfect gas, this expression simplifies considerably.

$$G - G(0) = -kT \ln Q + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad \text{From (15F.3)}$$

$$= -kT \ln Q + nRT \quad (\because pV = nRT) \quad \text{(Ideal Gas)} \quad (15F.7)$$

Replacing Q by $q^N / N!$ gives

$$\begin{aligned}G - G(0) &= -kT \ln(q^N / N!) + nRT \\&= -NkT \ln q + kT \ln N! + nRT \\&= -nRT \ln q + kT(N \ln N - N) + nRT && \text{(Ideal Gas)} \\&= -nRT \ln(q / N) && \text{(15F.9)}\end{aligned}$$

15B.2. How to Calculate the Molecular Partition Function?

Consider a system of non-interacting molecules, such as a perfect gas.

The molecules, however, are allowed to have an internal structure.

The energy of molecule has **the translational, rotational, vibrational, and electronic modes** of motion.

$$\varepsilon_j = \varepsilon^{\text{translation}} + \varepsilon^{\text{rotation}} + \varepsilon^{\text{vibration}} + \varepsilon^{\text{electronic}}$$

$$q = \sum_{\text{States}} \exp(-\beta\varepsilon^t - \beta\varepsilon^r - \beta\varepsilon^v - \beta\varepsilon^e)$$

(trans, rot, vib, elec)

$$= \sum_{\text{trans.}} \exp(-\beta\varepsilon^t) \sum_{\text{rot.}} \exp(-\beta\varepsilon^r) \sum_{\text{vib.}} \exp(-\beta\varepsilon^v) \sum_{\text{elec.}} \exp(-\beta\varepsilon^e)$$

$$= q^t q^r q^v q^e$$

- The modes are not completely **independent**.
- Vibration indep = when only the ground electronic state is occupied.

15B.2(a). The Translational Contribution

$$q^t = \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}} V = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} V \quad (15B.7a)$$

$$q^t = \frac{V}{\Lambda^3}, \quad \Lambda = \frac{h}{(2\pi m k T)^{1/2}} \quad \text{Thermal de Broglie wavelength}$$

The value of q^t rises to infinity as the temperature increases.

15B.2(b). The Rotational Contribution

One point to remember is that more than one rotational state may correspond to the same energy

$(2J + 1)$ degeneracy for the given J

$$q^r = \sum_{J=0} (2J + 1) \exp(-\beta E_J)$$

3-D

(15B.11)

Sec. 12B

The rotational energy levels of many molecules lie close enough together for a large number to be populated at room temperature. So, to a good approximation, the sum can be replaced by an integral.

For a **homonuclear diatomic molecule** or a **symmetric linear molecule**, rotation by 180° interchanges is indistinguishable from the original. So, we have to divide the integral by 2 to avoid counting indistinguishable orientations twice:

$$\text{homonuclear diatomic: } q^r \cong \frac{1}{2} \int_0^\infty (2J + 1) \exp(-\beta E_J) dJ$$

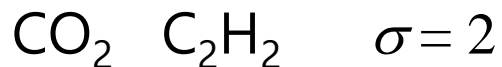
In the case of a heteronuclear diatomic, the rotation by 180° leads to a distinguishable orientation ($\text{HCl} \rightarrow \text{ClH}$) and so the factor $\frac{1}{2}$ does not appear.

In general form

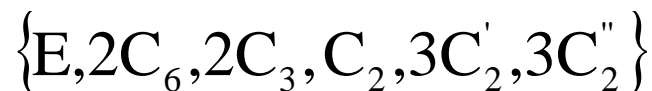
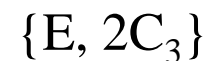
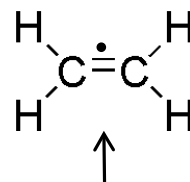
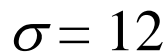
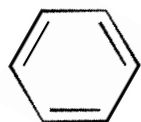
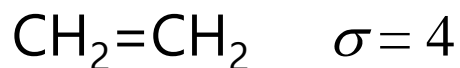
$$q^r \cong \frac{1}{\sigma} \int_0^\infty (2J + 1) \exp(-\beta E_J) dJ$$

where σ is the symmetry number.

Refer to Chapter 12 Molecular Symmetry.



more complex molecules more than two orientations



B = rotational constant
 σ = symmetry number

Sec. 12B

Linear Rotor (Molecule):

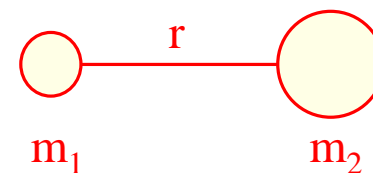
$$\underline{E_J = hcBJ(J + 1)}$$

where B : the rotational constant of the molecule and related to its moment of inertia

$$B = \frac{\hbar}{4\pi cI}$$

$$\therefore q^r \cong \frac{1}{\sigma} \int_0^\infty (2J + 1) \exp\{-\beta hcBJ(J + 1)\} dJ$$

$$q^r \approx \int_0^\infty \left(-\frac{1}{\sigma \beta hc B} \right) \left[\frac{d}{dJ} \exp\{-\beta hcBJ(J + 1)\} \right] dJ$$



$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2$$

Justif. 15B.2

3-D

$B = \text{rotational constant}$
 $\sigma = \text{symmetry number}$

The integral of a derivative of a function is the function itself, and so

$$q^r \approx \left(-\frac{1}{\sigma\beta hcB} \right) \exp\{-\beta hcBJ(J+1)\} \Big|_0^\infty = \frac{1}{\sigma\beta hcB}$$

The approximate form of the rotational partition function:

$$\underline{q^r} \approx \frac{kT}{\sigma hcB} = \frac{kT}{\sigma hc \frac{\hbar}{2\pi c l}} = \frac{2l kT}{\hbar^2 \sigma} \quad \left(\because \hbar = \frac{h}{2\pi} \right) \quad (15B.12a)$$

3-D

[skip] Approximate rotational partition function for other types of molecule can be found in the same way, leading to

$$q^r \approx \frac{\pi^{\frac{1}{2}}}{\sigma} \left\{ \left(\frac{2I_A kT}{\hbar^2} \right) \left(\frac{2I_B kT}{\hbar^2} \right) \left(\frac{2I_C kT}{\hbar^2} \right) \right\}^{\frac{1}{2}} \quad [\text{skip}]$$

where I_A , I_B and I_C are their three moments of inertia.

15B.2(c). The Vibrational Contribution

$$q^v = \sum_j \exp(-\beta \varepsilon_j^v)$$

In a polyatomic molecule, every normal mode of vibration has its own independent set of energy levels,

$$q^v = q^v(1)q^v(2)\cdots$$

where $q^v(K)$ is the partition function for the K^{th} normal mode.

$$\underline{E_n = \left(n + \frac{1}{2}\right) hc \tilde{\nu}} \quad n = 0, 1, 2, 3, \dots$$

where $\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$

k : the force constant
 μ : the reduced mass

Assumption:
simple harmonic approximation

3-D

$F = k \Delta r$
spring 1개

If we measure energies from the zero-point level, the permitted values are $E' = \nu h c \tilde{\nu}$.

$$q^{\nu} = \sum_n \exp(-nh\beta c\tilde{\nu}) = \sum_n \left(e^{-h\beta c\tilde{\nu}}\right)^n \quad n = 0, 1, 2, 3, \dots$$

$$\underline{q^{\nu} = \frac{1}{1 - \exp(-hc\tilde{\nu} / kT)}} \quad (15B.15)$$

$\tilde{\nu}$: wavenumber of the vibration mode

In many molecules the vibrational frequencies are so high that $hc\tilde{\nu}\beta > 1$.

e.g., the lowest vibrational wavenumber of methane:

Example 15B.2

$$1306 \text{ cm}^{-1} \Rightarrow hc\tilde{\nu}\beta \approx 6 \text{ at room temp.}$$

$$2850 \sim 2960 \text{ cm}^{-1} \Rightarrow hc\tilde{\nu}\beta \approx 14 \text{ at room temp.}$$

$$e^{-6} \cong 0.002$$

$\therefore q^{\nu} \approx 1$ implying that **only the lowest state is occupied.**

15B.2(d). The Electronic Contribution

Electronic energy separations are usually very large, and so the exponentials $\exp(-\beta\varepsilon^e)$ are all very small, except for the ground state, for which $\varepsilon^e = 0$.

Therefore, in most cases:

$$\underline{q^e = 1}$$

The Overall Partition Function

For a diatomic molecule,

$$q \approx \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V \left(\frac{kT}{\sigma hcB} \right) \left\{ \frac{1}{1 - \exp\left(-\frac{hc\tilde{\nu}}{kT}\right)} \right\}$$

1) Approximations: independent modes and harmonic vibrations.

2) Rotational levels are very close together.

15C.2(c). High-Temperature Limit for Vibration

[모순: Anharmonic Term 탄생]

$$q^v = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

At temperatures so high that $kT > hc\tilde{\nu}$, the partition function may be approximated by expanding the exponential

$$q^v = \frac{1}{1 - (1 - \beta hc\tilde{\nu} + \dots)} \cong \frac{1}{\beta hc\tilde{\nu}},$$

Hence,

$$q^v = \frac{kT}{hc\tilde{\nu}}$$

(15B.16)

(15C.9)

We can express the temperatures for which this expansion is valid in terms of the characteristic vibrational temperature θ_v , which is defined through:

$$\underline{k\theta_v = \hbar c\tilde{\nu}}$$

**Debye Temperature
(Solid State)**

(Table 15B.3)

Equation of State of a Perfect Gas

Non-Interacting Molecules Allowed for Internal Structures

$$Q = q^N / N!$$

$$p = kT \left(\frac{1}{Q} \right) \left(\frac{\partial Q}{\partial V} \right)_T = kT \left(\frac{N!}{q^N} \right) \left(\frac{\partial (q^N / N!)}{\partial V} \right)_T = kT \left(\frac{1}{q^N} \right) \left(\frac{\partial q^N}{\partial V} \right)_T$$

Since only q^t depends on the volume ($q^t = \frac{V}{\Lambda^3}$), this becomes

$$p = kT \left(\frac{1}{(q^t q^r q^v q^e)^N} \right) \left(\frac{\partial (q^t q^r q^v q^e)^N}{\partial V} \right)_T \quad \{q^e = 1\}$$

$$= kT \frac{1}{(q^t)^N} \left(\frac{\partial (q^t)^N}{\partial V} \right)_T = kT \frac{1}{(V / \Lambda^3)^N} \left(\frac{\partial (V / \Lambda^3)^N}{\partial V} \right)_T$$

$$= kT \frac{1}{(V / \Lambda^3)^N} \left(\frac{1}{\Lambda^3} \right)^N N V^{N-1} = NkT \frac{1}{V} = \frac{nLkT}{V} = \frac{nRT}{V}$$

Using Statistical Thermodynamics

Any thermodynamic properties can now be deduced from a knowledge of energy levels:

p. 476

Thermodynamics and Spectroscopy have been combined.

non-interacting molecules

15C. Average Energies and the Equipartition Principle

$\{q^e = 1\}$

$$\begin{aligned}U - U(0) &= -N \left(\frac{1}{q} \right) \left(\frac{\partial q}{\partial \beta} \right) = -N \left(\frac{1}{q^t q^r q^v q^e} \right) \left(\frac{\partial q^t q^r q^v q^e}{\partial \beta} \right) \\&= -N \left(\frac{1}{q^t q^r q^v q^e} \right) \left\{ q^r q^v q^e \frac{\partial q^t}{\partial \beta} + q^t q^v q^e \frac{\partial q^r}{\partial \beta} + q^t q^r q^e \frac{\partial q^v}{\partial \beta} \right. \\&\quad \left. + q^t q^r q^v \frac{\partial q^e}{\partial \beta} \right\} \\&= N \left\{ - \left(\frac{1}{q^t} \right) \left(\frac{\partial q^t}{\partial \beta} \right) - \left(\frac{1}{q^r} \right) \left(\frac{\partial q^r}{\partial \beta} \right) - \dots \right\}\end{aligned}$$

Since $[U - U(0)]/N$ is the sum of the mean energies of all the modes,

$$U - U(0) = N \left\{ \langle \varepsilon^t \rangle + \langle \varepsilon^r \rangle + \langle \varepsilon^v \rangle + \langle \varepsilon^e \rangle \right\}$$

$$\therefore \langle \varepsilon^m \rangle = - \left(\frac{1}{q^m} \right) \left(\frac{\partial q^m}{\partial \beta} \right)$$

Mean Energy of a Molecule

(15C.3)

$\{q^e = 1\}$

where each mode **m = translation, rotation, vibration, or electronic.**

15C.2(a). Mean Translational Energy

Can be found from the translational partition function.

Consider an one-dimensional system.

$$q^t = \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{1}{2}} X \quad m : \text{mass of a molecule}$$

$$\langle \varepsilon^t \rangle = \frac{1}{\left(\frac{2\pi m}{\beta h^2} \right)^{\frac{1}{2}} \cancel{X}} \left(\frac{\cancel{2\pi m}}{h^2} \right)^{\frac{1}{2}} \cancel{X} \left(-\frac{1}{2} \beta^{-\frac{3}{2}} \right) = \frac{1}{2\beta} = \frac{1}{2} kT$$

1-D

In three dimensions, the same calculation leads to

$$\langle \varepsilon^t \rangle = \frac{3}{2} kT \quad \mathbf{3-D}$$

**Mean energy: independent of
the mass of molecule and the size of container.**

In classical mechanics,
the kinetic energy T

$$T = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

↑ ↑ ↑

$$\frac{1}{2} kT \quad \frac{1}{2} kT \quad \frac{1}{2} kT$$

15C.2(b). Mean Rotational Energy of a linear molecule

$$\langle \varepsilon^r \rangle = - \left(\frac{1}{q^r} \right) \left(\frac{\partial q^r}{\partial \beta} \right)$$

$$q^r = \sum_J (2J + 1) \exp(-\beta hc B J(J + 1))$$

Low Temperature: we need term-by-term summation. $hcB \sim 10^{-5} \text{ eV}$

$$b = \beta hc B.$$

$$q^r = 1 + 3e^{-2\beta hc B} + 5e^{-6\beta hc B} + \dots = 1 + 3e^{-2b} + 5e^{-6b} + \dots$$

$$\langle \varepsilon^r \rangle = \frac{hcB \{6e^{-2b} + 30e^{-6b} + \dots\}}{\{1 + 3e^{-2b} + 5e^{-6b} + \dots\}}$$

(15C.6a)

$$T \rightarrow 0, \langle \varepsilon^r \rangle \rightarrow 0$$

Fig. 15C.2

Mean Rotational Energy of a linear molecule

High Temperature: many rotational levels are occupied.

$$hcB \sim 10^{-5} \text{ eV}$$

$$q^r \cong \frac{2IkT}{\hbar^2 \sigma} = \frac{kT}{\sigma hcB} \quad (15B.12a)$$

$$\langle \varepsilon^r \rangle = - \left(\frac{\hbar^2 \sigma}{2IkT} \right) \left(\frac{2I}{\hbar^2 \sigma} \right) (-\beta^{-2}) = \frac{1}{\beta} = kT \quad \begin{array}{l} \mathbf{3-D} \\ (15C.6b) \end{array}$$

The classical expression for the rotational energy of a linear molecule:

$$E_k = \frac{1}{2} I \omega_x^2 + \frac{1}{2} I \omega_y^2 : \text{two degrees of freedom}$$

$$2 \times \frac{1}{2} kT = kT$$

3-D

15C.2(c). Mean Vibrational Energy

$$q^v = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

$$\frac{\partial q^v}{\partial \beta} = -\frac{hc\tilde{\nu} e^{-\beta hc\tilde{\nu}}}{(1 - e^{-\beta hc\tilde{\nu}})^2}$$

$$\therefore \langle \varepsilon^v \rangle = \frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1}$$

$$hc\tilde{\nu} \sim 0.5 \text{ eV}$$

When the temperature is so high: $\beta hc\tilde{\nu} \ll 1$ ($T \gg \theta_v$)

$$\langle \varepsilon^v \rangle \cong hc\tilde{\nu} \left\{ \frac{1}{1 + \beta hc\tilde{\nu} - \dots - 1} \right\} \cong \frac{1}{\beta} = kT$$

3-D

- The classical expression for the Vibrational Energy:

$$E = T + V = \frac{1}{2} \mu v_x^2 + \frac{1}{2} kx^2$$

\downarrow \downarrow

kinetic E . potential E .

$\left(\frac{1}{2}kT\right)$ $\left(\frac{1}{2}kT\right)$

3-D

High-Temperature Limit

Equipartition Principle: the average energy of quadratic term in the energy expression has the same value, $\frac{1}{2}kT$.

Debye Temperature (Phonon in Solid Phase)

2,230 K in diamond

15E.1(b). Heat Capacities:

Detecting (Phase) Transitions

$$\underline{C_V} = \left(\frac{\partial U}{\partial T} \right)_V, \quad \beta = \frac{1}{kT}, \quad d\beta = -\frac{dT}{kT^2}$$
$$\therefore C_V = - \left(\frac{1}{kT^2} \right) \left(\frac{\partial U}{\partial \beta} \right)_V = -k\beta^2 \left(\frac{\partial U}{\partial \beta} \right)_V$$

The internal energy translational, rotational, vibrational and electronic contributions:

$$U - U(0) = N \left\{ \langle \varepsilon^t \rangle + \langle \varepsilon^r \rangle + \langle \varepsilon^v \rangle + \langle \varepsilon^e \rangle \right\}$$

$$\{g^e = 1\}$$

The heat capacity has contributions from each mode of motion:

$$C_V = C_V^t + C_V^r + C_V^v + C_V^e$$

$$\text{where } C_V^m = N \left(\frac{\partial \langle \epsilon^m \rangle}{\partial T} \right)_V$$

$$= - \left(\frac{N}{kT^2} \right) \left(\frac{\partial \langle \epsilon^m \rangle}{\partial \beta} \right)_V$$

**m = translation, rotation
vibration, or electronic**

Translational

$$C_V^t = N \left(\frac{\partial \frac{3}{2} kT}{\partial T} \right)_V = \frac{3}{2} Nk = \frac{3}{2} nR$$

In the case of monoatomic ideal gas,
the translational energy is the only contribution.

Rotational

$$\langle \epsilon^r \rangle = kT$$

$$C_V^r = Nk = nR$$

Valid at room temperature

$$hcB \sim 10^{-5} \text{ eV}$$

$$hcB \sim 10^{-5} \text{ eV}$$

Rotational

When the temperature is so low that only the lowest rotational state is occupied, $\langle \varepsilon^r \rangle = 0$ and there is no contribution to the heat capacity from the rotations.

An intermediate values the value of C_V^r can be

obtained by differentiating Eq. **(15C.6a)** ppt 15-54

$$\langle \varepsilon^r \rangle = \frac{hcB \{6e^{-2b} + 30e^{-6b} + \dots\}}{1 + 3e^{-2b} + 5e^{-6b} + \dots} \quad (kT < hcB)$$

where $b = \beta hcB$.

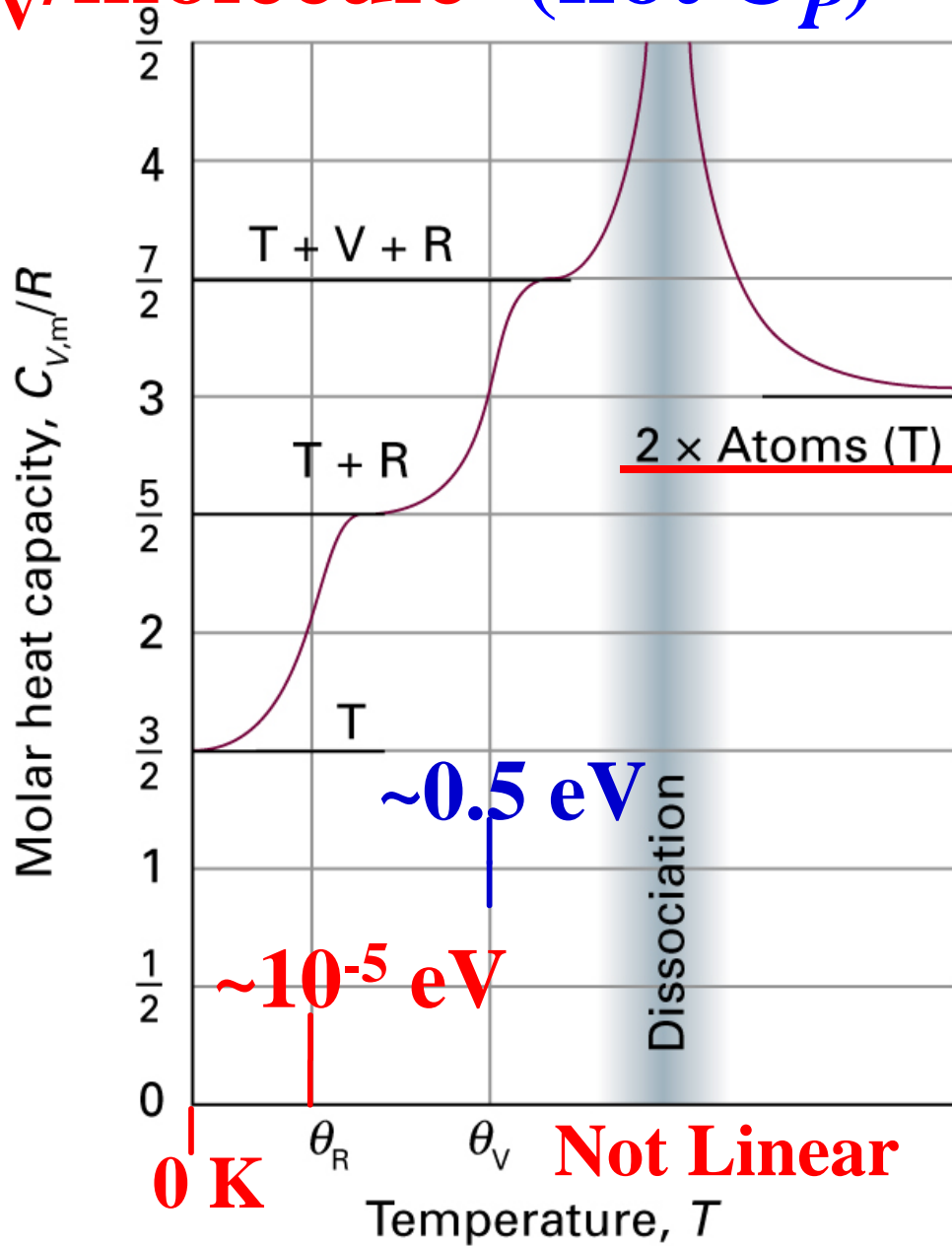
We can see that the rotational contribution to the heat capacity rises from zero ($kT < hcB$) to kT .

$$q^r = \sum_J (2J + 1) e^{-\beta E_J}$$

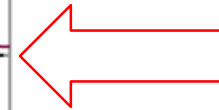
$$E_J = hcBJ(J + 1)$$

$$\langle \varepsilon^r \rangle = -\frac{1}{q^r} \left(\frac{\partial q^r}{\partial \beta} \right)$$

C_V /molecule (not C_P)



Linear Diatomic Molecules (Ideal Gas)



Temperature dependence of the heat capacity of linear molecules.

Assuming ideal gas at 0 K

Not Linear

The approximate form of the **rotational** partition function for a linear molecule.

$$q^r \cong \frac{kT}{\sigma hcB}$$

A useful way of expressing the temperature above which the approximation is valid to introduce the rotational temperature θ_r

The 'high temperature' means $T > \theta_r$. $hcB \sim 10^{-5} \text{ eV}$

$$q^v = \frac{kT}{hc\tilde{\nu}} \quad q^v = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \quad \text{span style="color: red;"> $hc\tilde{\nu} \sim 0.5 \text{ eV}$$$

We can express the temperature for which this expression is valid in terms of the characteristic **vibrational** temperature

In terms of the vibrational, 'high temperature' means $T > \theta_v$.

C_v /molecule for vibrational component

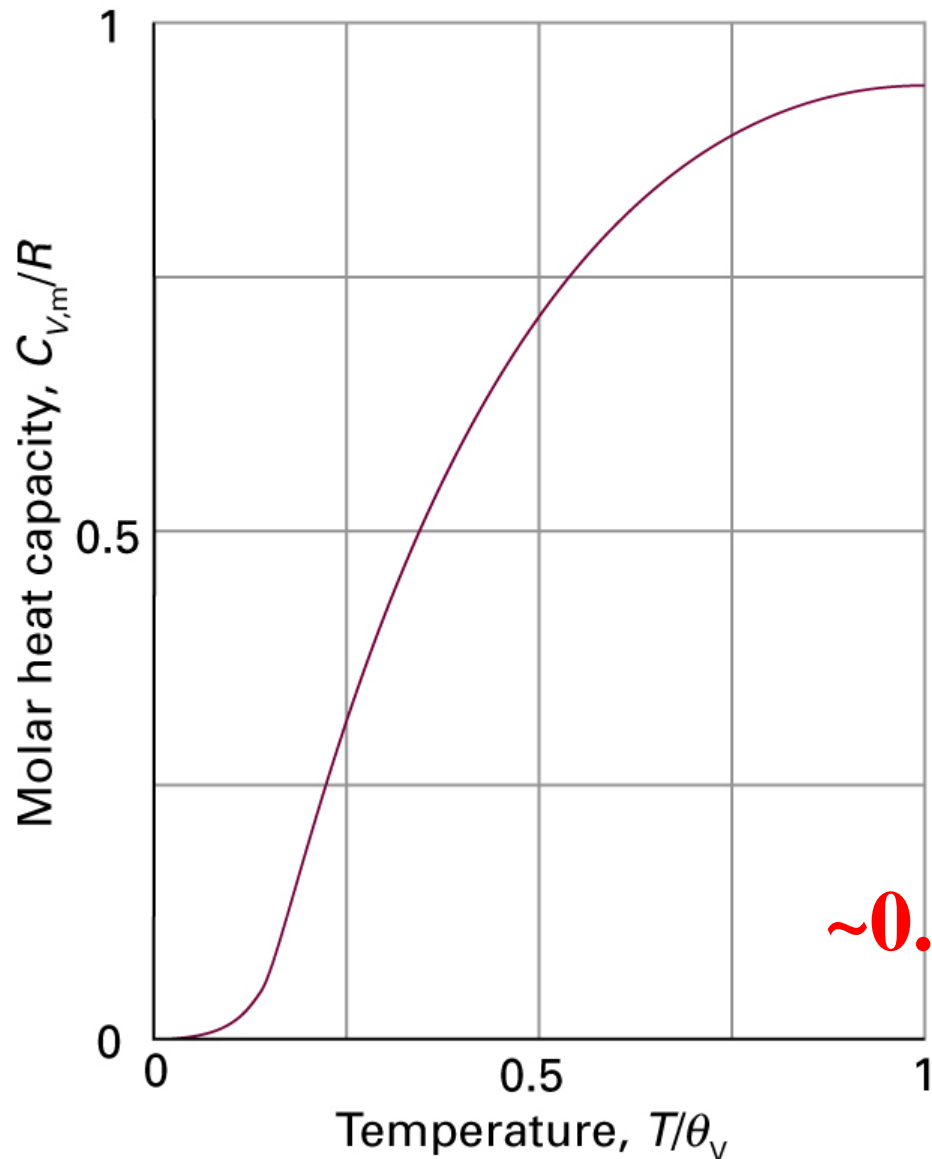


Figure 15C.3

Figure 15E.1

The temperature dependence of the vibrational heat capacity of a molecule in the harmonic approximation.

~0.5 eV

15E.2(e). Residual Entropies

Some disorder is present in solid even at absolute zero.

The entropy of solid at absolute zero is greater than zero, and is called **the residual entropy**.

The source and magnitude of the residual entropy:

Example: Consider a crystal composed of molecules AB, where A and B are of similar size.



→ The molecules adopt either orientation at random in the solid.

→ Since solidification is not an infinitely slow process

(metastable), the random array may be frozen in and survive even at absolute zero.

$$S = k \ln W$$

Suppose that two molecular orientations are equally probable, and that the sample contains N molecules.

2^N different ways for each member of ensemble

$$S = k \ln 2^N = Nk \ln 2 = nR \ln 2$$

This predicts a **residual entropy** of

(15E.14b)

$$k_B \ln 2 = 5.97 \times 10^{-5} \text{ eV/K (per molecule)}$$

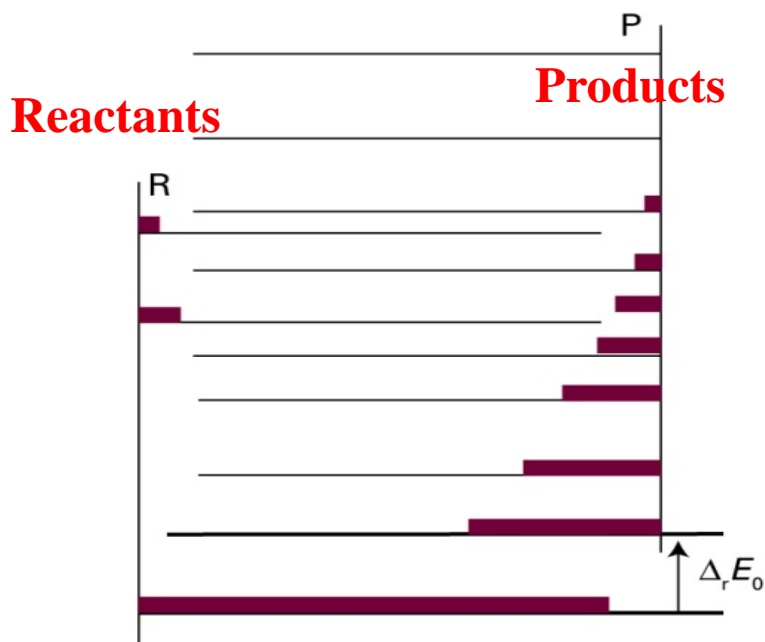
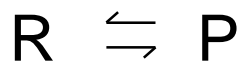
for molecules that can adopt either of two orientations at absolute zero.

Experimentally, entropy measurements by calorimetry (Chap. 3) or spectroscopic data.

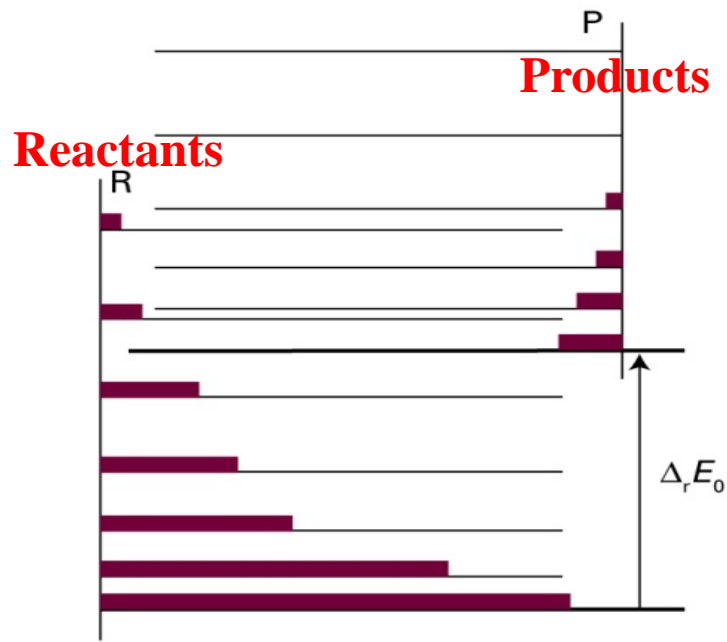
$$C_p = \left(\frac{dQ}{dT} \right)_p$$

15F.2. Equilibrium Constants

$$K = \exp(-\beta\Delta G_0)$$



Reactants will not dominate in the reaction mixture at equilibrium.



Reactants predominate in the reaction mixture.

Figs. 15F.2 and 15F.3. The array of energy levels for R and P molecules in the equilibrium $R \rightleftharpoons P$, and the dependence of equilibrium on the density of states. In classical thermodynamic terms, we need entropy and enthalpy to consider.

Independent Molecules

→ *Molecular Partition Function*

At some temperature T , the number of molecules in some state i of the joint system

$$n_i = \frac{N}{q} \exp(-\beta \varepsilon_i) \quad N : \text{the total number of molecules}$$

$$N_R = \sum_{i \text{ of R}} n_i = \frac{N}{q} \sum_R \exp(-\beta \varepsilon_R) \quad \text{Reactants}$$

$$N_P = \sum_{i \text{ of P}} n_i = \frac{N}{q} \sum_P \exp(-\beta \varepsilon_P) \quad \text{Products}$$

The sum over the states of R is nothing other than the molecular partition function for molecule (reactant), q_R :

$$N_R = \frac{Nq_R}{q}$$

Reactants (R) ↔ Products (P)

The sum over the states of P is also a partition function, but it is not quite the same as the ones met so far because the energies ε_P are measured from the ground state of the total system, which in the present example happens to be the ground state of A.

$$\varepsilon_P' = \varepsilon_P + \Delta E_0 \quad \varepsilon_P' : \text{Not from Zero} \quad \varepsilon_P : \text{from Zero}$$

ΔE_0 : the separation between the lowest levels of R and P

$$N_P = \frac{N}{q} \exp(-\beta \Delta E_0) \sum_P \exp(-\beta \varepsilon_P)$$

$$= \frac{N q_P}{q} \exp(-\beta \Delta E_0)$$

$$= \frac{N_R q_P}{q_R} \exp(-\beta \Delta E_0)$$

$$N_R = \frac{N q_R}{q}$$

Equilibrium constant of the reaction:

$$K = \frac{N_P}{N_R} = \frac{q_P}{q_R} \exp(-\beta\Delta E_0)$$

Derivation:

Assume Independence +
Given Volume

This gives a way of calculating the value of K simply from a knowledge of the partition function, and therefore from spectroscopic data or molecular properties.

Equilibrium Constant K of Reaction (in general)

$$K = \exp(-\beta\Delta G_0) \quad \textit{Given Pressure}$$

Problems from Chap. 15

D 15A.4

E 15A.1(b) 15A.3(b) 15A.4(b)

D 15B.2

E 15B.1(b) 15B.2(b) 15B.3(b) 15B.10(b)

E 15C.1(b) 15C.5(b)

D 15D.2 15D.4

D 15E.4 15E.6