

# **Chapter 1**

## **Boltzmann Probability Distribution and Entropy**



## Abstract

According to Boltzmann, energy was assumed countable. His idea was thought to be peculiar at his time. Boltzmann gave a statistical basis to the fact that pure different independent particles tend to be mixed spontaneously and occupy more space individually whereby increasing its randomness. Chemical process proceeds toward the state of lowered potential energy usually accompanied by increased randomness. He defined the average entropy of a system containing a large number of particles as  $S=k \ln\Omega$  where  $\Omega$  is the number of states given by counting the number of ways for placing certain number of indistinguishable particles in the possible number of different energy cells. If we have  $\Omega$  microstates, the probability to find any microstate is  $1/\Omega$ . The number of microstates measures disorder. Entropy is related to degree of disorder. For gases the number of microstates due to location in the space is very large. As a consequence, entropy of gases is very large and entropy of solid is small. At low temperature vibration and rotation of molecules are limited. That is why entropy is smaller at low temperature. When entropy is maximized, equilibrium is obtained in the isolated system.

## 1.1 Introduction

In the Boltzmann model, the distribution law is derived from the number of states given by counting the number of ways for placing certain number of indistinguishable particles in the possible number of different energy cells. It is also important to know how the given total amount of energy is distributed among the certain number of independent individuals. Energy was assumed countable. His idea was well understood and accepted later in the time of quantum mechanics. Boltzmann also gave a statistical basis to the fact that pure different independent particles tend to be mixed spontaneously and occupy

more space individually whereby increasing its randomness. Ludwig Boltzmann was born in 1844. A little more than a hundred years ago, he found out the famous formula  $S=k \ln\Omega$  that was carved on his tombstone. In order to reach his conclusion, we should recall the way of counting the number of permutations of  $N$  distinguishable objects. And then we start calculating the number of the cases that there will be  $i$  bits of something in the first individual if there are  $E$  bits of something to put into  $N$  individuals, which finally results in leading the probability distribution of the Boltzmann model. Bits of something could be coins and individuals could be people in economy. Bits of something could be energy and individuals could be molecules in chemistry.

The number of permutations of  $N$  distinguishable objects is  $N!$ . This is easy to explain. Any of the  $N$  objects can be in the first position, any of the other  $(N-1)$  in the second position, any of the remaining  $(N-2)$  in the third position, and so on.

If the  $N$  objects are indistinguishable, the number of permutations is  $N!/N!=1$ . If  $N$  is the sum of two different objects,  $N_A$  and  $N_B$ , the number of permutation is  $N!/N_A!N_B!$ .

Question 1-1 Each diatomic molecule oscillates in one direction and has one oscillator. How many ways are there putting a total of 6 energy bits into 4 diatomic molecules if each oscillator can hold any number of energy bits?

Answer: First we assume that  $E$  identical bits of energy are distinguishable as well as molecules. Then  $E$  identical bits of energy are numbered from 1 to  $E$ . Each molecule could have any amount of energy bits. We should admit special cases that some molecules have no energy bits and one molecule has all of  $E$  energy bits to oneself. We also admit some molecules have the same number of energy bits.

If we write the contents of the molecules in order, for example with  $E = 6$  and  $N = 4$  molecules we could have ( ,1 2 3, 4 5, 6) which means that none in the first molecule, 1, 2, 3 in the second, 4 and 5 in the third, and 6 in the fourth or ( ,5 2 4, 3, 6 1) which means that none in the first molecule, 5, 2, and 4 in the second, 3 in the third, and 6 and 1 in the fourth or (2, 5 4, 6 1, 3) which means that 2 in the first molecule, 5 and 4 in the second, 6 and 1 in the third, and 3 in the fourth. The first and the second permutation show the same number of energy bits in the first and second molecule. The first and the third permutation show the same number of energy bits in the fourth molecule.

Now we replace the commas representing boundaries between distinguishable molecules with letters, which can be in any order, although the first set of numbers still denotes the contents of the first molecule, the second set denotes the contents of the second, *etc.*

The first permutation above might be (A 1 2 3 B 4 5 C 6), (A 1 2 3 C 4 5 B 6), (B 1 2 3 A 4 5 C 6), (B 1 2 3 C 4 5 A 6), (C 1 2 3 A 4 5 B 6), or (C 1 2 3 B 4 5 A 6).

Clearly in any case the total number of permutations which is the number of possible ways of arranging 6 numbers and three letters is

$$\Omega = (6 + 3)! = 9!.$$

i.e.  $(E + N - 1)!$

Each of the 9! different outcomes is called a *microstate* in statistical mechanics. The total number of microstates is 9!.

Let's count the number of ways of putting a total of  $E$  energy bits into  $N$  molecules if each oscillator can hold any number of energy bits. Because the number of boundaries is fewer than the number of molecules by one, we have  $N - 1$  boundaries instead of  $N$ . There is a lot of over-counting in this way of

counting permutations, because actually we can't distinguish bits of energy from one another and also can't distinguish boundaries from one another because molecules are indistinguishable. To correct the counting of permutations we must divide by the number of ways of writing the energy numbers which is  $E!$  and by the number of ways of arranging the boundary labels which is  $(N - 1)!$ . After correction we obtain the total number of permutations,  $\Omega_{all}$  for arranging the  $E$  indistinguishable bits of energy into  $N$  identical molecules. We call  $\Omega_{all}$  the total number of microstates.

$$\Omega_{all} = \frac{(E+N-1)!}{E!(N-1)!} \quad (1.1)$$

$\Omega_{all}$  increases as  $E$  and  $N$  increases.

Question 1-2 If there are  $E$  bits of energy to put into  $N$  molecules, what is the probability that there will be  $\varepsilon_i$  bits in the first molecule?  $N$  and  $E$  are assumed constant, whereas  $\varepsilon_i$  is considered to be variable.

Answer: That is, what is the fraction of the number of permutations if we put  $\varepsilon_i$  bits in the first molecule and  $(E - \varepsilon_i)$  bits among the remaining  $N - 1$  molecules? Now let's calculate the number of ways to distribute the rest of energy  $(E - \varepsilon_i)$  bits among the remaining  $N - 1$  molecules. If there are  $\varepsilon_i$  bits in the first molecule, there must be  $(E - \varepsilon_i)$  bits left to distribute among the remaining  $N - 1$  molecules, which can be distributed in  $\Omega_{\varepsilon_i}$  ways.

$$\Omega(\varepsilon_i) = \frac{(E-\varepsilon_i+N-2)!}{(E-\varepsilon_i)!(N-2)!} \quad (1.2)$$

So if the  $E$  bits of energy are distributed equally likely among  $N$  molecules, the probability of having  $\varepsilon_i$  bits in the first molecule is  $p_i(\varepsilon_i) = \Omega(\varepsilon_i)/\Omega_{all}$ , and the number of microstates if we put  $\varepsilon_i$  bits in the first molecule is  $\Omega(\varepsilon_i)$ .

## 1.2 Finding the Boltzmann Probability Distribution

In order to eliminate these factorials in Eq. 1.2, we refer to James Stirling, a Scottish mathematician who led to the conclusion for very large  $N$ .

$N! \approx N^N e^{-N} \sqrt{2\pi N}$ . When  $N$  is very large, the contribution of the root is very small.

Derivation of Stirling's approximation is written below.

$$\begin{aligned} \int_1^N \ln X \, dX &< \ln N! = \ln 1 + \ln 2 + \ln 3 + \dots + \ln N = \sum_1^N \ln X \\ &< \int_1^N \ln X \, dX + \ln N. \\ \int_1^N \ln X \, dX &= [X \ln X - X]_1^N = N \ln N - N + 1 \end{aligned}$$

$$N \ln N - N + 1 < \ln N! < N \ln N - N + 1 + \ln N = (N + 1) \ln N - N + 1.$$

$N! \approx e^{N \ln N} e^{-N}$  when  $N$  is very large.

$$\frac{d \ln(N!)}{d N} \approx N \cdot \frac{1}{N} + \ln N - 1 = \ln N$$

We rewrite Eq. 1.2 in natural log form.

$$\ln \Omega(\varepsilon_i) = \ln(E - \varepsilon_i + N - 2)! - \ln(E - \varepsilon_i)! - \ln(N - 2)!$$

If  $E$  is very large,  $\varepsilon_i$  is considered a continuous variable.

Taking the derivatives with respect to  $\varepsilon_i$ , we get

$$\begin{aligned} \frac{d \ln \Omega(\varepsilon_i)}{d \varepsilon_i} &= \frac{d \ln(E - \varepsilon_i + N - 2)!}{d(E - \varepsilon_i + N - 2)} \times \frac{d(E - \varepsilon_i + N - 2)}{d \varepsilon_i} - \frac{d \ln(E - \varepsilon_i)!}{d(E - \varepsilon_i)} \times \frac{d(E - \varepsilon_i)}{d \varepsilon_i} \\ &= \frac{d \ln(E - \varepsilon_i + N - 2)!}{d(E - \varepsilon_i + N - 2)} \times (-1) - \frac{d \ln(E - \varepsilon_i)!}{d(E - \varepsilon_i)} \times (-1) \end{aligned}$$

since  $d(E - \varepsilon_i + N - 2)/d \varepsilon_i = -1$  and  $d(E - \varepsilon_i)/d \varepsilon_i = -1$ .

Now we apply the Stirling's Approximation,  $\frac{d \ln(N!)}{d N} \approx \ln N$  to the preceding equation since  $N$  and  $E$  are very large numbers.

$$\frac{d \ln \Omega(\varepsilon_i)}{d \varepsilon_i} \approx -\ln(E - \varepsilon_i + N - 2) + \ln(E - \varepsilon_i) = -\ln \frac{E - \varepsilon_i + N - 2}{E - \varepsilon_i} \quad (1.3)$$

We have a lot more total bits of energy than molecules, and the number of bits of energy in one molecule is never anything like as large as the total number of either molecules or total bits of energy.  $n_0$  is the number of molecules which has energy 0,  $n_1$  is the number of molecules with energy 1,  $n_2$  is the number of molecules with energy 2, and so on.  $n_E$  is the number of molecule with the total amount of energy  $E$ , which is one at most. The probability of having the total amount of energy,  $E$  in the first molecule and the rest has none, is nearly zero.  $p(E) = \Omega(E) / \Omega_{all} = 1 / \Omega_{all} \approx 0$ . It is clear that having a very large amount of energy,  $\varepsilon_i$  in the first molecule is far less likely to happen since it will decrease the number of ways of arranging the remaining energy into the remaining molecules. The number of molecules with higher energy might be smaller otherwise the resultant sum of energy will exceed the fixed value of total energy.  $\langle \varepsilon \rangle$  is the average energy per molecule. There are two constraints for the distribution of molecules in each energy compartment.

$$N = \sum_{i=0}^E n_i = n_0 + n_1 + n_2 + n_3 + \cdots + n_E$$

Putting more energy into the particular molecule will less likely happen because the number of ways of arranging the remaining energy into the remaining molecules will decrease.

$$\begin{aligned} E_{total} &= \sum_{i=0}^E n_i \times \varepsilon_i = N \cdot \langle \varepsilon \rangle \\ &= n_0 \times 0 + n_1 \times 1 + n_2 \times 2 + n_3 \times 3 + \cdots + n_{E-1} \times (E - 1) + n_E \times E \end{aligned}$$



Question 1-3 1) Why  $\Omega(E)$  equals one? 2) Why  $n_E$  is one at most? 3) What is the most probable value of  $n_i$ ? 4) Which is larger,  $n_3$  or  $n_5$ ?

Answer: 1) Substitute  $E$  for  $\varepsilon_i$  in Eq. 1.2. Then  $\Omega(E) = \frac{(E-E+N-2)!}{(E-E)!(N-2)!} = 1$  since  $0! = 1$ . 2)  $n_E$  is one at most since only one molecule can hold the total amount of energy  $E$ , which is unlikely to happen because  $p(E) = \frac{\Omega(E)}{\Omega_{all}} = \frac{1}{\Omega_{all}} \approx 0$  since  $\Omega_{all}$  is very large number. 3) The most probable value of  $n_i$  is zero. 4)  $n_3$ .

Question 1-4 Each atom oscillates in three directions and has 3 oscillators. Consider a solid that has a collection of  $N$  oscillators in  $N/3$  atoms for which the distribution of oscillators over energy is denoted by  $n_0, n_1, n_2, \dots, n_E$ . The  $n_0$  is the number of oscillators which has energy 0, The  $n_1$  is the number of oscillators with energy 1, The  $n_2$  is the number of oscillators with energy 2, and so on. Count the number of ways of placing  $n_0$  oscillators in the compartment of energy 0 and successively  $n_1$  oscillators in the compartment of energy 1. The number of counting is equal to the total number of microstates due to the successive arrangement.

Answer: We do not use Eq. 1.2 since we set the number of oscillators with energy 0 and 1 to  $n_0$  and  $n_1$  respectively. If we have a total of 3 oscillators and putting 2 oscillators from 3 into the compartment of energy 0 which has two rooms, the number of possible ways of arrangement in the compartment of energy 0 is three in the first energy room, and two ( $2=3-1$ ) in the second room. The number of total ways of the arrangement is  $3 \times 2$ . Since the oscillators are indistinguishable, we must divide  $3 \times 2$  by 2.

In general we have  $N \times (N-1) \times (N-2) \times \dots \times (N-n_0+1)/n_0!$  permutations to put  $n_0$  oscillators into the compartment of energy 0 from indistinguishable  $N$  oscillators.

If we successively put  $n_1$  oscillators in the compartment of energy 1, the number of ways of the arrangement is

$$(N - n_0)(N - n_0 - 1)(N - n_0 - 2) \dots (N - n_0 - n_1 + 1)/n_1!$$

Total number of microstates is not additive but multiple since we have the number of ways of the successive arrangement corresponding to each of the first starting arrangement.

$$\begin{aligned} \Omega_{all} &= \frac{N(N-1)(N-2) \dots (N-n_0+1)}{n_0!} \times \frac{(N-n_0)(N-n_0-1)(N-n_0-2) \dots (N-n_0-n_1+1)}{n_1!} \\ &= \frac{N!}{n_0! n_1! (N-n_0-n_1)!} \end{aligned}$$

We assume that  $E \gg \varepsilon_i = i$  and  $E \gg 2$ .

So we will make no significant error in Eq. 1.3 above even if we ignore the smaller energy bits,  $\varepsilon_i$  and 2, but we can't ignore  $N$ .

$$\frac{d \ln \Omega(\varepsilon_i)}{d \varepsilon_i} \approx -\ln \frac{E+N}{E} = -\ln \left( 1 + \frac{N}{E} \right)$$

But for very small  $x$ ,  $e^x \approx 1 + x$ . Since we are considering  $E \gg N$ ,  $x = \frac{N}{E}$  is very small number, but not zero. We get the following approximation.

$$\begin{aligned} \frac{d \ln \Omega(\varepsilon_i)}{d \varepsilon_i} &\approx -\ln (e^{N/E}) = -\frac{N}{E} \\ \int d \ln \Omega(\varepsilon_i) &\approx -\frac{N}{E} \int d\varepsilon_i \\ \ln \Omega(\varepsilon_i) &\approx -\frac{\varepsilon_i}{E/N} + \text{const} \end{aligned}$$

This says that a plot of the log of  $\Omega(\varepsilon_i)$  vs. the number of energy bits is a straight line whose slope is  $-N/E$ . The probability of putting a certain number of energy bits into the particular molecule is proportional to  $e^{-\frac{\varepsilon_i}{E/N}}$ .

$$p_i(\varepsilon_i) \propto e^{-\frac{\varepsilon_i}{E/N}}$$

This is called the Boltzmann distribution where  $E/N$ , the total number of bits of energy divided by the number of molecules is the average energy per molecule. In the Boltzmann model the average is assumed to be  $kT$  (see the next page) which has the same units of  $\varepsilon_i$ .  $k$  is the Boltzmann constant and  $T$  is temperature.

**Table 1.1** Number of molecules with the amount of energy  $i$ .

Amount of energy, $\varepsilon_i$	0	1	2	3	4	$E$
Number of molecules, $n_i$	$n_0$	$n_1$	$n_2$	$n_3$	$n_4$	$n_E$

$\varepsilon_i = 0, 1, 2, 3, \dots, E$ . A total amount of energy,  $E$  increases with increasing temperature.

$n_i$  is the number of molecules which have the energy  $\varepsilon_i = i$ .

$n_E$  is one at most since only one molecule can hold the total amount of energy, which is unlikely to happen.  $n_0$  is the largest among  $n_i$ .

Probability function of a molecule in state  $i$  with energy  $\varepsilon_i$  can be described as  $p_i(\varepsilon_i) = a e^{-\frac{\varepsilon_i}{kT}}$ .

$$\ln p_i(\varepsilon_i) = \ln a - \frac{\varepsilon_i}{kT}$$

What is  $a$ ?

$$\sum p_i(\varepsilon_i) = 1 = a \sum_{i=0} e^{-\varepsilon_i/kT} \quad a = \frac{1}{\sum_{i=0} e^{-\varepsilon_i/kT}}$$

$$p_i(\varepsilon_i) = \frac{e^{-\varepsilon_i/kT}}{q} \quad \text{where } q = \frac{1}{a} = \sum_{i=0} e^{-\varepsilon_i/kT}$$

is called *molecular partition function*.

(1.4)

If the total number of molecules is  $\sum_{i=0}^E n_i = N$ , we obtain

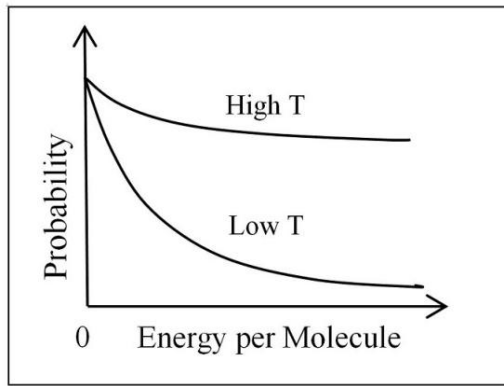
$$n_i = Np_i(\varepsilon_i) = \frac{Ne^{-\varepsilon_i/kT}}{q} \text{ and } p_i(\varepsilon_i) = \frac{n_i}{N} = \frac{e^{-\varepsilon_i/kT}}{q}. \quad (1.5)$$

Since  $\frac{n_0}{N} = \frac{e^{-0/kT}}{q} = \frac{1}{q}$ , we get the following equation.

$$n_i = n_0 e^{-\varepsilon_i/kT} \quad (1.6)$$

$$\frac{p_i(\varepsilon_i)}{p_j(\varepsilon_j)} = \frac{n_i}{n_j} = e^{-(\varepsilon_i - \varepsilon_j)/kT} \quad (1.7)$$

$$\Delta\varepsilon = (\varepsilon_j - \varepsilon_i) = kT \ln \frac{n_i}{n_j}$$



**Figure 1.1** Probability versus individual energy.

Why  $p_i(\varepsilon_i)$  and  $n_i$  is maximum at  $\varepsilon_i = 0$  and decreases steadily with increasing  $\varepsilon_i$ ? We have a given total amount of energy. Putting more energy into the particular molecule will decrease the number of ways of arranging the remaining energy into the remaining molecules.

The expected value of energy is defined as follows.

$$E(\varepsilon) = \sum_{\varepsilon_i=0} \varepsilon_i p_i(\varepsilon_i) = \frac{\sum_{\varepsilon_i=0} \varepsilon_i n_i}{N}.$$

Replacing  $\frac{n_i}{N}$  by  $\frac{e^{-\varepsilon_i/kT}}{q}$  from Eq. 1.5, we get

$$E(\varepsilon) = \frac{\sum_{\varepsilon_i=0} \varepsilon_i n_i}{N} = \frac{1}{q} \sum_{\varepsilon_i=0} \varepsilon_i e^{-\varepsilon_i/kT}.$$

If the energy levels are spaced equally and close together relative to  $kT$ , then we can convert the sum into integrals without introduction of state density. Kinetic energy from translation, rotation and vibration, and potential energy of oscillator can be described in the form of  $\varepsilon = ay^2$ .

$$q = \int_0^{\infty} e^{-\varepsilon/kT} d\varepsilon = 2kT \int_0^{\infty} x e^{-x^2} dx$$

$$E(\varepsilon) = \frac{1}{q} \int_0^{\infty} \varepsilon e^{-\varepsilon/kT} d\varepsilon = \frac{kT \int_0^{\infty} x^3 e^{-x^2} dx}{\int_0^{\infty} x e^{-x^2} dx}$$

where  $x^2 = \frac{ay^2}{kT} = \frac{\varepsilon}{kT}$  and  $d\varepsilon = 2kTx dx$ .

Integrating by parts we get  $\int_0^{\infty} x^3 e^{-x^2} dx = \frac{1}{2}$  and  $\int_0^{\infty} x e^{-x^2} dx = \frac{1}{2}$ .

$$E(\varepsilon) = kT$$

The average energy per molecule of the Boltzmann model is set as  $kT$ . So it is reasonable to get  $kT$  if you calculate the average energy using the Boltzmann equation. It is also known that solving the Schrodinger equation for harmonic oscillator of diatomic molecules, the energy spacing between successive states is constant.  $\varepsilon_i = \left(i + \frac{1}{2}\right)hf$ . So we can calculate the average energy of the vibration model just like the Boltzmann model without introduction of state density. But for translational energy in a box, the energy spacing between successive states is progressively larger as  $i$  increases. We will consider it later in 1.12 along with the translational energy of monatomic gas.

Example 1-1 Assume perfect atomic lattice with a collection of oscillators at  $T \approx 0 K$ . Set ground state energy  $\varepsilon_0 = 0$ . Calculate  $q$  and  $p_0$ .

If energies of all other states are much larger than  $kT$ ,

$$q = \sum_{i=0}^E e^{-\varepsilon_i/kT} = e^{-0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT} + e^{-\varepsilon_3/kT} + \dots + e^{-\varepsilon_E/kT} \approx 1.$$

$$p(\varepsilon_0 = 0) = \frac{e^{-\varepsilon_0/kT}}{q} \approx 1. \quad p(\varepsilon_1) \approx p(\varepsilon_2) \approx p(\varepsilon_i \neq 0) \approx 0.$$

At  $T \approx 0 \text{ K}$  all the oscillators are at ground state. The constituent atoms sit at the particular position without translation, rotation, and vibration. All of them don't have any energy except bonding energy.

Example 1-2 Let's calculate probability,  $p_i(\varepsilon_i)$  at very high temperature. Consider atomic lattice of solid that has a collection of  $N$  oscillators. Set ground state energy equals zero. What is the average energy of the solid with  $N$  oscillators?

If  $\varepsilon_i$  is relatively very small compared to  $kT$ ,  $n_i = n_0 e^{-\varepsilon_i/kT} \approx n_0$ .

$$p_i(\varepsilon_i) = \frac{n_i}{N} \approx \frac{n_0}{N}.$$

In a range of smaller  $\varepsilon_i$ , the oscillators are equally distributed among all states at very high temperature. The average energy of the solid is  $Nkt$ .

### 1.3 Interacting System

Actually in the universe particles in a system are interacting. Consider a system which contains a number of solids and in the system these are interacting with each other. Since energy consists of discrete energy bits, the energy of a solid also have discrete values  $E_1, E_2, E_3, \dots, E_E$ . Each solid can exchange energy with each other. If we make a number of observations of a solid at different times, we will observe that a solid might have a different  $E_i$  at each time. The thermodynamic internal energy is defined as the average energy of all solids in the system when measured in a large number of observations.

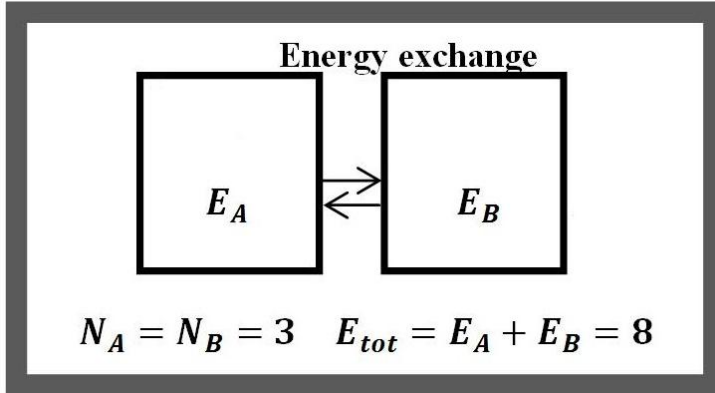
Our simple model is now a system of two small identical interacting solids in contact with a large reservoir isolated from the rest of the universe and each

solid oscillates in three directions and has 3 oscillators. Solids with  $E_A$  and  $E_B$  can exchange energy. We assume a total energy of all solids is constant since the system is isolated from the rest of the universe. *The total energy,  $E_{tot} = E_A + E_B$  is fixed and constant.*

There are some microstates for the interacting system specified by the temporary constrained values of  $E_A$  and  $E_B$ . Using the following equation below, the calculated results of microstates are shown in Table 1.2.

$$\Omega(E) = \frac{(E+N-1)!}{E!(N-1)!} \text{ where } E = 0, 1, 2, 3, 4, 5, \dots, E \text{ and } N \text{ oscillators.}$$

If  $E_{tot} = 8$  and  $N_A = N_B = 3$  for each solid, over a long time scales the number of total microstates possibly appearing to the system is 1287 as shown in Table 1.2. All 1287 microstates are equally probable. *If you look at the system at any instant, you are equally likely to find one microstate in any of 1287 microstates. This assumption is called the fundamental assumption of statistical mechanics.* In Table 1.2 you will see the maximum of  $\Omega_{all}(E)$  is at  $E_A = E_B = E_{tot}/2 = \langle E \rangle = 4$ . We assume that at equilibrium  $E_A$  is about the same as  $E_B$ . So the many of  $\Omega_{all}$  will appear about the average energy,  $\langle E \rangle$ . The peak of  $\Omega_{all}$  will become higher and its width gets narrower when  $N$  gets larger. It will be justified mathematically.



**Figure 1.2** Each solid A and B has 3 oscillators and they can exchange energy.

**Table 1.2** Combined system and multiplicities.

$E_A$	$\Omega_A(E_A)$	$E_B$	$\Omega_B(E_B)$	$\Omega_{all} = \Omega_A \Omega_B$
0	1	8	45	45
1	3	7	36	108
2	6	6	28	168
3	10	5	21	210
4	15	4	15	225
5	21	3	10	210
6	28	2	6	168
7	36	1	3	108
8	45	0	1	45
				Total=1287

Now we will make a mathematical justification for a system with two large interacting solids where atoms of a solid cannot exchange positions, but solids can exchange their energy. Each polyatomic solid has a huge number of oscillators( $N$ ), and the total energy( $E$ ) in the system is assumed constant since the system is isolated from the rest of the universe.

If  $N$  is huge, Eq. 1.1 becomes 
$$\Omega(E) = \frac{(E+N-1)!}{E!(N-1)!} \approx \frac{(E+N)!}{E! N!}.$$



We will take the natural logarithm of Eq. 1.1, apply Stirling's approximation and rewrite it below.

$$\begin{aligned} \ln \Omega(E) &= \ln \frac{(E+N)!}{E!(N)!} = \ln (E+N)! - \ln E! - \ln N! \\ &\approx (E+N) \ln (E+N) - (E+N) - E \ln E + E - N \ln N + N \\ \ln \Omega(E) &\approx (E+N) \ln (E+N) - E \ln E - N \ln N. \quad (1.8) \\ \ln (E+N) &= \ln E(1+N/E) = \ln E + \ln(1+N/E) \end{aligned}$$

Since we assume  $E \gg N$ ,  $N/E$  is very small and so we obtain the following approximation using Taylor's expansion of the logarithm,  $\ln(1+x) \approx x$  for  $x \ll 1$ .

$$\ln(E+N) \approx \ln E + N/E$$

Substituting  $\ln E + N/E$  for  $\ln(E+N)$  in Eq. 1.8, we obtain

$$\begin{aligned} \ln \Omega(E) &\approx (E+N)(\ln E + N/E) - E \ln E - N \ln N \\ &= N \ln E - N \ln N + N + N^2/E. \\ \ln \Omega &\approx N (\ln E/N) + N + N^2/E \quad (1.9) \end{aligned}$$

The last term is negligible compared to the others with the assumption of  $E \gg N$ .

$$\begin{aligned} \ln \Omega(E) &\approx N (\ln E/N) + N \\ \Omega(E) &\approx e^{N (\ln E/N)} e^N = (eE/N)^N \quad (1.10) \end{aligned}$$

It is easily understandable that  $\Omega$  is a very large number and will increase a lot by a small positive change of  $E$  and  $N$  in Eq. 1.10.

Let's apply the result to a system with two large interacting solids model.

$$\Omega_{all}(E) = (eE_A/N)^N (eE_B/N)^N = (e/N)^{2N} (E_A E_B)^N \quad (1.11)$$

It might have a peak at  $E_A = E_B = E_{tot}/2 = \langle E \rangle$ .

$$\Omega_{max} = (e/N)^{2N} (E_{tot}/2)^{2N} \quad (1.12)$$

To find what the graph looks like near the peak, we substitute  $E_{tot}/2 + \Delta E$  and  $\frac{E_{tot}}{2} - \Delta E$  for  $E_A$  and  $E_B$  respectively in Eq. 1.11.

$$\Omega_{all}(E) = (e/N)^{2N} (E_A E_B)^N = (e/N)^{2N} [(E_{tot}/2)^2 - \Delta E^2]^N \quad (1.13)$$

We take the logarithm to simplify the second factor of Eq. 1.12.

$$\begin{aligned} & \ln[(E_{tot}/2)^2 - \Delta E^2]^N \\ &= N \ln [(E_{tot}/2)^2 - \Delta E^2] = N \ln [(E_{tot}/2)^2 (1 - (2\Delta E/E_{tot})^2)] \\ &= N [\ln (E_{tot}/2)^2 + \ln (1 - (2\Delta E/E_{tot})^2)] \approx N \left[ \ln \left( \frac{E_{tot}}{2} \right)^2 - \left( \frac{2\Delta E}{E_{tot}} \right)^2 \right]. \end{aligned}$$

By exponentiation of the last expression, we obtain

$$[(E_{tot}/2)^2 - \Delta E^2]^N \approx e^N [\ln (E_{tot}/2)^2 - (2\Delta E/E_{tot})^2].$$

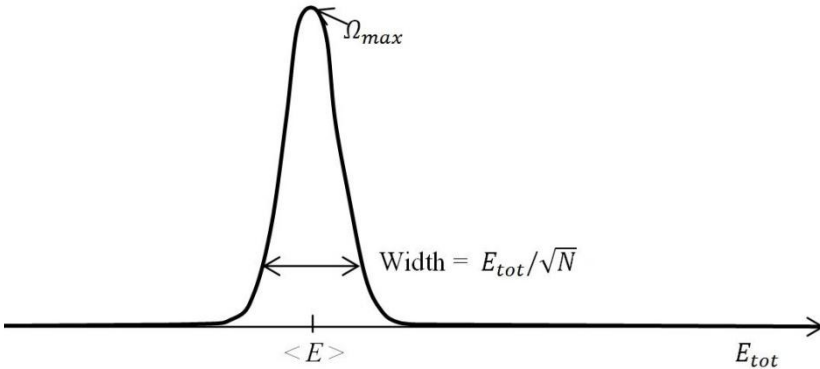
Putting this back into Eq. 1.13, we will find a function called a Gaussian.

$$\begin{aligned} \Omega_{all}(E) &= (e/N)^{2N} [(E_{tot}/2)^2 - \Delta E^2]^N \\ &\approx (e/N)^{2N} e^{N \ln (E_{tot}/2)^2} e^{-N (2\Delta E/E_{tot})^2} = \Omega_{max} e^{-N (2\Delta E/E_{tot})^2}. \end{aligned}$$

The number of microstates falls down to  $1/e$  of its maximum value when  $\Delta E = E_{tot}/2\sqrt{N}$ .

The width of a peak is about  $E_{tot}/\sqrt{N}$ . If  $N = 10^{20}$ , the width is  $E_{tot} \times 10^{-10}$  which is very narrow.

Two large interacting solids have a very narrow high peak of  $\Omega_{all}(E)$  and so  $\Omega_{all}(E)$  is not be scattered. The maximum number of microstates,  $\Omega_{max}(E)$  appears about  $E_A = E_B = \langle E \rangle$ .



**Figure 1.3** The distribution of total microstates about  $\langle E \rangle$  as a function of  $E$  in a large interacting system.

When two large interacting solids are at equilibrium in an isolated system, all microstates will have about the same energy,  $\langle E \rangle$  and then all degenerate microstates have the same probability to appear at  $\langle E \rangle$ .

This can be true for more than two identical interacting solids system. Solids can be replaced with identical molecules which interact with each other. When identical interacting molecules are at equilibrium in an isolated system, all microstates will have about the same energy,  $\langle E \rangle$  and then all degenerate microstates have the same probability to appear at  $\langle E \rangle$ .

## 1.4 Partition Functions and Degeneracy

If there are some numbers of microstates with the same energy, the states are said to be *degenerate*. The state of being degenerate is called *degeneracy*. An interacting system has degenerate microstates at  $\langle E \rangle$  as described in 1.3. Locational exchanges of gaseous particles in the space also cause degenerate microstates if there is no potential energy in a system.

$g_{\varepsilon_i}$  is the number of degenerate microstates with the same molecular energy  $\varepsilon_i$ .

Molecular partition function ( $q$ ) is  $q = \sum_{i=0} e^{-\varepsilon_i/kT} = \sum_{\varepsilon_i=0} g_{\varepsilon_i} e^{-\varepsilon_i/kT}$ .

Canonical partition function ( $Q$ ) is *the partition function* for a system which is composed of a number of solids or particles.

$$Q = \sum_{i=0} e^{-E_i/kT} = \sum_{E_i=0} \Omega_{E_i} e^{-E_i/kT}.$$

$E_i$  is *the system energy of microstate  $i$* .  $\Omega_{E_i}$  is the number of degenerate microstates with the system energy,  $E_i$ .

System energy is considered as the sum of the energy of each particle,  $n_1, n_2, n_3, \dots, n_N$ .

$$E_i = \varepsilon_{n_1,i} + \varepsilon_{n_2,i} + \varepsilon_{n_3,i} + \dots + \varepsilon_{n_N,i}$$

$Q$  can be expressed by  $q$  after separating the partition function for a system.

$$\begin{aligned} Q &= \sum_{i=0} e^{-E_i/kT} = \sum_{i=0} e^{-(\varepsilon_{n_1,i} + \varepsilon_{n_2,i} + \varepsilon_{n_3,i} + \dots + \varepsilon_{n_N,i})/kT} \\ &= \left( \sum_{n_1,i=0} e^{-\varepsilon_{n_1,i}/kT} \right) \left( \sum_{n_2,i=0} e^{-\varepsilon_{n_2,i}/kT} \right) \left( \sum_{n_3,i=0} e^{-\varepsilon_{n_3,i}/kT} \right) \dots \left( \sum_{n_N,i=0} e^{-\varepsilon_{n_N,i}/kT} \right) = q^N. \end{aligned}$$

$Q = q^N$  for distinguishable particles that can exchange positions.

$Q = q^N/N!$  for indistinguishable particles that can exchange positions.

## 1.5 Translational Distribution of Gasses

In contrast to solid the number of microstates of gaseous molecules largely depends on its volume because of the outcome of exchanging positions. So the number of microstates of gases is much greater than solids due to a huge number of its possible location for a particle. Here we will discuss the number of microstates for gaseous particles in the space. *An ideal gas is assumed to have no microstates associated with molecular rotation, vibration, interaction and etc., but it has translational kinetic energy.*

Now we have the gaseous molecule whose molecular size is assumed to be  $10^{-30} m^3$ . If total volume of the space is  $1m^3$ , then each gaseous molecule can take  $10^{30}$  possible locations. One molecule can enter one of  $10^{30}$  energy cells in the space of  $1m^3$ . So the number of microstates provided for one molecule is equal to  $10^{30}$ . We assume that there is no potential energy in the space and so the molecule does not obtain the potential energy due to changing its location. Hence the number of degenerate microstates due to location is  $10^{30}$ .

Let's calculate the number of microstates caused by location of  $N$  gaseous molecules in  $1m^3$ .

The number of degenerate microstates for distinguishable  $N$  molecules in the space is

$$\Omega_{location} = 10^{30}(10^{30} - 1)(10^{30} - 2) \dots (10^{30} - N + 1) \approx 10^{30N}.$$

For indistinguishable  $N$  molecules,  $\Omega_{location} \approx 10^{30N}/N!$ .

Example 1-3 We consider the gaseous molecule which molecular size is assumed to be  $10^{-30} m^3$ . We assume that all molecules are indistinguishable and potential energy in the space is negligible. We have  $10^{30}$  energy cells available for each molecule in the space of  $1m^3$ . If the system has one mole of gaseous molecules, count the number of degenerate microstates due to locational disorder in the space of  $1m^3$ .  $N_a$ (Avogadro's constant) =  $6.02 \times 10^{23}$

The number of degenerate microstates for distinguishable  $N$  molecules is

$$\Omega_{location} = (10^{30}) (10^{30} - 1) (10^{30} - 2) \dots (10^{30} - N_a + 1) \approx (10^{30 \times N_a}).$$

The number of degenerate microstates for indistinguishable  $N$  molecules is  $\Omega_{location} \approx (10^{30 \times N_a})/N_a!$  since  $N$  distinguishable particles have  $N!$  times more permutations than that of indistinguishable particles have.

Since  $N$  is large, we can apply the Stirling's approximation,  $N! \approx e^{-N} N^N$ .

$$\Omega_{location} = \frac{(10^{30 \times N_a})}{e^{-N_a(N_a)^{N_a}}} \approx e^{N_a} (10^6)^{N_a} \approx (10^{0.4})^{N_a} (10^6)^{N_a} = (10^{6.4})^{N_a}.$$

For gases, the number of microstates is huge as a result of the translational distribution in the space. However for liquids and solids, all space is filled with molecules and so the number of microstates arose from location largely depends on their impurity, and much smaller compared to that of gases. The number of microstates for pure solid is considered to be one at 0 K and increases as temperature goes up due to starting of vibrations.

Question 1-5 If the ideal liquid molecules is composed of 100 molecules of A and 400 molecules of B, count the number of microstates after mixing. We do not consider additional states which are associated with rotation, vibration, and etc.

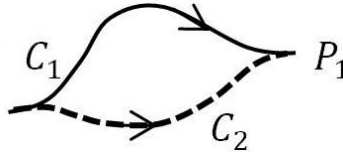
$$\text{Answer: } \Omega_{mix} = \frac{500!}{100! \times 400!}$$

## 1.6 Changes in Energy and Enthalpy in Relation to Changes in States of the System

### 1.6.1 Internal Energy as a State Function

The first law of thermodynamics is stated from the experience as follows. The work done to the surroundings is equal to the heat withdrawn from the surroundings if the process of a system is carried out in any cyclic transformation.  $\oint (dq + dw) = 0$  for all cycles.

The system cannot do work without the equivalent quantity of heat supply in a cyclic system.



**Figure 1.4** Two different paths between two thermodynamic states.

$$\oint (dq + dw) = \int_{C_1} (dq + dw) - \int_{C_2} (dq + dw) = 0$$

$$\int_{C_1} (dq + dw) = \int_{C_2} (dq + dw)$$

Corollary, the sum of  $q$  and  $w$  is independent of path whereas  $w$  and  $q$  depends on path individually. This means that there is a state function whose differential is  $dq + dw$ .

The differentials of the internal energy is defined by

$$dU \equiv dq + dw = dq - p_{ext}dV, \oint dU = 0 \quad (1.14)$$

where  $q$  is heat and the sign of heat transfer,  $dq$  from the surrounding to the system is positive.  $P_{ext}$  is external pressure and  $V$  is volume. If  $dV$  is positive,  $dw = -p_{ext}dV$  is the work done to the outside that is negative.

The difference in energy only depends on the initial and final states of the system.

$$\Delta U = \int_{state1}^{state2} dU = U_2 - U_1 = q + w$$

The internal energy of the universe is constant, in other words it is conserved.

$$\Delta U_{universe} = \Delta U_{system} + \Delta U_{surrounding} = 0$$

The energy has a definite value when the state of a system is specified by two of state properties such as pressure ( $P$ ), volume ( $V$ ) or temperature ( $T$ ). Since

the internal energy is a function of  $T$  and  $V$ , the differential of the internal energy is expressed mathematically below.

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (1.15)$$

The difference of energy between the value at initial condition and the value at final condition can be measurable at certain condition described below.

If the system changes at constant volume,  $dU = dq_V - p_{ext} \times 0 = dq_V = \left(\frac{\partial U}{\partial T}\right)_V dT$ .

$q_V$  denotes the amount of heat transfer under constant volume.  $\left(\frac{\partial U}{\partial T}\right)_V = \frac{dq_V}{dT} = C_V$ . The sign  $C_V$  is the heat capacity of the system at constant volume and easily obtained by drawing tangent line of  $q_V$  versus temperature. The heat capacity is the amount of heat transfer needed to raise one degree of its temperature. The substance with a large heat capacity like a thick porcelain container needs more heat supply to raise its temperature and the temperature drops slowly when it is left.

$$dU = C_V dT$$

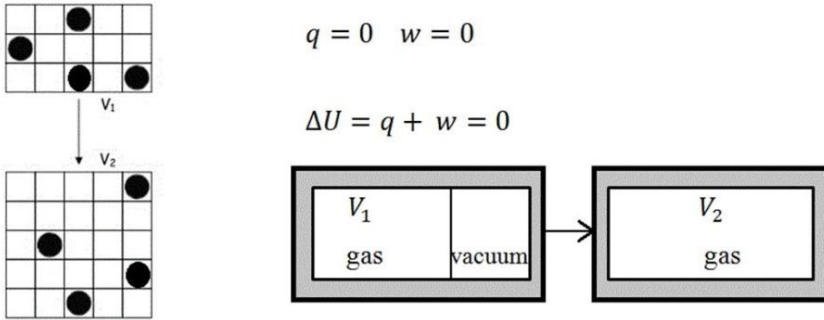
$$\Delta U = \int_{T_1}^{T_2} C_V(T) dT \quad (1.16)$$

*The internal energy is defined as expected value of the net energy of molecules as a whole.  $U \equiv E(E) = \sum_i E_i p_i$  where  $E_i$  is the system energy in an assembly of molecules of state  $i$ .* The internal energy of an ideal gas is calculated in 1.12. The result is  $U = (3/2)RT$  (Eq. 1.33) and  $C_V = (3/2)R$  for one mole of ideal gas. An ideal gas has no vibration and no rotation like a monoatomic gas and is assumed no interaction between molecules. It has only translational energy and is considered that there is no contribution of bonding energy of molecules to the properties of the system.



### 1.6.2 Joule Free Expansion of Gasses

Joule free expansion is a process of adiabatic gas expansion to vacuum where no heat exchanges and no works are done. Very small temperature changes are observed for real gases experimentally. We will calculate the change of internal energy associated with the free expansion.



**Figure 1.5** Adiabatic expansion of a gas to vacuum.

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = 0$$

What does  $\left(\frac{\partial U}{\partial V}\right)_T$  mean? We want to know the value of  $\left(\frac{\partial U}{\partial V}\right)_T$ . We need to convert it into the measurable term.

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V \left(\frac{\partial T}{\partial V}\right)_U \tag{1.17}$$

$\left(\frac{\partial T}{\partial V}\right)_U$  is named Joule coefficient and measured experimentally. They found it was a very small and negative value for real gases. For an ideal gas the Joule coefficient is considered zero.  $dU = C_V dT$ . It is always true for ideal gas. It is almost true for monatomic gases and approximately true for other gases. Because  $\left(\frac{\partial U}{\partial V}\right)_T \approx 0$ , the equation  $dU = C_V dT$  doesn't require that the transformation should be carried out under constant volume.  $C_V/R$  of monatomic gases such as He, Ne, Ar and Kr at 298.15 K is 1.5 /mole which is

smaller than the other gases. Those of diatomic gases are from 2.5 to 3.4 per mole. Those of triatomic gases are from 3.5 to 4.0 per mole.

Example 1-4 Calculate  $\Delta U$  and  $q_V$  for the transformation of one mole of He from 25 °C to 37°C. We assume there is almost no interaction between molecules.

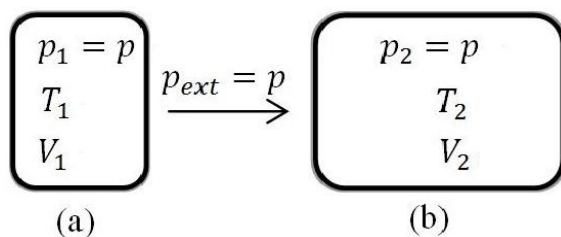
$$\Delta U = \frac{3}{2}R\Delta T = \frac{3}{2}R(12\text{K}) . \Delta U = 1.5(8.31 \text{ J/K} \cdot \text{mol})(12\text{K}) = 150 \text{ J/mol.}$$

$$q_V = \Delta U = 150 \text{ J/mol}$$

Since we assumed there is almost no interaction between molecules, the gas is considered as an ideal gas.

### 1.6.3 Enthalpy as a State Function

If the system changes at constant pressure and if the system does only reversible  $pV$  work, external pressure is assumed to be in equilibrium to internal pressure during the system change. The sign  $q_p$  denotes the amount of heat transfer under constant pressure. If it is positive, the system gains an increase in temperature and so the internal energy will increase but at the same time the system will do work to the outside as the volume increases.



**Figure 1.6** The system changes at constant pressure. (a) Initial state. (b) Final state.

$$\Delta U = q_p - p\Delta V$$

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

$$U_2 + p_2V_2 - (U_1 + p_1V_1) = q_p$$

since  $p_1 = p_2 = p$ .

We define enthalpy as  $H \equiv U + pV$ . Enthalpy depends on the state of a system. Like the internal energy, it has a definite value when the state of a system is specified by two of state properties such as  $p$ ,  $V$  or  $T$ . It doesn't depend on the path of a process. That is, enthalpy is a state function.

Under a constant pressure,

$$\Delta H = H_2 - H_1 = q_p . \quad (1.18)$$

The heat transfer at constant pressure between the system and the surroundings is equal to the change in enthalpy. The heat withdrawn from the surrounding is equal to the increase in enthalpy.

Relationship between the internal energy and enthalpy under constant pressure is as follows.

$$\Delta U = q_p - p\Delta V = \Delta H - p\Delta V. \quad \Delta H = \Delta U + p\Delta V.$$

For gases,  $\Delta H$  and  $\Delta U$  differ by one to two percent. For liquids and solids, the difference is negligible.  $\Delta H$  is easily measurable.

Example 1-5  $\left(\frac{\partial U}{\partial T}\right)_p = \frac{dq_p}{dT} = C_p$  is the heat capacity of the system at constant pressure. Calculate  $C_p$  for one mole of an ideal gas and  $C_p/C_v$ . Use the formula,  $pV = nRT$  for an ideal gas.

$q_p$  denotes the amount of heat transfer under constant pressure. If it is positive, the system gains an increase in temperature and so the internal energy will increase but at the same time the system will do work to the outside as the volume increases. For one mole of an ideal gas  $\Delta U = \left(\frac{3}{2}\right)R\Delta T$  and  $\Delta U = q_p - p\Delta V = q_p - R\Delta T$ .

$$q_p = (5/2)R\Delta T. \quad C_p = 5/2 R.$$

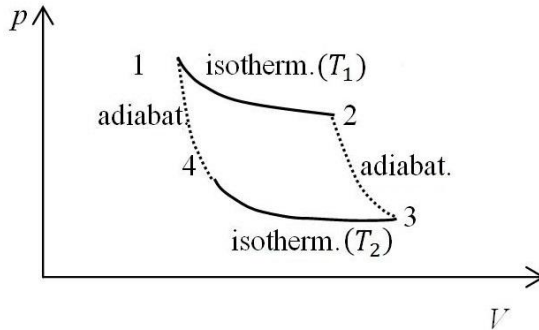
For an ideal gas  $C_V = 3/2 R$  as described following Eq. 1.16.

$$C_p/C_v = 5/3 = 1.667$$

## 1.7 Changes in Entropy and Gibbs Free Energy

### 1.7.1 Entropy as a State Function

$S = \frac{q_{rev}}{T}$  is called entropy and we will prove below that it is a state function by using Carnot cycle for one mole of an ideal gas. All the paths of the Carnot cycle are assumed to be reversible.



**Figure 1.7** The Carnot cycle is a typical heat engine which has all paths are reversible.

Path (1 → 2): Isothermal process.

$$dU = \frac{3}{2} R dT = 0$$

$$q_1 = -w_1 = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{RT_1}{V} dV = RT_1 \ln \left( \frac{V_2}{V_1} \right)$$

Path (2 → 3): Adiabatic process.

$$q = 0, \quad dU = -p dV = -\frac{RT}{V} dV = C_V dT.$$

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_2}^{V_3} \frac{dV}{V}. \quad C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_3}{V_2}. \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{R/C_V}.$$

Path(4 → 1): Adiabatic process.  $q = 0$ ,  $\left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{R/C_V}$

Path(3 → 4): Isothermal process.

$$\Delta U = 0, \quad q_2 = -w_2 = \int_{V_3}^{V_4} p dV = \int_{V_3}^{V_4} \frac{RT_2}{V} dV = RT_2 \ln \left(\frac{V_4}{V_3}\right).$$

$$\left(\frac{V_1}{V_4}\right)^{R/C_V} = \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{R/C_V}. \quad \frac{V_4}{V_3} = \frac{V_1}{V_2}, \quad \ln \left(\frac{V_4}{V_3}\right) = -\ln \left(\frac{V_2}{V_1}\right).$$

$$\frac{q_2}{q_1} = \frac{T_2 \ln \left(\frac{V_4}{V_3}\right)}{T_1 \ln \left(\frac{V_2}{V_1}\right)} = -\frac{T_2}{T_1}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \quad \rightarrow \quad \oint \frac{dq_{rev}}{T} = 0$$

where  $q_{rev}$  denotes amount of heat transfer in a reversible process.

Since  $\oint \frac{dq_{rev}}{T} = 0$  for any reversible cycle, we define *entropy* as a function of state like the internal energy and enthalpy.

$$S = \frac{q_{rev}}{T}. \quad dS = \frac{dq_{rev}}{T} \quad (1.19)$$

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T}$$

Because  $dq$  is path dependent, it is necessary to express  $dq$  in terms of state variables.

$$dq_{rev} = TdS$$

For reversible process  $p_{ext} = p$  and  $dq = dq_{rev} = TdS$ .

$$dU = dq - p_{ext}dV = TdS - pdV \quad (1.20)$$

$$dH = dU + d(pV) = dU + pdV + Vdp.$$

Substituting  $TdS - pdV$  for  $dU$  in the preceding equation,

$$dH = TdS + Vdp \quad (1.21)$$

At constant pressure and for reversible process,  $dH = TdS = dq_p = C_p dT$  where  $C_p$  is the heat capacity of the system at constant pressure.

$$TdS = C_p dT$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad (1.22)$$

### 1.7.2 Spontaneous Changes

Irreversible changes are real changes. Spontaneous process is always irreversible. According to the second law of thermodynamics, an irreversible cycle is less efficient than a reversible one.

If the work done by the system to the surrounding is expressed as  $(-w) > 0$ , then  $0 < (-work)_{irrev} < (-work)_{rev}$ .

$$0 > (work)_{irrev} > (work)_{rev}$$

$$\Delta U = q_{irrev} + w_{irrev} = q_{rev} + w_{rev}.$$

$$q_{irrev} < q_{rev}, \quad \frac{dq_{irrev}}{T} < \frac{dq_{rev}}{T} = dS.$$

$$dq_{irrev} < TdS$$

$$dU = dq_{irrev} + dw_{irrev} < TdS + dw_{irrev}$$

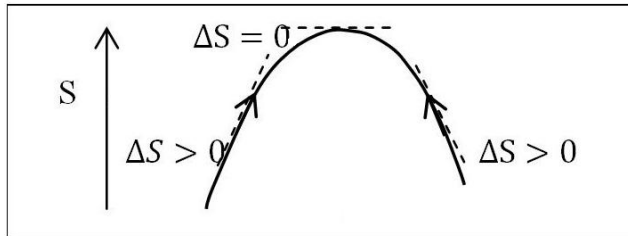
$$dU - dw_{irrev} - TdS < 0$$

$$dU + p_{ext}dV - TdS < 0 \quad (1.23)$$

(1) If  $q = w = 0$  in an isolated system like a thermos bottle,  $dU = 0$  and  $dV = 0$ .

$(dS)_{U,V} > 0$  is the condition for irreversible process for isolated system according to Eq. 1.23.

Since spontaneous process is always irreversible,  $(dS)_{U,V} > 0$  is the condition for spontaneity for isolated system.



**Figure 1.8.1** In an isolated system, equilibrium is achieved when the entropy is maximized.

Equilibrium is achieved when entropy is maximized.

(2) If  $H$  and  $p_{ext}$  are constant,  $dH = dU + p_{ext}dV = 0$ .

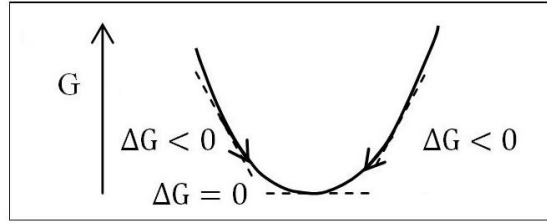
$(dS)_{H,p} > 0$  is the condition for spontaneity under constant  $H$  and constant  $p_{ext}$ .

(3) If  $T$  and  $V$  are constant,  $dU - TdS = d(U - TS) < 0$ .  $A = U - TS$  is defined as the Helmholtz free energy.

$(dA)_{T,V} < 0$  is the condition for spontaneity under constant  $T$  and constant  $V$ .

(4) If  $T$  and  $p_{ext}$  are constant,  $dU + p_{ext}dV - TdS = d(U + p_{ext}V - TS) < 0$ .

$G = U + p_{ext}V - TS = H - TS = A + p_{ext}V$  where  $G$  is defined as the Gibbs free energy.



**Figure 1.8.2** At constant  $p_{ext}$  and constant temperature, equilibrium is achieved when the Gibbs free energy is minimized.

$(dG)_{T,p} < 0$  is the condition for spontaneity under constant  $T$  and constant  $p_{ext}$ . At constant  $p_{ext}$  and constant temperature, equilibrium is achieved when the Gibbs free energy is minimized.

Example 1-6 Prove  $\left(\frac{\partial G}{\partial T}\right)_p = -S$  for reversible constant pressure process.

From the definition,  $dG = dH - TdS - SdT$ .

At constant pressure, putting  $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$  from Eq. 1.22 and  $\left(\frac{\partial H}{\partial T}\right)_p = C_p$  into the next equation,

$$\left(\frac{\partial G}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S = C_p - T\left(\frac{C_p}{T}\right) - S = -S$$

Alternative solution:  $dH = TdS + Vdp$  from Eq. 1.21

$$dG = dH - TdS - SdT = (TdS + Vdp) - TdS - SdT = -SdT + Vdp.$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp. \quad \left(\frac{\partial G}{\partial T}\right)_p = -S.$$

Example 1-7 What is integrated solution for  $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$  as temperature changes  $T_1$  to  $T_2$  under constant pressure?

$$\Delta S = C_p \ln \left(\frac{T_1}{T_2}\right)$$



Example 1-8 Phase conversion of liquid water to water vapor is considered a reversible constant pressure process because it is carried out under the atmospheric pressure which is about the same as the vapor pressure of the liquid. If the process is carried out at one atmospheric pressure and the normal boiling point of 100°C, calculate  $\Delta S_{vap}$  from the value of  $\Delta H_{vap}$  (40.657 kJ/mole).

At constant pressure and for reversible process,  $T_b = T_1 = T_2 = 373.15 \text{ K}$ .

$$\Delta H_{vap} = q_p = 40,658 \text{ J/mol}$$

$$\Delta S_{vap} = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T} = \frac{q_p}{T_b} = \frac{\Delta H_{vap}}{T_b} = \frac{40,658 \frac{\text{J}}{\text{mol}}}{373.15 \text{ K}} = 108.96 \frac{\text{J}}{\text{K}} \cdot \text{mol}^{-1}.$$

Question 1-6 Calculate  $\Delta G_{vap}$  at one atmospheric pressure and the normal boiling point of 100°C.

Answer:

$$\begin{aligned} \Delta G_{vap} &= \Delta H_{vap} - T \Delta S_{vap} \\ &= 40657 \text{ J} \cdot \text{mol}^{-1} - [(373.15 \text{ K})(108.96 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] = 0 \text{ J} \cdot \text{mol}^{-1}. \end{aligned}$$

## 1.8 Definition of Entropy

If we have a system which is composed of identical  $N$  molecules at constant temperature in a large reservoir, and making number of observations of the system over time, we will find molecules are in a different state with different  $\varepsilon_i$ . Instead of observing one system many times, we count the total number of ways for placing  $n_0$  molecules in the compartment 0,  $n_1$  molecules in the compartment 1 and so on. The compartments are energy cells with  $\varepsilon_i$ . The number of states of a system containing  $N$  molecules,  $\Omega_N$ , is calculated below using Stirling's approximation since  $N$  is assumed to be very large. If  $N$  and  $E$  are very large,  $n_i$  and  $\varepsilon_i$  are considered to be continuous variables.

$$\begin{aligned} \Omega_N &= N! / n_0! n_1! n_2! n_3! \dots \\ &\approx \frac{N^N e^{-N}}{n_0^{n_0} \times n_1^{n_1} \times n_2^{n_2} \times n_3^{n_3} \times \dots \times e^{-n_0 - n_1 - n_2 - n_3 \dots}} \\ &= \frac{N^N}{n_0^{n_0} \times n_1^{n_1} \times n_2^{n_2} \times n_3^{n_3} \times \dots} \quad \text{where } \sum_{i=0} n_i = N. \end{aligned}$$

Let's rewrite in natural log form.

$$\begin{aligned} \ln \Omega_N &= N \ln N - N - (n_0 \ln n_0 - n_0 + n_1 \ln n_1 - n_1 + n_2 \ln n_2 - n_2 + n_3 \ln n_3 - n_3 \dots) \\ &= N \ln N - \sum_{i=0} n_i \ln n_i = N \ln N - \sum_i p_i N \ln p_i N \\ &= N \ln N - \sum_i p_i N (\ln p_i + \ln N) \\ &= N \ln N - \sum_i p_i N \ln p_i - \sum_i p_i N \ln N = - \sum_i p_i N \ln p_i. \end{aligned}$$

$$S_N = k \ln \Omega_N = -Nk \sum_{i=0} p_i \ln p_i$$

$$S = \frac{S_N}{N} = k \ln \Omega = -k \sum_{i=0} p_i \ln p_i \quad \text{where } \Omega^N = \Omega_N. \quad (1.24)$$

The number of microstates is determined by counting the number of ways of positioning an assembly of particles in the space and counting number of ways of putting particles into its energy compartments that an assembly of particles possesses. If we have  $\Omega_1$  for a system 1 and  $\Omega_2$  for system 2, total microstates are  $\Omega_{total} = \Omega_1 \Omega_2$ .

Because entropy is a state function, it should be additive.  $S_{total} = S_1 + S_2$ .

Then entropy is defined as a function of  $\ln \Omega$ .

$$S \propto \ln \Omega$$

Using constant  $k$ , the average entropy per particle in a system containing a large number of particles is defined by Boltzmann as  $S = k \ln \Omega$  and will be

discussed again in 1.10. Eq. 1.24 tells us that *average entropy of a molecule is a function of the number of microstates and also a function of expected value of logarithm of the inverse probability of finding a particular microstate of a molecule*. Eq. 1.24 is consistent with the fundamental assumption of statistical mechanics. If you look at the system at any instant, you are equally likely to find one microstate in any of all  $\Omega$  microstates. If we have  $\Omega$  microstates, the probability to find any one microstate is  $1/\Omega$ .

The maximizing ways of arranging molecules into huge number of energy compartments results in the maximizing microstates and is the same as maximizing entropy of the system with constrains of  $\sum_{i=0} n_i = N$  and  $E_{total} = \sum_{i=0} n_i \varepsilon_i$ .

Question 1-9 We have a system containing  $N$  molecules. Calculate the number of microstates when we put all the molecules but one into the energy compartment 0 and successively put one into the energy compartment 1.

$$\text{Answer: } \Omega = N! / (N-1)! 1! 0! 0! 0! \cdots = N$$

Example 1-9 Maximize  $\Omega_N$  to obtain the Boltzmann distribution with constrains of  $\sum_{i=0} n_i = N$ ,  $E_{total} = \sum_{i=0} n_i \varepsilon_i = N \cdot \langle \varepsilon \rangle$ , and  $\sum_i p_i = 1$  where  $p_i = \frac{n_i}{N}$ . When a system is isolated and in equilibrium, entropy is the maximum from 1.7.2 (1), and the number of identical molecules,  $N$  and total energy,  $E$  are assumed constant at equilibrium in an isolated system.

$$\begin{aligned} \ln \Omega_N &= \ln \left( \frac{N!}{n_0! n_1! n_2! n_3! \cdots} \right) \\ &= N \ln N - N - (n_0 \ln n_0 - n_0 + n_1 \ln n_1 - n_1 + n_2 \ln n_2 - n_2 + n_3 \ln n_3 - n_3 \cdots) \\ &= N \ln N - \sum_i n_i \ln n_i. \end{aligned}$$

If  $N$  and  $E$  are very large,  $n_i$  and  $\varepsilon_i$  are considered to be continuous variables.

When  $\Omega_N$  is maximum,

$$d \ln \Omega_N = - \left( \sum_i \ln n_i + \sum_i n_i \frac{1}{n_i} \right) dn_i = 0 \quad \text{a)}$$

where  $N = \sum_i n_i = \text{constant}$ , and  $E_{total} = \sum_{i=0} n_i \varepsilon_i = \text{constant}$ .

$$(\alpha - 1) dN = (\alpha - 1) \sum_i dn_i = 0 \quad \text{b)}$$

$$\beta dE = \beta \sum_{i=0} \varepsilon_i dn_i = 0 \quad \text{c)}$$

We sum up a), b) and c), when  $\Omega_N$  is maximized.

$$\sum_i (\ln n_i + \alpha + \beta \varepsilon_i) dn_i = 0$$

$$\ln n_i + \alpha + \beta \varepsilon_i = 0$$

$n_i = e^{-\alpha - \beta \varepsilon_i} = n_0 e^{-\beta \varepsilon_i}$ , where  $n_0 = e^{-\alpha}$  is the number of identical molecules which has no energy.

The maximized way of arranging molecules into huge number of energy compartments results in the maximized microstates and we obtain the Boltzmann distribution. Entropy is the maximum when the ways of arranging molecules are maximized. In the isolated system at equilibrium we have the maximum entropy and the Boltzmann distribution of a system.

## 1.9 Entropy Expressed by Partition Function

All the thermodynamic functions can be calculated from the partition functions. The thermodynamic internal energy ( $U$ ) is defined as the average of the system energy when measured in a large number of observations. The system energy is the total energy of all molecules in a system. We first start to

express the expected value of system energy,  $U \equiv E(E)$  by the partition function. Then we will express entropy by partition function.

$$p_i = \frac{e^{-\beta E_i}}{Q}, \quad \beta = 1/kT. \quad Q = \sum_{i=0} e^{-E_i/kT} = \sum_{i=0} e^{-\beta E_i}.$$

$$U \equiv E(E) = \sum_{i=0} E_i p_i = \frac{1}{Q} \sum_{i=0} E_i e^{-\beta E_i} \quad (1.25)$$

$$\left(\frac{\partial Q}{\partial \beta}\right)_V = \left(\frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i}\right)_V = - \sum_{i=0} E_i e^{-\beta E_i}$$

$$U = E(E) = \frac{1}{Q} \sum_{i=0} E_i e^{-\beta E_i} = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V$$

$$U = -\left(\frac{\partial \ln Q}{\partial T}\right)_V \left(\frac{\partial T}{\partial \beta}\right)_V \quad (1.26)$$

$$\left(\frac{\partial \beta}{\partial T}\right)_V = \frac{\partial}{\partial T} \left(\frac{1}{kT}\right) = -\frac{1}{kT^2}$$

Substituting  $-kT^2$  for  $\left(\frac{\partial \beta}{\partial T}\right)_V$  in Eq. 1.26, we obtain the following equation.

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V \quad (1.27)$$

$$dU = dq_{rev} - pdV = T dS - pdV$$

$$A \equiv U - TS, \quad dA = dU - T dS - S dT = -pdV - SdT.$$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V \quad (1.28)$$

Substituting  $-\left(\frac{\partial A}{\partial T}\right)_V$  for  $S$  in  $A \equiv U - TS$ , we get  $A = U + T \left(\frac{\partial A}{\partial T}\right)_V$ .

Dividing  $A = U + T \left(\frac{\partial A}{\partial T}\right)_V$  by  $T^2$ , we obtain  $-\frac{U}{T^2} = \frac{1}{T} \left(\frac{\partial A}{\partial T}\right)_V - \frac{A}{T^2} = \left(\frac{\partial A/T}{\partial T}\right)_V$ .

$$U = -T^2 \left( \frac{\partial A/T}{\partial T} \right)_V = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V \text{ from Eq. 1.27.}$$

Integrating the above equation with respect to  $T$ , the following equation is obtained.

$$\frac{A}{T} = -k \ln Q \text{ (constant of integration is taken to be zero)}$$

$$A = -kT \ln Q \quad (1.29)$$

Now we can express  $S$  with  $k$ ,  $T$ , and  $Q$ .

$$S = -\frac{A}{T} + \frac{U}{T} = k \ln Q + kT \left( \frac{\partial \ln Q}{\partial T} \right)_V$$

Question 1-8 Express  $p$ ,  $H$  and  $G$  with  $k$ ,  $T$ ,  $V$ , and  $Q$ .  $H \equiv U + pV$ ,  $G \equiv H - TS$ .

$$\text{Answer: } p = -\left( \frac{\partial A}{\partial V} \right)_T = kT \left( \frac{\partial \ln Q}{\partial V} \right)_T, \quad H = kT \left[ T \left( \frac{\partial \ln Q}{\partial T} \right)_V + V \left( \frac{\partial \ln Q}{\partial V} \right)_T \right],$$

$$G = -kT \left[ \ln Q - V \left( \frac{\partial \ln Q}{\partial V} \right)_T \right]$$

## 1.10 Entropy as the Function of Microstates and Probability of Finding a Particular Microstate of a Molecule

We will prove that classically defined entropy is a function of expected value of logarithm of the inverse probability of finding a particular microstate of a molecule.

$$S = -\frac{A}{T} + \frac{U}{T}$$

$$\frac{S}{k} = \frac{U - A}{kT} = \frac{1}{kT} \frac{1}{Q} \sum_{i=0} E_i e^{-\beta E_i} + \ln Q$$

$$-\frac{E_i}{kT} = -\beta E_i = \ln e^{-\beta E_i}. \quad E_i = -kT \ln e^{-\beta E_i}.$$

$$\frac{S}{k} = - \sum_{i=0} \frac{e^{-\beta E_i}}{Q} (\ln e^{-\beta E_i}) + \ln Q$$

$$\sum_{i=0} \frac{e^{-\beta E_i}}{Q} = \sum_{i=0} p_i = 1$$

$$\frac{S}{k} = - \sum_{i=0} \frac{e^{-\beta E_i}}{Q} (\ln e^{-\beta E_i}) + \sum_{i=0} \frac{e^{-\beta E_i}}{Q} \ln Q = - \sum_{i=0} \frac{e^{-\beta E_i}}{Q} \ln \left( \frac{e^{-\beta E_i}}{Q} \right).$$

$$S = -k \sum_{i=0} p_i \ln p_i \quad (1.30)$$

What does " $-\sum_{i=0} p_i \ln p_i$ " mean? It is the expected value of  $\ln 1/p$ .

Eq. 1.24 tells us that the number of microstates per molecule is a function of expected value of logarithm of the inverse probability of finding a particular microstate of a molecule. Equation 1.30 says entropy is a function of expected value of logarithm of the inverse probability of finding a particular microstate of an assembly of molecules.

Using constant  $k$ , the average entropy per particle in an assembly is defined as

$$S = k \ln \Omega. \quad (1.31)$$

$$S = k \ln \Omega = -k \sum_{i=0} p_i \ln p_i.$$

If the system is isolated and at equilibrium, the system energy and a total number of molecules becomes constant and the system obtains the maximum entropy due to the maximum  $\Omega$ .

The number of microstates measures disorder. Entropy is related to degree of disorder. For gases, the number of microstates is very large. As a consequence entropy of gases is very large. For liquids and solids, all positions in space are occupied by molecules or atoms and so the number of microstates for them largely depends on their impurity and temperature. Entropy of liquids and solids

is smaller than gases and gets smaller as it becomes pure. If there are more energy compartments in them, the number of microstates becomes larger and as a consequence entropy gets greater.

This is the amazing conclusion. Eq. 1.31 gives approximate values of entropy of gas and liquid mixtures.

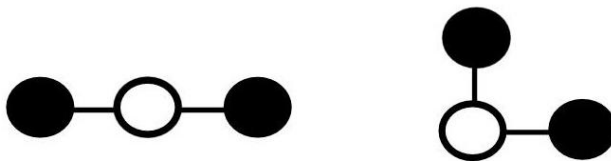
Question 1-9 When we increase temperature of a system, entropy increases. Please explain why it happens?

Example 1-10 Calculate  $S$  at  $0\text{ K}$  for perfect pure crystal.

$$\Omega = 1, \quad S = k \ln 1 = 0.$$

Since  $\Omega = 1$  at  $0\text{ K}$ ,  $S = 0$  is an exact value if the crystal is pure crystal with no holes. We should also realize that it is impossible to have  $0\text{ K}$ .

Example 1-11 There are gaseous molecules with 2 distinct configurations with the same energy. Rotation around a single bond interconverts the 2 different conformers. The molecular size is assumed to be  $10^{-30}\text{ m}^3$ . We have  $N$  molecules in the gas phase, molecular volume =  $v$  and total volume =  $V = 1\text{ m}^3$ . Count the number of microstates due to configuration and location and calculate the approximate value of entropy due to configuration and location. We assume that potential energy in the space is negligible. We do not think of states due to vibration and rotation and etc. in this problem.



**Figure 1.9** The gaseous molecule has two different configurations.

The number of microstates due to configurations for one molecule is

$$\Omega_{conf} = 2.$$



The number of microstates due to location for one molecule is

$$= V/v.$$

The number of microstates due to location for  $N$  molecule is

$$\approx (V/v)^N/N!.$$

The number of microstates due to configuration for  $N$  molecules is

$$\Omega_{conf} = 2^N$$

The total number of microstates is

$$\Omega_N = \Omega_{location} \Omega_{conf} \approx 2^N (V/v)^N/N! = 2^N (10^{30})^N/N!.$$

Average entropy on configuration and location per molecule is

$$S = k \ln \Omega = k \ln (\Omega_N)^{1/N} \approx k \ln (2 \times 10^{30}/N!).$$

## 1.11 Separation of Partition Functions

The system energy is considered as the sum of the energy of each molecule,  $n_1, n_2, n_3, \dots, n_N$ .

$$E_i = \varepsilon_{n_1,i} + \varepsilon_{n_2,i} + \varepsilon_{n_3,i} + \dots + \varepsilon_{n_N,i}$$

$$\begin{aligned} Q &= \sum_{i=0} e^{-E_i/kT} = \sum_{i=0} e^{-(\varepsilon_{n_1,i} + \varepsilon_{n_2,i} + \varepsilon_{n_3,i} + \dots + \varepsilon_{n_N,i})/kT} \\ &= \left( \sum_{n_1,i=0} e^{-\varepsilon_{n_1,i}/kT} \right) \left( \sum_{n_2,i=0} e^{-\varepsilon_{n_2,i}/kT} \right) \left( \sum_{n_3,i=0} e^{-\varepsilon_{n_3,i}/kT} \right) \dots \left( \sum_{n_N,i=0} e^{-\varepsilon_{n_N,i}/kT} \right) \\ &= q^N. \end{aligned}$$

$Q = q^N$  for distinguishable particles that can interchange positions.

$Q = q^N/N!$  for indistinguishable particles that can interchange positions.

Using the Stirling's approximation, the last formula is expressed in log form.  
 $\ln Q = N \ln q - N \ln N + N$ .

All thermodynamic functions can be expressed in terms of  $\ln q$  instead of  $\ln Q$ .

## 1.12 Application to Monatomic Gas with Translational Energy

We assume no contribution of bonding energy of molecules to the properties of a system and there is no potential energy. The gas is assumed to be ideal. Molecules of the gas are considered monoatomic. They do not interact with each other and are confined in a container. Only kinetic energy is considered.

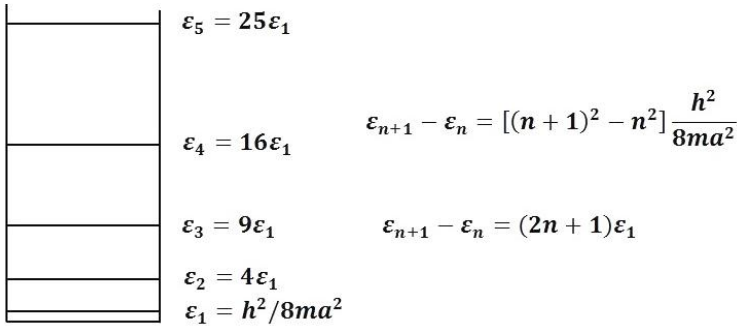
$$\varepsilon_{trans} = \varepsilon_x + \varepsilon_y + \varepsilon_z$$

$$q_{trans} = \sum_{i=0} e^{-(\varepsilon_{xi} + \varepsilon_{yi} + \varepsilon_{zi})/kT} = q_x q_y q_z$$

The energy states for translation are considered to be the same as the energy states for a particle in a box which we will discuss later in the chapter 3. If the width of the box in the  $x$  direction is  $a$ ,  $\varepsilon_x = \frac{h^2 n^2}{8ma^2}$ ,  $n = 1, 2, 3, \dots$

$$n = \left( \frac{8ma^2 \varepsilon_x}{h^2} \right)^{\frac{1}{2}}$$

$$\varepsilon_1 = \frac{h^2}{8ma^2}, \quad \varepsilon_2 = 4\varepsilon_1, \quad \varepsilon_3 = 9\varepsilon_1, \quad \varepsilon_4 = 16\varepsilon_1, \quad \varepsilon_5 = 25\varepsilon_1.$$



**Figure 1.10** Energy levels for a particle in a box with rigid walls.

The energy spacing between successive states gets progressively larger as  $n$  increases.

$$\varepsilon_{n+1} - \varepsilon_n = (2n+1) \frac{h^2}{8ma^2}$$

If  $n$  is very large,  $2n + 1 \approx 2n = 2 \left( \frac{8ma^2\varepsilon_x}{h^2} \right)^{\frac{1}{2}} = \frac{4a}{h} (2m\varepsilon_x)^{\frac{1}{2}}$ .

$$\varepsilon_{n+1} - \varepsilon_n = \frac{4a}{h} (2m\varepsilon_x)^{\frac{1}{2}} \frac{h^2}{8ma^2} = \frac{h}{a} \left( \frac{\varepsilon_x}{2m} \right)^{\frac{1}{2}}$$

The number of degenerate states in the range  $d\varepsilon$  is  $g = \frac{d\varepsilon}{\varepsilon_{n+1} - \varepsilon_n} =$

$$\frac{a}{h} \left( \frac{2m}{\varepsilon} \right)^{\frac{1}{2}} d\varepsilon.$$

$$q_x = \int_0^\infty \frac{a}{h} \left( \frac{2m}{\varepsilon} \right)^{\frac{1}{2}} e^{-\varepsilon/kT} d\varepsilon$$

$$y^2 = \varepsilon/kT. \quad d\varepsilon = 2kTydy.$$

$$q_x = \frac{a}{h} \int_0^\infty \left( \frac{2m}{kT} \right)^{\frac{1}{2}} 2kT e^{-y^2} dy = \frac{2a}{h} (2mkT)^{\frac{1}{2}} \left( \frac{\sqrt{\pi}}{2} \right) = \frac{a}{h} (2\pi mkT)^{\frac{1}{2}}.$$

$$q_{trans} = q_x q_y q_z = \frac{abc}{h^3} (2\pi mkT)^{\frac{3}{2}} = \frac{V}{h^3} (2\pi mkT)^{\frac{3}{2}}$$

$$Q = q_{trans}^N / N!$$

Using Stirling's approximation  $\ln N! \approx N \ln N - N$ ,

$$\ln Q \approx N \ln(q_{trans}) - N \ln N + N. \quad (1.32)$$

We differentiate Eq. 1.32 with respect to  $T$ .

$$\begin{aligned} \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} &\approx N \frac{1}{q_{trans}} \left(\frac{\partial q_{trans}}{\partial T}\right)_V \\ &= N \frac{h^3}{V} (2\pi mkT)^{-\frac{3}{2}} \left[ \frac{3V}{2h^3} (2\pi mkT)^{\frac{1}{2}} 2\pi mk \right] = \frac{3N}{2T} \\ U_{trans} = \langle E_{trans} \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} = \frac{3}{2} NkT = \frac{3}{2} nR \end{aligned} \quad (1.33)$$

$N = nN_a$ ,  $Nk = nkN_a = nR$ .  $N_a$  is Avogadro's constant.

$$A \equiv U - TS. \quad A = -kT \ln Q.$$

$$dA = dU - TdS - SdT = TdS - pdV - TdS - SdT = -pdV - SdT.$$

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

We get the derivative of Eq. 1.32 with respect to  $V$ .

$$\begin{aligned} \left(\frac{\partial \ln Q}{\partial V}\right)_T &= N \frac{1}{q_{trans}} \left(\frac{\partial q_{trans}}{\partial V}\right)_T = N \frac{h^3}{V} (2\pi mkT)^{-\frac{3}{2}} \left[ \frac{1}{h^3} (2\pi mkT)^{\frac{3}{2}} \right] = N/V \\ p &= \frac{NkT}{V} = \frac{nRT}{V} \end{aligned} \quad (1.34)$$

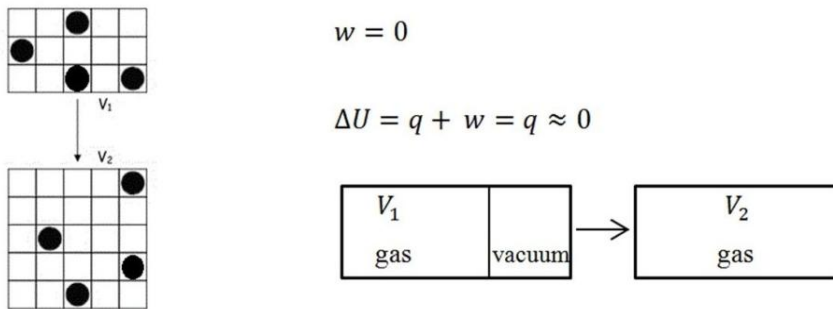
This formula is well known and well describes monatomic gases in which the interaction energy between molecules is very small. A gas which has no vibration and no rotation like a monoatomic gas and has no interaction between molecules is called an ideal gas. An ideal gas satisfies Eq. 1.34. It is approximately true for real gases.

## 1.13 Calculation of Entropy Change Microscopically

### 1.13.1 Free Expansion of a Gas

Free expansion is a process of gas expansion to vacuum where no works are done. The temperature change was negligible experimentally. We assume that potential energy in the space is negligible. Kinetic energy of molecules is constant before and after the expansion. We will calculate the change of entropy associated with the free expansion of  $N$  gaseous molecules.

Since there are no works and negligible heat exchange, the internal energy is constant during the free expansion.



**Figure 1.11** Free expansion of a gas to vacuum.

We are considering gases of which all molecules are indistinguishable. Let molecular volume be  $v$  and total volume be  $V$ .

The number of degenerate microstates which is the number of ways of positioning a molecule in the space is

$$\Omega_{location} = V/v$$

The number of total degenerate microstates which is the number of ways of positioning  $N$  molecules in the space is  $\Omega_{location} = \Omega^N / N! = (V/v)^N / N!$ .

Entropy changes during the free expansion as volume changes from  $V_1$  to  $V_2$  and pressure changes from  $p_1$  to  $p_2$ .

$$\Delta S_N = k \ln \Omega_2 - k \ln \Omega_1 = k \ln \frac{\Omega_2}{\Omega_1} = k \ln \frac{(V_2/v)^N / N!}{(V_1/v)^N / N!}$$

$$\Delta S_N = Nk \ln \frac{V_2}{V_1} = nR \ln \frac{V_2}{V_1} > 0 \quad (1.35)$$

$$\Delta G_N = \Delta H - T\Delta S \approx -nRT \ln \frac{V_2}{V_1} < 0 \quad (1.36)$$

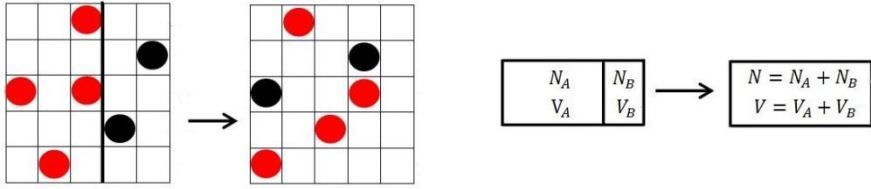
The system moves toward the state with increasing disorder. As a gas diffuses, its pressure decreases and entropy increases which is accompanied by decreasing Gibbs free energy,  $G$ . The free expansion proceeds spontaneously. Since  $\Delta U \approx 0$ , and  $w = p_{ext}dV = 0$ ,  $\Delta S > 0$  is the condition for spontaneity from 1.7.2 (1).

Question 1-10 Prove  $\Delta H \approx 0$  during free expansion of a gas.

Answer: Free expansion.  $q \approx 0$   $w = 0 \rightarrow \Delta U \approx 0$  Since  $\Delta T \approx 0 \rightarrow p_2V_2 \approx p_1V_1$ .  $\Delta H = \Delta U + \Delta(pV) = \Delta U + (p_2V_2 - p_1V_1) \approx 0$ .

### 1.13.2 Ideal Gas Mixture

We will calculate the change of entropy when two ideal pure gases are mixed under constant pressure and temperature. We let molecular volume be equal for different two gases. Since gases are ideal, we don't concern about microstates associated with molecular rotation, vibration, interaction and etc.. Kinetic energy is constant before and after the mixing since temperature does not change during mixing. We assume that potential energy in the space is negligible. We calculate only degenerate microstates which result from positional disorder to find entropy change due to mixing.



**Figure 1.12** Two ideal pure gases are mixed under constant pressure and temperature.

Entropy before mixing:

$$\begin{aligned} S_i &= k \ln \Omega_{\text{location } A} + k \ln \Omega_{\text{location } B} = k \ln \Omega_{\text{location } A} \Omega_{\text{location } B} \\ &= k \ln \frac{(V_A/v)^{N_A} (V_B/v)^{N_B}}{N_A! N_B!} \end{aligned}$$

Entropy after mixing: We count how many ways to distribute  $N_A$  molecules of A and  $N_B$  molecules of B among the  $(V/v)$  lattice sites.

$$\begin{aligned} S_f &= k \ln \Omega_{\text{location}} = k \ln \frac{(V/v)^{N_A+N_B}}{N_A! N_B!} \\ \Delta S_N &= S_f - S_i = k \ln \frac{(V/v)^{N_A+N_B}}{N_A! N_B!} - k \ln \frac{(V_A/v)^{N_A} (V_B/v)^{N_B}}{N_A! N_B!} \\ &= k \ln \frac{(V/v)^{N_A+N_B}}{(V_A/v)^{N_A} (V_B/v)^{N_B}} = k \ln \frac{V^{N_A} V^{N_B}}{V_A^{N_A} V_B^{N_B}} > 0 \end{aligned}$$

Since the initial pressures are the same, the initial volumes are in the ratio of the number of molecules.

$$\begin{aligned} V_A &= (N_A/N)V = X_A V. & V_B &= (N_B/N)V = X_B V. \\ N_A &= X_A N. & N_B &= X_B N. \end{aligned}$$

$$\begin{aligned} \Delta S_N &= k \ln \frac{V^{N_A} V^{N_B}}{V_A^{N_A} V_B^{N_B}} = k \ln \frac{1}{X_A^{N_A} X_B^{N_B}} = -k \ln X_A^{N_A} - k \ln X_B^{N_B} \\ &= -k(N_A \ln X_A + N_B \ln X_B). \end{aligned}$$

$$\Delta S_N = -kN(X_A \ln X_A + X_B \ln X_B) = -nR(X_A \ln X_A + X_B \ln X_B) > 0 \quad (1.37)$$

since  $X_A < 1$  and  $X_B < 1$ .

When two pure gases are mixed, entropy always increases. As  $\Delta G$  is negative, the mixing proceeds spontaneously under constant temperature and pressure from 1.7.2 (4).

Question 1-11 For ideal gas mixing under constant pressure and temperature, find  $\Delta U = 0$  and  $\Delta H = 0$  and calculate  $\Delta G$ .

Answer: For ideal gas,  $U = (3/2)nRT$  from Eq. 1.33.  $\Delta U = 0$  under constant temperature.

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = 0$$

$$\Delta G = \Delta H - T\Delta S = nRT(X_A \ln X_A + X_B \ln X_B) < 0$$

### 1.13.3 Ideal Liquid Mixture

Here we calculate the change of entropy when two ideal pure liquid are mixed under constant pressure and temperature. We assume two different liquid molecules do not interact and the sizes of molecular volume are about the same.  $\Delta H_{mix}$  of an ideal mixture is zero because no bonds are made or broken between molecules. Lattice model of liquid is different from gas in that all the space cells are occupied by the molecule. We assume pure ideal liquid has no disorder in location. We assume that potential energy in the space is negligible.

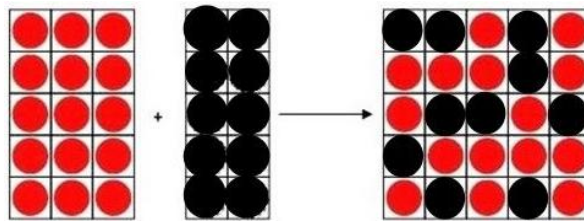


Figure 1.13 Two pure liquids are mixed.

$$S_A = k \ln \Omega_A = k \ln 1 = 0$$

$$S_B = k \ln \Omega_B = k \ln 1 = 0$$



We assume two different molecules have the same molecular volume and lattice cell sizes.

$$\Omega_{mix} = \frac{N!}{N_A! N_B!}$$

$$\Delta S_{mix} = S_{mix} - (S_A + S_B) = k \ln \Omega_{mix} = k \ln \frac{N!}{N_A! N_B!}$$

$$\ln N! = N \ln N - N$$

$$\begin{aligned} \Delta S_{mix} &= Nk \ln N - Nk - (N_A k \ln N_A - N_A k + N_B k \ln N_B - N_B k) \\ &= (N_A + N_B)k \ln N - N_A k \ln N_A - N_B k \ln N_B = N_A k \ln \frac{N}{N_A} + N_B k \ln \frac{N}{N_B} \\ \Delta S_{mix} &= -Nk(X_A \ln X_A + X_B \ln X_B) > 0 \quad \text{since } N_A = NX_A \text{ and } N_B = NX_B. \quad (1.38) \end{aligned}$$

In contrast to an ideal liquid, real liquids are considered to have additional states which are associated with molecular rotation, vibration, interaction and etc. besides of positional disorder, but these additional states occur in both the pure and mixed liquid. That's why  $\Delta S_{mix}$  is dominated by the disorder in molecular location. For real liquids heat of mixing,  $\Delta H_{mix}$  is not zero but negligible since no bonds are made or broken.  $\Delta S_{mix}$  will matter. For ideal mixture,  $\Delta H_{mix} = C_p \Delta T = 0$ .  $\Delta G_{mix} = -T \Delta S_{mix} = NkT(X_A \ln X_A + X_B \ln X_B) < 0$ . The mixing goes spontaneously under constant temperature and pressure since  $\Delta G_{mix}$  is negative.

## 1.14 Double-stranded Polymer Model

Each strand of polymer bonds with the other strand by H-bonding. We assume the interaction energy for each H-bonding is  $-\epsilon$ . The strand unzips from the one end, rupturing the H-bonding of the end, then the next one, then the next and so on as we increase temperature. It resembles the denaturation of DNA. Each ruptured interaction raises the energy by  $\epsilon$ .

This is a variation of the Boltzmann model which has nondegenerate evenly spaced states separated by tiny constant energy  $\epsilon$ .  $n_i$  is the number of molecules with energy  $\epsilon_i$ .  $i$  increases with increasing temperature.

**Table 1.3** Number of molecules with the amount of energy,  $\epsilon_i = i\epsilon$ .

Amount of Energy, $i\epsilon$	0	$\epsilon$	$2\epsilon$	$3\epsilon$	$4\epsilon$	$i\epsilon$
Number of molecules, $n_i$	$n_0$	$n_1$	$n_2$	$n_3$	$n_4$	$n_i$

From the Boltzmann law,  $n_i = n_0 e^{-\epsilon_i/kT}$ .

$$N = \sum_{i=0}^{\infty} n_i = n_0 + n_0 e^{-\epsilon/kT} + n_0 e^{-2\epsilon/kT} + n_0 e^{-3\epsilon/kT} + \dots$$

If we set  $x = e^{-\epsilon/kT}$ , the above equation becomes  $N = n_0(1 + x + x^2 + x^3 + \dots) = \frac{n_0}{1-x}$ .

Average value of energy is given by  $\langle \epsilon_{conf} \rangle = \frac{1}{N}(n_0 \cdot 0 + n_1 \cdot \epsilon + n_2 \cdot 2\epsilon + n_3 \cdot 3\epsilon + \dots)$ .

$$\begin{aligned} \langle \epsilon_{conf} \rangle &= \frac{1}{N} \{n_0 \epsilon (x + 2x^2 + 3x^3 + \dots)\} \\ &= \frac{1}{N} \{n_0 \epsilon x (1 + 2x + 3x^2 + \dots)\} \end{aligned}$$

$$\begin{aligned} (1 + 2x + 3x^2 + \dots) &= \frac{d}{dx} (1 + x + x^2 + x^3 + \dots) = \frac{d \left[ \frac{1}{1-x} \right]}{dx} \\ &= 1/(1-x)^2 \end{aligned}$$

Since  $N = \frac{n_0}{1-x}$ ,

$$\langle \epsilon_{conf} \rangle = n_0 \epsilon x / N (1-x)^2 = \epsilon e^{-\epsilon/kT} / (1 - e^{-\epsilon/kT}) = \frac{\epsilon}{e^{\epsilon/kT} - 1}$$

$$U_{conf} = N \langle \epsilon_{conf} \rangle = N \frac{\epsilon}{e^{\epsilon/kT} - 1}$$

$$q_{conf} = \sum_i e^{-i\varepsilon/kT} = 1 + x + x^2 + x^3 + \dots = \frac{1}{1-x} = \frac{1}{1-e^{-\varepsilon/kT}}$$

$$Q_{conf} = (q_{conf})^N = \left( \frac{1}{1-e^{-\varepsilon/kT}} \right)^N$$

$$A_{conf} = -kT \ln Q_{conf} = -NkT \ln \left( \frac{1}{1-e^{-\varepsilon/kT}} \right) = NkT \ln(1-e^{-\varepsilon/kT})$$

$$S_{conf} = -\frac{A_{conf}}{T} + \frac{U_{conf}}{T} = Nk \left[ -\ln(1-e^{-\varepsilon/kT}) + \frac{\frac{\varepsilon}{kT}}{e^{\varepsilon/kT}-1} \right] \quad (1.39)$$

When temperature is very small,  $\lim_{T \rightarrow 0} U_{conf} = \lim_{T \rightarrow 0} \frac{N\varepsilon}{e^{\varepsilon/kT}-1} = 0$ .

When temperature is very high,

$$e^{\varepsilon/kT} \approx 1 + \left(\frac{\varepsilon}{k}\right) \frac{1}{T} \text{ as } \frac{1}{T} \approx 0$$

$$\text{and } \lim_{T \rightarrow \infty} U_{conf} = N\varepsilon/(1 + \varepsilon/kT - 1) = NkT. \quad (1.40)$$

Question 1-12 Calculate  $\lim_{T \rightarrow 0} C_{Vconf}$  and  $\lim_{T \rightarrow \infty} C_{Vconf}$ .

Answer:  $C_{Vconf} = \frac{dU_{conf}}{dT} \lim_{T \rightarrow 0} C_{Vconf} = 0$ ,  $\lim_{T \rightarrow \infty} C_{Vconf} = Nk = nR$ .

## 1.15 Activation Energy

Arrhenius presented a qualitative theory for molecular reaction. His original idea has been made more quantitative by later theories. Arrhenius considered that any reaction process can proceed first by means of the formation of “high-energy species” which we call the activation complex and secondly by the breakdown of this complex into products. If the activated complex has an activated energy,  $E_a$ , greater than the reactants, then the number of activated complex molecules over the number of the reactant molecules can be written as follows.

$$\frac{[\text{activated complex molecules}]}{[\text{reactant molecules}]} = e^{-E_a/RT} \quad \text{from Eq. 1.7.}$$

Where  $E_a$  = system energy of activated complex molecules  
– system energy of reactant molecules.

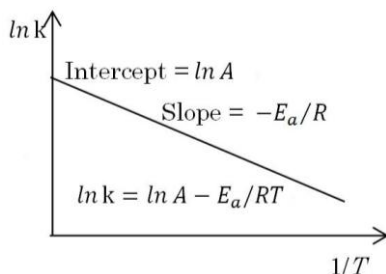
Since molecules having more than  $E_a$  have a chance to succeed the reaction, the reaction rate is considered to be proportional to the concentration of activated complex molecules.

$$\text{Rate} \propto [\text{activated complex molecules}]$$

$$\text{Rate} = A \times e^{-E_a/RT} \times [\text{reactant molecules}]$$

Rate =  $k$  [reactant molecules] where  $k$  is called the rate constant.

$$k = A e^{-E_a/RT} \quad (1.41)$$



**Figure 1.14**  $\ln k$  versus inverse temperature.

Factor  $A$  does not depend on temperature. It depends on the nature of the material involved. Factor  $A$  is the rate constant at infinitely high temperature. As the value of  $E_a$  increases, the energy requirement increases and it becomes more difficult to acquire this energy. The amount of  $e^{-E_a/kT}$  increases rapidly with increasing temperature. In order for reaction to proceed rapidly we increase temperature or lower the activation energy by catalysis. To assure the reaction going forward we have to take the products away, which prevents the backward reaction.

Example 1-12 The rate constant for a first order reaction at 27°C is observed to be 0.0404 /s and changes to 2.23 /s at 67°C. Estimate the rate constant (in s<sup>-1</sup>) of the reaction at 47°C. The first order reaction, such as H<sub>2</sub>O<sub>2</sub> or radioactive decay do not require molecular collisions.

$$k_1 = Ae^{-E_a/RT_1}, \quad k_2 = Ae^{-E_a/RT_2}, \quad \frac{k_1}{k_2} = e^{\frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\ln \frac{k_1}{k_2} = \frac{-E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$T_1 = 27^\circ\text{C} = 300\text{K}, \quad k_1 = 0.0404 \text{ s}^{-1}$$

$$T_2 = 67^\circ\text{C} = 340\text{K}, \quad k_2 = 2.23 \text{ s}^{-1}$$

$$T_3 = 47^\circ\text{C} = 320\text{K}, \quad k_3 = ?$$

$$\frac{-E_a}{R} = -10227.9, \quad k_3 = 0.3402 \text{ s}^{-1}.$$

Question 1-13 The hydrolysis of sucrose to form a molecule of glucose and a molecule of fructose is a part of digestive process.  $E_a = 108\text{KJ/mol}$ ,  $k = 1.0 \times 10^{-3}\text{M}^{-1}\text{s}^{-1}$  at 37°C. What is  $k$  at 35°C?

Answer:  $k = 7.6 \times 10^{-4}\text{M}^{-1}\text{s}^{-1}$ . The reaction is slowed down due to impaired function of the enzyme.

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