

Statistical Thermodynamic and Surface Chemistry

(Course No. 3102)

**Physical Chemistry Course delivered to B. Sc, third year
chemistry students.**

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Statistical Thermodynamics

Topic to be covered:

1. Introduction

1.1. Terminology and Basic Concepts

1.2. Basic Statistics

1.3. Statistics of Particles

1.4. Distribution Functions

1.5. Partition Function

1.6. Thermodynamic Functions

1.7. Statistical Mechanics of Ensembles

1.8. Thermodynamic Properties of Ideal Gas

1. Introduction

Statistical Mechanics (or Statistical Thermodynamics, as it is often called) is concerned with predicting and as far as possible interpreting the macroscopic properties of a system in terms of the properties of its microscopic constituents (molecules, atoms, electrons, etc).

For example, thermodynamics can inter-relate all kinds of macroscopic properties, such as energy, entropy, and so forth, and may ultimately express these quantities in terms of the heat capacity of the material. Thermodynamics, however, cannot predict the heat capacities: statistical mechanics can.

There is another difference. Thermodynamics (meaning macroscopic thermodynamics) is not applicable to small systems ($\sim 10^{12}$ molecules or less) to large systems in the critical region. In both instances, failure is attributed to large fluctuations, which thermodynamics does not take into account, whereas statistical mechanics does.

How are the microscopic and macroscopic properties related? The former are described in terms of position, momentum, pressure, energy levels, wave functions, and other mechanical properties. The latter are described in terms of heat capacities, temperature, entropy, and others—that is, in terms of thermodynamic properties. Until about the mid-nineteenth century, the two seemingly different disciplines were considered to be separate sciences, with no apparent connection between them. Mechanics was associated with names like Newton, LaGrange, and Hamilton and more recently with Schrodinger, Heisenberg, and Dirac. Thermodynamics was

associated with names like Carnot, Clausius, Helmholtz, Gibbs, and more recently with Carathéodory, Born, and others. *Statistical mechanics is the branch of science that interconnects these two seemingly different subjects.* But statistical mechanics is not a mere extension of mechanics and thermodynamics. Statistical mechanics has its own laws (postulates) and a distinguished slate of scientists, such as Boltzmann, Gibbs, and Einstein, who are credited with founding the subject.

PRELIMINARY DISCUSSION—SIMPLE PROBLEM

The following simple (silly) problem is introduced to illustrate with a concrete example what statistical mechanics purports to do, how it does it, and the underlying assumptions on which it is based.

Consider a system composed of three particles (1, 2, and 3) having a fixed volume and a fixed energy, E . Each of the particles can be in any of the particle energy levels, ϵ_i , shown in Figure 1. We take the total energy, E , to be equal to 6 units.

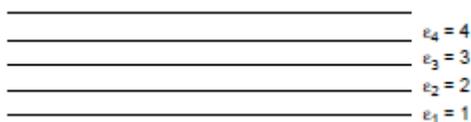


Figure 1: Representation of a set of equally spaced energy levels.

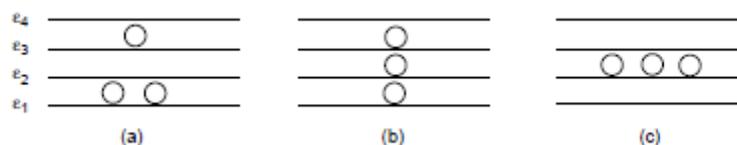


Figure 2: Distribution of three particles among the set of energy levels of figure 1 having a total energy of 6 units.

In the example discussed here, we have for simplicity taken the energy levels to be non-degenerate and equally spaced. Figure 2 illustrates how the particles can be distributed among the energy levels under the constraint of total constant energy of 6 units. Although the total energy is the same regardless of how the particles are distributed, it is reasonable to assume that some properties of the system, other than the energy, E , will depend on the arrangement of the particles among the energy states. These arrangements are called *microstates* (or micromolecular states).

TIME AND ENSEMBLE AVERAGES

During the time of measurement on a single system, the system undergoes a large number of changes from one microstate to another. The observed macroscopic properties of the system are time averages of the properties of the instantaneous microstates—that is, of the mechanical properties. Time-average calculations are virtually impossible to carry out. A way to get around this difficulty is to replace the time average of a single system by an ensemble average of a very large collection of systems. That is, instead of looking at one system over a period of time, one looks at a (mental) collection of a large number of systems (all of which are replicas of the system under consideration) at a given instance of time. Thus, in an ensemble of systems, all systems have certain properties in common (such as same N , V , E) but differ in their microscopic specifications; that is, they have different microstates. The assumption that the time average may be replaced by an ensemble average is stated as postulate:

- **Postulate I:** *the observed property of a single system over a period of time is the same as the average over all microstates (taken at an instant of time).*

NUMBER OF MICROSTATES, Ω_D , DISTRIBUTIONS D_i

For the system under consideration, we can construct 10 microstates (Figure 3). We might characterize these microstates by the symbols Ψ_1 , Ψ_2 , and so forth. (In quantum mechanics, the Ψ symbols could represent wave functions.) The microstates can be grouped into three different classes, characterized by the particle distributions D_1 , D_2 , D_3 . Let Ω_D denote the number of microstates belonging to distribution D_1 , etc. Thus, $\Omega_{D_1} = 3$, $\Omega_{D_2} = 6$, and $\Omega_{D_3} = 1$.

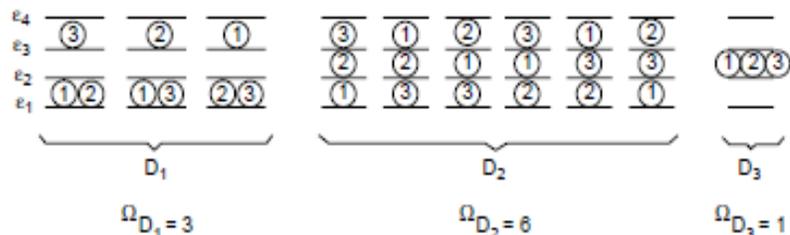


Figure 3: Identity of the particles corresponding to the arrangements in figure 2. The symbol Ω_{D_i} represents the number of quantum states associated with distribution D_i

Each of the systems constituting the ensemble made up of these microstates has the same N , V , and E , as noted before, but other properties may be different, depending on the distribution. Specifically, let χ_1 be a property of the systems when the system is in the distribution D_1 , χ_2 when

the distribution is D_2 , and χ_3 when the distribution is D_3 . The ensemble average, which we say is equal to the time average (and thus to the observed property) is

$$\langle \chi \rangle_{ensemble} = \chi_{obs} = (3\chi_1 + 6\chi_2 + \chi_3) / 10 \quad 1$$

This result is based on a number of assumptions, in addition to the time average postulate, assumptions that are implied but not stated. In particular

1) *Equation 1* assumes that all microstates are equally probable. (Attempts to prove this have been only partially successful.) This assumption is so important that it is adopted as a fundamental postulate of statistical mechanics.

- **Postulate II:** *all microstates have equal a priori probability.*

2) Although we refer to the microscopic entities as “particles,” we are noncommittal as to the nature of the particles. They can mean elementary particles (electrons, protons, etc.), composites of elementary particles, aggregates of molecules, or even large systems.

3) In this example, the assumption was made that each particle retains its own set of *private* energy level. This is generally not true—interaction between the particles causes changes in the energy levels. Neglecting the interactions holds for ideal gases and ideal solids but not for real systems.

4) In drawing pictures of the 10 microstates, it was assumed that all particles are distinguishable, that is, that they can be labeled. This is true classically, but not quantum mechanically. In quantum mechanics, identical particles (and in our example, the particles are identical) are *indistinguishable*. Thus, instead of there being three different microstates in distribution D_1 , there is only one, i.e., $\Omega_{D1} = 1$. Similarly, $\Omega_{D2} = 1$ and $\Omega_{D3} = 1$.

In summary, attention must be paid to the nature of the particles in deciding what statistical count is appropriate.

- 1) If the particles are classical, i.e., *distinguishable*, we must use a certain type of statistical count, namely the *Maxwell-Boltzmann* statistical count.
- 2) If the particles are quantal, that is, *indistinguishable and there are no restrictions as to the number of particles per energy state*, we have to use the *Bose-Einstein* statistical count.
- 3) If the particles are quantal, that is, *indistinguishable and restricted to no more than one particle per state*, then we must use the *Fermi-Dirac* statistical count.

4) Although pictures may be drawn to illustrate how the particles are distributed among the energy levels and how the number of microstates can be counted in a given distribution, this can only be accomplished when the number of particles is small. If the number is large (approaching Avogadro's number), this would be an impossible task. Fortunately, it need not be done. What is important, as will be shown, knows the *number of microstates*, Ω_{D^*} , *belonging to the most probable distribution*. There are mathematical techniques for obtaining such information, called *Combinatory Analysis*.

1.1. Terminology and Basic Concepts

Probability

If an event can occur in n ways (i.e. there are n possible outcomes) and a particular result can occur in m ways, then the probability of the particular result occurring is m/n .

Example

Spinning a coin gives rise to 2 possible outcomes: H (Heads) or T (Tails) H occurs in 1 way; therefore the probability of a H result is $\frac{1}{2}$

Note:

1. The sum of the probabilities for all possible results is unity: in the above example, the probability of T occurring is also $\frac{1}{2}$ and the probability of obtaining either an H or a T (i.e. encompassing all possible results) is therefore equal to $(\frac{1}{2} + \frac{1}{2}) = 1$

2. Probabilities may be expressed as fractions, in decimal format or as percentages; so the following probabilities are all equivalent - $\frac{1}{2}$, 0.5, 50%.

Example

A standard dice has six faces (with faces numbered 1 ... 6) and rolling it gives rise to 6 possible outcomes. A 3 occurs in 1 way; therefore the probability of throwing a 3 is $\frac{1}{6}$

Permutations and Combinations

- An arrangement where order is important is called a **permutation**.
- An arrangement where order is not important is called **combination**.

If we have n different items, then the number of ways of arranging them in a row is given by the factorial $n!$

Proof by Example

Consider how many arrangements are possible for the 26 letters of the alphabet. The first letter could be chosen in 26 different ways - leaving 25. Thus 25 choices are possible for the second

letter. The third choice is then made from the 24 remaining letters and so on. The number of different arrangements possible for just the first two choices is thus 26×25 ; and when the third is included, $26 \times 25 \times 24$. This process can be continued until all the letters of the alphabet are used up and the number of different possible arrangements is $26 \times 25 \times 24 \times 23 \times \dots \times 4 \times 3 \times 2 \times 1$ - such a multiplication series is called a *factorial* and in this case the number of arrangements would be written as $26!$

A above arrangement is an example of a permutation because the arrangement of the “n” objects is in a specific order. Since the order is important for a permutation.

- ***Permutation of n different objects*** The number of permutations of n objects taken all at a time, denoted by the symbol ${}^n P_n$, is given by

$${}^n P_n = n!$$

- The number of permutations of n objects taken r at a time, where $0 < r \leq n$, denoted by ${}^n P_r$, is given by

$${}^n P_r = \frac{n!}{n! - r!}$$

- ***When repetition of objects is allowed*** The number of permutations of n things taken all at a time, when repetition of objects is allowed is n^n .
- The number of permutations of n objects, taken r at a time, when repetition of objects is allowed, is n^r .
- ***Permutations when the objects are not distinct*** The number of permutations of n objects of which p_1 are of one kind, p_2 are of second kind, ..., p_k are of k^{th} kind and the rest if any, are of different kinds is

$$\frac{n!}{p_1! p_2! \dots p_k!}$$

- ***Combinations*** On many occasions we are not interested in arranging but only in selecting r objects from given n objects. A combination is a selection of some or all of a number of different objects where the order of selection is immaterial. The number of selections of r objects from the given n objects is denoted by ${}^n C_r$, and is given by

$${}^n C_r = \frac{n!}{r!(n-r)!}$$

Example

With three different letters, ABC, then $n = 3$ and $n! = 6$, corresponding to the six possible

arrangements which are: ABC, ACB, BAC, BCA, CAB, CBA

Example 1 : Cl and Cl₂

Chlorine has two stable isotopes of RAM 35 and 37. Their relative abundance is about 3:1. This can be expressed as " the chance of encountering a Cl atom of mass 35 in a collection of free chlorine atoms is 75% " or the *probability* of any particular Cl atom having mass 35 is 0.75.

This means that a mass spectrum of chlorine atoms shows two peaks at masses 35 and 37, the former three times as intense as the latter.

What happens in the chlorine molecule (Cl₂)? Clearly several combinations of isotopes are possible, (i) both atoms are of mass 35, giving ³⁵Cl₂, (ii) one 35 and one 37, giving ³⁵Cl³⁷Cl, or (iii) both are of mass 37, giving ³⁷Cl₂. These possible combinations give rise to three peaks in the mass spectrum, corresponding to Cl₂⁺ ions with relative masses of 70, 72, and 74.

There are several ways of tackling the problem of identifying the exact probability of each molecular mass occurring. We will start with the least sophisticated approach.

If we choose the first atom in the molecule to be ³⁵Cl then this choice has a probability of 0.75; this atom may then be associated with either another ³⁵Cl atom, again with a probability of 0.75, or with a ³⁷Cl atom, with a probability of 0.25.

The pattern of all possible combinations, taking account of these relative probabilities is shown in Table 1. For this table we have chosen to work with four chlorine atoms in the first instance, since the relative abundances then indicate that on average three will be 35 and one 37. *Each* of these atoms can then be associated with four other atoms, and again three will be 35 and one 37, giving the sixteen possible Cl₂ molecules shown in the table.

Table 1: Possible Ways of Combining Chlorine Isotopes

First Cl	35				35				35				37			
Second Cl	35	35	35	37	35	35	35	37	35	35	35	37	35	35	35	37
Total mass	70	70	70	72	70	70	70	72	70	70	70	72	72	72	72	74

Total number of molecules = 16

No. of molecules of mass 70 = 9 ⇒ Relative probability = $\frac{9}{16} = 0.5625$

No. of molecules of mass 72 = 6 ⇒ Relative probability = $\frac{6}{16} = 0.3750$

No. of molecules of mass 74 = 1 ⇒ Relative probability = $\frac{1}{16} = 0.0625$

Cross-checking:

Total number of molecules = 9 + 6 + 1 = 16

Total probability of all outcomes = 0.5625 + 0.3750 + 0.0625 = 1.0000

Note that the total number of possible isotopic arrangements in the final molecule arises by multiplying the number of choices for the first atom by the number of choices for the second. In this case four for the first times four for the second i.e. sixteen.

If the only way in which these molecules can be distinguished is by mass then the relative probabilities will be as shown on the right hand side of the lower part of the table – of the sixteen arrangements, nine correspond to a total molecular mass of 70, six correspond to a total mass of 72 and one corresponds to a total mass of 74.

1.2. Basic Statistics

Different physical situations encountered in nature are described by three types of statistics, *viz.*, **the Maxwell-Boltzmann (or M-B) statistics, the Bose-Einstein (or B-E) statistics and the Fermi-Dirac (or F-D) statistics.** The **M-B** statistics, developed long before the advent of quantum mechanics, is also called **classical statistics** whereas the **Bose-Einstein and Fermi-Dirac statistics** are collectively called **quantum statistics**. The characteristics of the three types of statistics are summed up as follows:

1. In **Maxwell-Boltzmann** statistics, the particles are assumed to be *distinguishable* and *any number of particles may occupy the same energy levels*. Particles obeying **M-B** statistics are called *boltzmannons or maxwellons*.
2. In **Bose-Einstein** statistics, the particles are *indistinguishable* and *any number of particles may occupy a given energy level*. This statistics is obeyed by particles having *integral spin*, such as hydrogen (H_2), Deuterium (D_2), nitrogen (N_2), helium-4 (He^4) and photons. Particles obeying **B-E** statistics are called *bosons*.
3. In **Fermi-Dirac** statistics, the particles are *indistinguishable but only one particle may occupy a given energy level*. This statistics is obeyed by particles having *half-integral spin*, e.g., the protons, electrons, helium-3 (He^3) and nitric oxide (NO). Particles obeying **F-D** statistics are called *fermions*.

Fermions are those species whose wave functions are *antisymmetric* with respect to the *exchange of particles* whereas **bosons** are those species whose wave functions are *symmetric* with respect to the *exchange of particles*.

1.3. Statistics of Particles

(i) Maxwell-Boltzmann Statistics

Consider a system of N *distinguishable* particles occupying energy levels $\epsilon_0, \epsilon_1, \epsilon_2$, etc. The total number of arrangements for placing n_0 particles in the ground state energy level ϵ_0 , n_1 particles in the first excited energy level ϵ_1 , n_2 particles in the second excited energy level ϵ_2 , and so on, is known as the **thermodynamics probability, W** , of the given macrostate. It is, in general, a very large number. Our problem is to determine W , i.e., to determine how many microstates correspond to a given macrostate. It can be shown that W is given by

$$W = \frac{N!}{n_1! n_2! n_3! \dots n_j!} = \frac{N!}{\prod n_i!} \quad (1)$$

Where $N = \sum n_i$

In Eq.1, N is the total number of particles and the summation is over all the energy levels. It is possible to realize a given energy level in more than one way, *i.e.*, more than one quantum state has the same energy. When this happens, the energy level is said to be degenerate, let g_i be the **degeneracy (multiplicity)** of the energy level ϵ_i . This means that if there is one particle in the i th energy level, there are g_i ways of distributing it. For two particles in the i th level, there are g_i^2 possible distributions. Thus, for n_i particles in the i th level, there are $g_i^{n_i}$ possible distributions. Hence, the thermodynamic probability for the system of N particles is given by

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i!} \quad (2)$$

It is well known that the entropy S and probability W of a given state of a system are related by the Boltzmann equation, the most famous equation in statistical mechanics, *viz.*,

$$S = k \ln W \quad (3)$$

The probability must be a maximum for an equilibrium state so that at equilibrium

$$S = k \ln W_{\max} \quad (4)$$

We are thus interested in finding a distribution that will make W a maximum. It is more convenient, however, to maximize the logarithm of W . It is known from calculus that at the maximum, the derivative of a function vanishes. Hence, at equilibrium,

$$d \ln W = \frac{\partial \ln W}{\partial n_1} dn_1 + \frac{\partial \ln W}{\partial n_2} dn_2 + \dots$$

$$d \ln W = \sum_i \frac{\partial \ln W}{\partial n_i} dn_i = 0 \quad (5)$$

If we confine our investigation to a *closed system of independent particles*, it meets the following two requirements:

- (i) The total number of particles is *constant, i.e.*,

$$N = \sum_i n_i = \text{constant} \quad (6)$$

- (ii) The total energy, U , of the system is *constant, i.e.*,

$$U = \sum_i n_i \varepsilon_i = \text{constant} \quad (7)$$

The constancy of the total number of particles implies that

$$dN = \sum_i dn_i = 0 \quad (8)$$

And the constancy of the total energy implies that

$$dU = \sum_i dn_i \varepsilon_i = 0 \quad (9)$$

From Eq. 2, taking logarithms both sides, we get

$$\ln W = \ln N! + \sum_i n_i \ln g_i - \sum_i \ln n_i! + \text{constant} \quad (10)$$

Using *Stirling's approximation* according to which, for large x ,

$$\ln x! = x \ln x - x \quad (11)$$

Using this approximation for $\ln N!$, Eq. **10** becomes

$$\begin{aligned} \ln W &= \ln N! + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \sum_i n_i + \text{constant} \\ \ln W &= (N \ln N - N) + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + N + \text{constant} \\ \ln W &= N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \text{constant} \end{aligned} \quad (12)$$

Differentiating and bearing in mind that N and g_i are constants, we get

$$d \ln W = \sum_i \ln g_i dn_i - \sum_i \ln n_i dn_i - \sum_i n_i d \ln n_i \quad (13)$$

Now,
$$\sum_i n_i d \ln n_i = \sum_i n_i \frac{dn_i}{n_i} = \sum_i dn_i = 0 \quad (14)$$

Hence, at equilibrium,

$$d \ln W = \sum_i \ln g_i dn_i - \sum_i \ln n_i dn_i = 0 \quad (15)$$

Eq. (15) gives the change in $\ln W$ which results when the number of particles in each energy level is varied.

If our system were *open*, then n_i would vary without restriction and the variations would be *independent* of one another. It would then be possible to solve **Eq. 15** by setting each of the coefficients of the dn_i terms in **Eq. 15** equal to zero. However, our system is not open but closed and since N is constant, the values of dn_i are not independent of one another, as is seen from **Eq.14**. Again, the energy of the system is constant, too.

The desired solution is obtained by applying the method of *Lagrange's undetermined multipliers*. Rewriting **Eq. 15**, we have

$$\sum_i \ln \frac{g_i}{n_i} dn_i = 0 \quad (16)$$

Multiplying **Eqs. 8** and **9** by the arbitrary constants α and β (known as **Lagrange's undetermined multipliers**) and subtracting from **Eq. 16**, we get

$$\sum_i \left[\ln \frac{g_i}{n_i} - \alpha - \beta \varepsilon_i \right] dn_i = 0 \quad (17)$$

We can now select values of α and β in such a manner that one of the terms in the summation (say, $i = 1$) is zero, the value of dn_i being immaterial. The remaining dn_i terms then become independent of one another since dn_i can be obtained from these dn_i terms (Eq. 8). We are now in a position to set each of the coefficients of dn_i in Eq. 17 equal to zero. Thus,

$$\begin{aligned} \ln \frac{g_i}{n_i} - \alpha - \beta \varepsilon_i = 0 \quad \text{or} \quad \ln \frac{g_i}{n_i} = \alpha + \beta \varepsilon_i \quad \text{or} \quad \ln n_i = \ln g_i - \alpha - \beta \varepsilon_i \quad \text{or} \\ n_i = g_i e^{-\alpha - \beta \varepsilon_i} \end{aligned} \quad (18)$$

Eq. (18) which is one form of the **Boltzmann distribution law**, gives the **most probable distribution for a macrostate**, *i.e.*, it gives the occupation numbers of the molecular energy levels for the most probable distribution in terms of the energies ε_i , the degeneracy g_i and the undetermined multipliers α and β .

Evaluation of Lagrange's Undetermined Multipliers: We now proceed to determine α and β .

Since $N = \sum_i n_i$, hence from Eq. 18,

$$\begin{aligned} N &= \sum_i g_i e^{-\alpha - \beta \varepsilon_i} \quad \text{or} \\ e^{-\alpha} &= N / \sum_i g_i e^{-\beta \varepsilon_i} \end{aligned} \quad (19)$$

Defining a quantity q , called the **molecular partition function**, as

$$q = \sum_i g_i e^{-\beta \epsilon_i} \quad (20)$$

We obtain

$$e^{-\alpha} = N/q \quad (21)$$

Accordingly, the **Boltzmann distribution law equation becomes**

$$n_i = N g_i e^{-\beta \epsilon_i} / q \quad (22)$$

The partition function, q , is a quantity of immense importance in statistical thermodynamics. We shall see presently that by evaluating the partition function for a system we can calculate the value of any thermodynamic function for that system.

However, before we proceed with the task of evaluating the partition function, let us determine the constant β . Taking logs of Eq. 2 and applying Stirling's approximation to

$$\ln W = \ln N! + \sum_i (n_i \ln g_i - \ln n_i!) \quad (23)$$

$$\ln W = (N \ln N - N) + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \sum_i n_i$$

$$\ln W = N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i \quad (24)$$

Taking logs of Eq.22, we have

$$\ln n_i = \ln N - \ln q + \ln g_i - \beta \epsilon_i \quad (25)$$

Substituting in Eq. 24, we get

$$\begin{aligned} \ln W &= N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln N - \ln q + \ln g_i - \beta \epsilon_i \\ &= N \ln N + \sum_i n_i \ln g_i - N \ln N + N \ln q - \sum_i n_i \ln g_i + \beta \sum_i n_i \epsilon_i \\ &= N \ln q + \beta U \end{aligned} \quad (26)$$

Substituting this result into the **Boltzmann** equation (*viz.*, Eq.3), we have,

$$S = k \ln W = N k \ln q + k \beta U \quad (27)$$

From the combined result of the First Law and Second law of thermodynamics, we know that for a simple system,

$$dU = TdS - PdV \quad (28)$$

$$\text{At constant volume (V = constant ; } dV = 0), dU = TdS \quad (29)$$

$$\therefore \left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad (30)$$

Differentiating Eq. 27 with respect to U at constant V , we get

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{Nk}{q} \left(\frac{\partial q}{\partial U}\right)_V + k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_V = \frac{Nk}{q} \frac{dq}{d\beta} \left(\frac{\partial \beta}{\partial U}\right)_V + k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_V \quad (31)$$

Also, from Eq. 20,

$$\frac{dq}{d\beta} = -Uq/N \quad (32)$$

Substituting of Eq. 32 in 31 results in cancellation of the first and the last terms, giving

$$\left(\frac{\partial S}{\partial U}\right)_V = k\beta \quad (33)$$

Comparing Eqs. 30 and 33, we find that

$$\beta = 1/kT \quad (34)$$

Hence, from Eq. 21, the molecular partition function q becomes

$$q = \sum_i g_i e^{-\epsilon_i/kT} \quad (35)$$

And **Maxwell – Boltzmann distribution** equation becomes

$$n_i = Ng_i e^{-\epsilon_i/kT} / q \quad (36)$$

From Eq. 36 we can easily obtain the ratio of the populations, *i.e.*, the number of particles in any two energy levels ϵ_i and ϵ_j . Thus,

$$n_i / n_j = g_i / g_j e^{-(\epsilon_i - \epsilon_j)/kT} \quad (37)$$

(ii) Bose – Einstein Statistics

Consider a system of N *indistinguishable* particles such that n_i particles are in the i th energy level with degeneracy g_i . The n_i particles have to be distributed among g_i states. For the sake of simplicity, imagine that the i th energy level has $g_i - 1$ partitions which are sufficient to separate the energy level into g_i intervals. Now the possible number of distributions of n_i particles among the g_i states may be determined by permuting the array of partitions and particles. The total number of permutations of n_i particles and $(g_i - 1)$ partitions is $(n_i + g_i - 1)!$. However, *the partitions and the particles are indistinguishable*. This implies that interchanging two partitions does not alter an arrangement; also interchanging two particles does not alter an arrangement. Hence, we must divide $(n_i + g_i - 1)!$ by the number of permutations of the $(g_i - 1)$ partitions, *viz.*, $(g_i - 1)!$ and the number of permutations of n_i particles, *viz.*, $n_i!$ to obtain the number of possible arrangements of the n_i particles in the energy level ϵ_i . Thus,

$$\text{The number of arrangements} = \frac{(n_i + g_i - 1)}{n_i!(g_i - 1)!} \quad (1)$$

As in the case of **Maxwell – Boltzmann** statistics, we assume that in the present case also the total number of particles is constant and the total energy of the system is also constant, *i.e.*,

$$N = \sum_i n_i = \text{const } t$$

$$U = \sum_i n_i \varepsilon_i = \text{const } t$$

Thus, the thermodynamic probability **W** for the system of N particles (*i.e.*, the number of ways of distributing N particles among the various energy levels) is given by

$$W = \prod_i \frac{(n_i + g_i - 1)}{n_i!(g_i - 1)!} x^{\text{const } t} \quad (2)$$

Taking logarithms of both sides of Eq. 2, we get

$$\ln W = \sum_i [\ln(n_i + g_i - 1)! - \ln n_i! - \ln(g_i - 1)!] + \text{const } t \quad (3)$$

Here, too, since n_i and g_i are very large numbers, we can invoke *Stirling's approximation*, *viz.*,

$\ln x! = x \ln x - x$, to obtain

$$\ln W = \sum_i [(n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i] + \text{const } t \quad (4)$$

Where we have set $n_i + g_i - 1 = n_i + g_i$ and $g_i - 1 = g_i$. Since, n_i is very large, it can be treated as a *continuous variable*. Differentiation of Eq. 3, with respect to n_i and setting the differential equal to zero gives for the most probable thermodynamic state of the system,

$$d \ln W = \sum_i [\ln n_i - \ln(n_i + g_i)] dn_i = 0 \quad \text{or} \quad \sum_i \left[\ln \frac{n_i}{(n_i + g_i)} \right] dn_i = 0 \quad (5)$$

We know that,

$$dN = \sum_i dn_i = 0 \quad (6)$$

$$dU = \sum_i \varepsilon_i dn_i = 0 \quad (7)$$

Applying the method of Lagrange's undetermined multipliers to Eqs. 5, 6 and 7, we get

$$\sum_i \left[\ln \frac{n_i}{(n_i + g_i)} + \alpha + \beta \varepsilon_i \right] dn_i = 0 \quad (8)$$

Since the variations dn_i are independent of one another, hence

$$\ln \frac{n_i}{(n_i + g_i)} + \alpha + \beta \varepsilon_i = 0 \quad (9)$$

Whence
$$\ln \left[\frac{g_i}{(n_i)} + 1 \right] = \alpha + \beta \varepsilon_i \quad \text{or} \quad \frac{g_i}{n_i} + 1 = e^{\alpha + \beta \varepsilon_i} \quad (10)$$

$$\therefore n_i = g_i / [\exp(\alpha + \beta \varepsilon_i) - 1] \quad (11)$$

Eq. 11 is the expression for the most probable distribution of N particles among the various energy levels according to the **Bose – Einstein** statistics.

(iii) Fermi – Dirac Statistics

Consider that the n_i particles are distributed among the g_i states ($n_i < g_i$) where g_i , as before, is the degeneracy of the i^{th} energy level. Imagine that the particles are **indistinguishable**. This implies that the first particle may be placed in any one of the g_i states and for each one of these choices, the second particle may be placed in any one of the remaining $g_i - 1$ states, and so on. Thus, the number of arrangements is given by the expression $g_i! / (g_i - n_i)!$. Since the particles are **indistinguishable**, the above expression has to be divided by the possible number of permutations of n_i particles, *viz.*, $n_i!$. Hence, the number of arrangements of n_i particles in the i^{th} energy level is given by the expression $g_i! / (n_i! (g_i - n_i)!)$.

Thus, the thermodynamics probability W for the system of N particles (i.e., the number of ways of distributing N particles among the various energy levels) is given by

$$W = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \times \text{const } t \quad (1)$$

Taking logarithms of both sides of Eq. 1, we have

$$\ln W = \sum_i [\ln g_i! - \ln n_i! - \ln(g_i - n_i)!] + \text{const } t \quad (2)$$

Assuming that n_i , g_i and $g_i - n_i$ are very large, we can apply Stirling's approximation, obtaining

$$\ln W = \sum_i [(n_i - g_i) \ln(g_i - n_i) - n_i \ln n_i + g_i \ln g_i] + \text{const } t \quad (3)$$

Thus, for the most probable state,

$$\ln W = \sum_i [\ln n_i - \ln(g_i - n_i)] dn_i = 0$$

or
$$\sum_i \left[\ln \frac{n_i}{(g_i - n_i)} \right] dn_i = 0 \quad (4)$$

Since
$$N = \sum_i n_i = \text{const } t \quad \text{and} \quad U = \sum_i n_i \varepsilon_i = \text{const } t,$$

Hence,
$$dN = \sum_i dn_i = 0 \text{ and } dU = \sum_i \varepsilon_i dn_i = 0 \quad (5)$$

Applying Lagrange's method of undetermined multipliers, we obtain

$$\sum_i \left[\ln \frac{n_i}{(g_i - n_i)} + \alpha + \beta \varepsilon_i \right] dn_i = 0 \quad (6)$$

Since the variations dn_i are independent of one another, hence.

$$\ln \frac{n_i}{(g_i - n_i)} + \alpha + \beta \varepsilon_i = 0 \text{ or } \ln \left[\left(\frac{g_i}{n_i} \right) - 1 \right] = \alpha + \beta \varepsilon_i$$

or
$$\left(\frac{g_i}{n_i} \right) - 1 = e^{\alpha + \beta \varepsilon_i} \quad (7)$$

$$\therefore n_i = g_i / [\exp(\alpha + \beta \varepsilon_i) + 1] \quad (8)$$

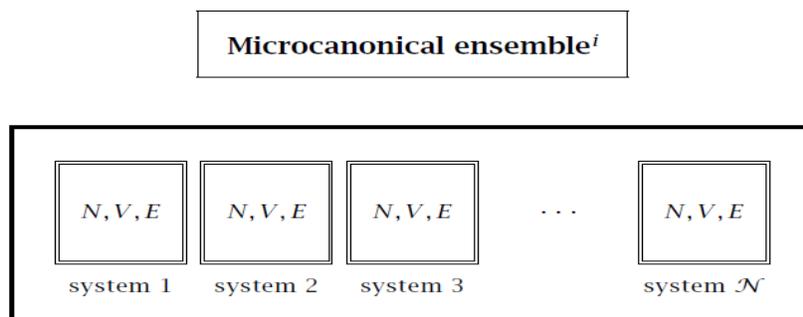
Eq. 8, is the expression for the most probable distribution of N particles among the energy levels according to the **Fermi – Dirac** statistics.

1.4. Ensemble Partition Function

Equilibrium statistical mechanics is based on the idea that, when we make a controlled measurement on a macroscopic system, microscopic fluctuations are so rapid that the system passes through a sequence of many microscopic states during the finite time needed to make the measurement. Consequently the measured value of a physical quantity is actually a long-time average of a fluctuating quantity. We assume that this long-time average is equivalent to an average over a hypothetical ensemble of infinitely many copies of the system, the systems belonging to the ensemble being in different microscopic states consistent with specified values of a small number of macroscopic variables. The statistical weight attached to each microstate is determined by requiring that the probability distribution should be stationary (since we are trying to describe a system in equilibrium) when each system in the ensemble evolves with time according to the microscopic equations of motion. There are actually several different types of partition functions, each corresponding to different types of statistical ensemble (or, equivalently, different types of free energy.)

- (1) The Micro-canonical ensemble describes an isolated system.
- (2) The Canonical ensemble describes a system in contact with a heat bath.
- (3) The Grand Canonical ensemble describes a system in contact with a heat and particle bath.

The Microcanonical Ensemble



A system (a solid, liquid or a gas) which is completely isolated from its surroundings has constant energy E and a constant number of particles N . We will suppose it is also contained at constant volume V . If the system has a number of different types of particles (a number of components), the number of each component, N_1, N_2, \dots is also constant. A micro-canonical ensemble is an assembly of mental copies of this isolated system. Since the energy of each copy is the same, E the need to consider an ensemble is really superfluous. One system will do.

$$S(E, V, N) = k \ln[\Omega(E, V, N)]$$

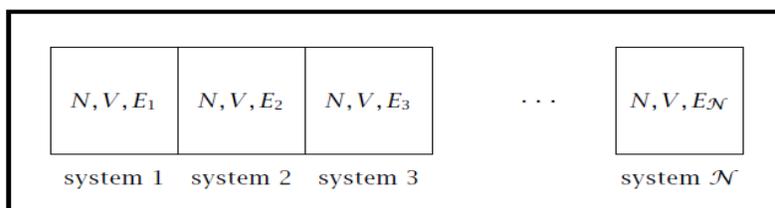
where k is Boltzmann constant; $\Omega(E, V, N)$ is number of microstates that are consistent with the total energy E . We use the notation E for this fixed energy and U for the average of a fluctuating total energy). Since isolated systems are difficult to realize in practice, the microcanonical ensemble is not often used.

The Canonical Ensemble

The canonical ensemble describes a system that has a fixed number N of particles and fixed volume of V but is in thermal contact (and in thermal equilibrium) with a heat bath, with which it can exchange energy. The condition of thermal equilibrium implies that the system has a definite temperature T , which is a property of the heat bath. Statistical weight for a microstate of energy E is $p(E) = Z(T, V, N)^{-1} e^{-\beta E}$, where $\beta = 1/kT$ and the normalizing factor $Z(T, V, N)$ is called as **Canonical partition function**.

$$Z(T, V, N) = \sum_V e^{-\beta E_V} = \sum_E \Omega(E, V, N) e^{-\beta E}$$

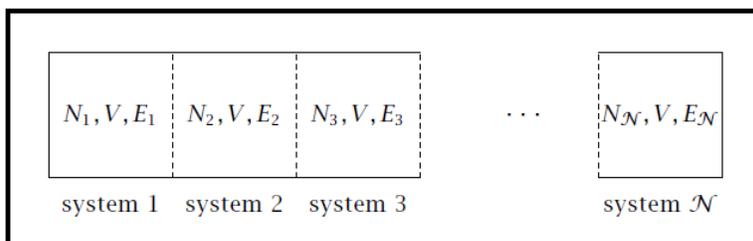
Canonical ensemble


The Grandcanonical Ensemble

The grand canonical ensemble describes an open system, whose volume V is fixed, in equilibrium with a reservoir with which it can exchange both energy and particles. A macroscopic state of this system is characterized by its volume, together with definite values of the temperature T and chemical potential μ both of which are properties of the reservoir. A microstate is now specified by both the energy E and the number N of particles that find themselves instantaneously inside the system and its statistical weight is $p(E, N) = Z(T, V, \mu)^{-1} e^{\beta\mu N} e^{-\beta E}$ where grand canonical partition function is

$$Z(T, V, \mu) = \sum_N e^{\beta\mu N} Z(T, V, N)$$

Grand canonical ensemble



Micro canonical Ensemble: N, V, E common

Canonical ensemble: N, V, T common

Grand canonical ensemble: μ, V, T common

Since an ensemble is a collection of imaginary replications of the system, so we are free to let the number of members be as large as we like; when appropriate, we can let N become infinite. The number of members of the ensemble in a state with energy E_i is denoted n_i , and we can speak of the configuration of the ensemble.

(a) Molecular Partition Functions for an Ideal Gas

The molecular energy levels needed for the evaluation of the molecular partition functions are obtained from the solution of the Schrödinger equation. According to the Born-Oppenheimer approximation, the total energy of a molecule is composed of contributions from the translational, rotational, vibrational and electronic mode of motion. Thus,

$$\varepsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el} \dots \dots \dots (1)$$

This equation holds good if there is no coupling between the different modes of motion. It is only for the simplest atoms that expressions for the electronic energy, ε_{el} , can be explicitly obtained. For molecules it is generally not possible to do so. Hence, the concept of an electronic energy level has limited usefulness. We will, therefore, not include the electronic energy in Eq. 1 and instead will write

$$\varepsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} \dots \dots \dots (2)$$

According to the laws of conservation of momentum, angular momentum and energy, there cannot be any interaction between the translational motion of a body and the internal motions (rotational and vibrational motions) when the motion is taking place in the field-free environment. However, there is always some coupling between the rotational and vibrational modes of motion. In the present discussion we will neglect such coupling and assume that Eq. 2 holds.

Using Eqs. 39 and 2, the molecular partition function can be written as

$$q = \sum_i \sum_j \sum_k g_i \exp[(\varepsilon_{i,tr} + \varepsilon_{j,rot} + \varepsilon_{k,vib})/kT]$$

$$q = \sum_i g_i \exp[-\varepsilon_{i,tr}/kT] \times \sum_j g_j \exp[-\varepsilon_{j,rot}/kT] \times \sum_k g_k \exp[-\varepsilon_{k,vib}/kT] \dots \dots (3)$$

$$q = q_{tr} \times q_{rot} \times q_{vib} \dots \dots \dots (4)$$

Thus, the **total partition function** of a molecule is the product of the translational, rotational and vibrational partition functions. This is known as the **multiplication theorem for the partition functions**.

(b) Translational Partition Function

For a particle of mass m , moving in an infinite three-dimensional box of sides a , b and c , assuming that the potential is zero within the box, the energy levels obtained by the solution of the Schrödinger equation are given by the expression

$$\varepsilon_{n_x, n_y, n_z} = \varepsilon_{tr} = (h^2/8m) \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \dots \dots \dots (5)$$

Where each of the quantum numbers n_x , n_y , n_z vary from one to infinity. Using Eqs. 39 and 5, the translational partition function, neglecting degeneracy, is given by

$$q_{tr} = \sum_{n_x} \sum_{n_y} \sum_{n_z} \exp\left[-\frac{h^2}{8mkT} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\right] \dots \dots \dots (6)$$

Where the triple summation is taken over all integral values of n_x , n_y and n_z from one to infinity. The motion of the particle in the three x, y and z directions being independent, we can replace the triple summation as a product of three summations. Thus,

$$q_{tr} = \sum_{n_x=1}^{\infty} \exp\left[-\frac{n_x^2 h^2}{8ma^2 kT}\right] \times \sum_{n_y=1}^{\infty} \exp\left[-\frac{n_y^2 h^2}{8mb^2 kT}\right] \times \sum_{n_z=1}^{\infty} \exp\left[-\frac{n_z^2 h^2}{8mc^2 kT}\right] \dots \dots (7)$$

It is well known that the spacing between the energy levels of the particle in a three-dimensional box is very small compared with the thermal energy, kT . Hence, we can replace the summation by integration. Accordingly,

$$q_{tr} = \int_0^{\infty} \exp\left[-\frac{n_x^2 h^2}{8ma^2 kT}\right] dn_x \times \int_0^{\infty} \exp\left[-\frac{n_y^2 h^2}{8mb^2 kT}\right] dn_y \times \int_0^{\infty} \exp\left[-\frac{n_z^2 h^2}{8mc^2 kT}\right] dn_z (8)$$

From calculus, it is known that the standard integral

$$\int_0^{\infty} e^{-ax^2} dx = \left(\frac{1}{2}\right) \left(\frac{\pi}{a}\right)^{1/2} \dots \dots \dots (9)$$

Using this result, the three integrals in Eq. 8 which are identical except for the constants a, b and c, can be calculated, giving

$$\begin{aligned} q_{tr} &= \left(\frac{a}{h}\right) (2\pi mkT)^{1/2} \times \left(\frac{b}{h}\right) (2\pi mkT)^{1/2} \times \left(\frac{c}{h}\right) (2\pi mkT)^{1/2} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \times abc \\ &= \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \times V \dots \dots \dots (10) \end{aligned}$$

Where $V(=abc)$ is the volume of the box in which the molecule moves. Eq. 10 can also be written as

$$q_{tr} = q_{tr}^o \times V \dots \dots \dots (11)$$

where q_{tr}^o is the partition function per unit volume. From Eq. 10 we see that the translational partition function depends upon temperature and volume.

If M is the mass per mole the $m = M/N_A$ where N_A is Avogadro's number. Also, $k = R/N_A$. Hence,

$$q_{tr} = [(2\pi MRT)^{3/2} \times V_m] / (h^2 N_A^2) \dots \dots \dots (12)$$

where V_m is the volume per mole.

Sometimes we are interested in calculating the quantity q_{tr}/N_A . For a gas at 1 atm pressure (101.325 kNm^{-2}), the volume per mole, viz., $V_m = (8.206 \times 10^{-5})Tm^3$. Hence, Eq. 12 takes the form

$$\frac{q_{tr}^o}{N_A} = 0.02559 M^{3/2} T^{5/2} \dots \dots \dots (13)$$

where q_{tr}^o is the translational partition function per unit volume evaluated for the gas at 1 atm pressure. Thus, for H_2 at 27°C and 1 atm pressure, we have

$$\frac{q_{tr}^o}{N_A} \approx 10^5 \dots \dots \dots (14)$$

Using the Boltzmann distribution, the number of molecules in any translational state I is given by

$$n_{i,tr} = \frac{N e^{-\frac{\epsilon_{i,tr}}{kT}}}{q_{tr}} \dots \dots \dots (15)$$

where N is the total number of molecules.

Since the factor $\epsilon_{i,tr}/kT$ is a positive number, $n_{i,tr}$ cannot be greater than N/q_{tr} . It follows from Eq. 14 that $N/q_{tr} \approx 10^{-5}$

The above result implies that though the number of molecules (N) is very large, the number of available quantum states (or energy level), i.e., q_{tr} , is even larger so that the probability of any one quantum state being occupied by a given molecules is very small. The quantity $h/(2\pi mkT)^{1/2}$ in Eq. 10, is called the **thermal de Broglie wave length** and is represented by the symbol Λ . Thus, $q = V/\Lambda^3$

(c) Rotational Partition Function

The simplest system that undergoes rotational motion is a diatomic molecule. The rotational energy levels of a rigid diatomic rotor (i.e., a rotor whose internuclear distance remains fixed during rotation), obtained by solving the Schrodinger wave equation, are

$$q_{rot} \equiv \epsilon_J = \frac{J(J+1)h^2}{8\pi^2 I} \dots \dots \dots (16)$$

Where the rotational quantum number J has the values 0, 1, 2, 3,....., and I is the moment of inertia of the molecule about an axis perpendicular to the internuclear axis.

The degeneracy, g_j , of rotational energy levels is equal to $(2J+1)$. Thus, using Eqs. 39 and 16, the rotational partition function of a rigid diatomic rotor is given by

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{J(J+1)h^2}{8\pi^2IkT}\right] = \sum_{J=0}^{\infty} (2J+1) \exp[-J(J+1)C] \dots \dots \dots (17)$$

where $C = h^2/8\pi^2IkT$

When $kT \gg h^2/8\pi^2I$, the spacing between the neighboring rotational energy levels. Still it is found that for practically all diatomics (exceptions are the hydrogen isotopes at low temperatures), $h^2/8\pi^2IkT$ is small so that the successive rotational energy levels are closer to one another. It is thus possible to replace the summation in Eq. 75 by integration. Accordingly,

$$q_{rot} = \int_0^{\infty} (2J+1) \exp[-J(J+1)C] dJ \dots \dots \dots (18)$$

Let $x = J^2 + J$. Therefore, $dx = (2J+1)dJ$

$$\therefore q_{rot} = \int_0^{\infty} e^{-Cx} dx = -\frac{[e^{-\infty} - e^0]}{C} = \frac{1}{C} \dots \dots \dots (19)$$

Substituting for C , we have

$$q_{rot} = \frac{8\pi^2IkT}{h^2} \dots \dots \dots (20)$$

The quantity $h^2/8\pi^2Ik$ in Eq. 20 has the dimensions of temperature and is called **Characteristic rotational temperature** which can be written as

$$\Theta_{rot} = \frac{T}{q_{rot}} \dots \dots \dots (21)$$

From Eq. 16 we see that the value of Θ/T gives an idea as to how close the energy levels are to kT . The assumption of the replacement of summation by integration used in evaluating q_{rot} is valid when Θ_{rot} is far less than T .

Eq. 20 can be applied to rotational degrees of freedom in which identical configurations occur only after a rotation of 2π . If the molecule has elements of symmetry number such that identical configurations occur after a rotation of $2\pi/\sigma$ where σ is the symmetry number, then the rotational partition function is given by

$$q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{T}{\sigma \Theta_{rot}} \dots \dots \dots (22)$$

The symmetry number ensures the avoidance of too many identical configurations being taken into account. For homonuclear diatomic molecules such as H₂, O₂, N₂, etc., $\sigma = 2$ whereas for heteronuclear diatomic molecules such as CO, NO, HD, HCl, etc., $\sigma = 1$.

We can also write Eq. 22 as

$$q_{rot} = \frac{kT}{\sigma hcB} \dots \dots \dots (23)$$

Where B is the **rotational constant** of the diatomic rotor defined as

$$B = \frac{h}{8\pi^2 Ic} \dots \dots \dots (24)$$

(d) Vibrational Partition Function

For a diatomic molecule vibrating as a simple harmonic oscillator (SHO), the vibrational energy levels, obtained by the solution of the Schrodinger wave equation, are given by

$$E = \left(v + \frac{1}{2} \right) h\nu \dots \dots \dots (25)$$

where ν is the vibrational frequency and v is the vibrational quantum number which has the values $v = 0, 1, 2, 3, \dots$

The energy levels are non-degenerate, i.e., the degeneracy, g , is unity. Using Eqs. 39 and 25, the vibrational partition function of the diatomic molecule is given by

$$q_{vib} = \sum_{v=0}^{\infty} \exp \left[-\frac{\left(v + \frac{1}{2} \right) h\nu}{kT} \right] = e^{-h\nu/2kT} \sum_{v=0}^{\infty} \exp \left[-\frac{vh\nu}{kT} \right] \dots \dots \dots (26)$$

In the case of a simple harmonic oscillator, the spacing between the neighbouring energy levels (which are equally spaced by an amount $h\nu$) is very large compared with the translational or the rotational energy levels. In other words, $h\nu \gg kT$. Hence, the summation cannot be replaced by integration. The summation can, however, be carried out as follows:

Let $x = h\nu/kT$. Then,

$$\sum_{v=0}^{\infty} \exp \left[-\frac{vh\nu}{kT} \right] = \sum_{v=0}^{\infty} e^{-vx} = 1 + e^{-x} + e^{-2x} + e^{-3x} + \dots \dots \dots (27)$$

$$= \frac{1}{1 - e^{-x}} = \frac{1}{1 - e^{-h\nu/kT}} \dots \dots \dots (28)$$

Hence, from, Eq. 26

$$q_{vib} = \frac{e^{-\frac{h\nu}{2kT}}}{1 - e^{-\frac{h\nu}{kT}}} \dots \dots \dots (29)$$

If we define Θ_{vib} , the **characteristic Vibration temperature**, of the oscillator as

$$\Theta_{vib} = \frac{h\nu}{k} \dots \dots \dots (30)$$

Then, the vibrational partition function is given by

$$q_{vib} = \frac{e^{-\frac{\Theta_{vib}}{2T}}}{1 - e^{-\frac{\Theta_{vib}}{T}}} \dots \dots \dots (31)$$

According to Heisenberg’s uncertainty principle, the oscillator cannot have a total energy of zero because this would imply that both the position and the momentum of the oscillator can be precisely determined. Thus, as seen from Eq. 25, even in the ground vibrational state ($v = 0$), the oscillator possesses an energy $\left(\frac{h\nu}{2}\right)$, called the **zero-point energy**, above the classical energy zero. Sometimes it is convenient to measure the energies of the various quantum states from the ground state rather than from the classical energy zero. Hence, the energy level expression (Eq. 25) for the SHO is modified to

$$\epsilon = \nu h\nu \quad (\nu = 0, 1, 2, 3, \dots) \dots \dots (32)$$

Hence the new vibrational partition function is given by

$$q'_{vib} = \sum_{\nu=0}^{\infty} \exp\left[-\frac{\nu h\nu}{kT}\right] = 1 + x + x^2 + x^3 + \dots \dots \dots (33)$$

where $x = \exp\left(-\frac{h\nu}{kT}\right) < 1$

$$\text{For } x < 1, 1 + x + x^2 + x^3 + \dots = 1/(1 - x)$$

Since $\exp\left(-\frac{h\nu}{kT}\right) < 1$, we have

$$q'_{vib} = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} = \frac{1}{1 - e^{-\frac{\Theta_{vib}}{T}}} \dots \dots \dots (34)$$

If the temperature is very high or very low, Eq. 89 can assume a simpler form as illustrated below.

Case I: T is very low so that $\frac{\Theta_{vib}}{T} \gg 1$. Then, $\exp(-\frac{\Theta_{vib}}{T})$ is negligible compared with unity in the denominator of Eq. 31 and we obtain

$$q_{vib} = e^{-\Theta_{vib}/2T} \quad (\text{at low temperature}) \dots\dots (35)$$

Case II: T is very high so that $\frac{\Theta_{vib}}{T} \ll 1$. Then, the exponential in the denominator can be expanded as a series, retaining only the first two terms:

$$e^{-\frac{\Theta_{vib}}{T}} = 1 - \frac{\Theta_{vib}}{T} + \dots \dots\dots (36)$$

Hence,

$$q_{vib} = \frac{T e^{-\frac{\Theta_{vib}}{2T}}}{\Theta_{vib}} \quad (\text{at high temperature}) \dots\dots (37)$$

The value of ν , and hence Θ_{vib} , is obtained from the vibrational (infrared) spectrum of a molecule.

(e) Electronic Partition Function

Though it is possible, in principle, to solve Schrodinger equation for the electronic states and energies of molecules, it is more convenient to obtain this information from the spectroscopic data. For most of the molecules, the excited electronic energy level lie so far above the ground state compared with kT (a typical excited state value being greater than $2eV \approx 3 \times 10^{-19}J$) that all the molecules may be considered to be in the ground state at ordinary temperatures. Thus, contributions to the electronic partition function arising from excited electronic states may be neglected. The electronic partition function is given by

$$q_{el} = \sum_i g_{el,i} e^{-\epsilon_i/kT} = g_0 e^0 + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} + \dots \dots\dots (38)$$

$$q_{el} = g_0 \dots\dots\dots (39)$$

Since the second, and third and subsequent terms are considered negligible.

Thus, the electronic partition function is simply the degeneracy, g_0 , of the ground electronic state.

1.5. Thermodynamic Functions

We can use the **Boltzmann** distribution law and the related partition functions to calculate the macroscopic (thermodynamic) properties such as internal energy, enthalpy, entropy, free energy,

etc., of matter from molecular properties. The partition functions are, therefore, of great importance in statistical thermodynamics.

Internal Energy, U : The internal energy, U , of a system consisting of N independent particles (atoms or molecules) is equal to the sum of the energies of individual particles. Thus,

$$U = \sum_i N_i \varepsilon_i = N \bar{\varepsilon} \quad (1)$$

Where $\bar{\varepsilon}$ is the *average energy* of the particles defined by

$$\bar{\varepsilon} = \frac{\sum_i N_i \varepsilon_i}{\sum_i N_i} = \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}} = \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{q} \quad (2)$$

Now,
$$\left(\frac{\partial q}{\partial \beta} \right)_V = \frac{\partial \left[\sum_i e^{-\beta \varepsilon_i} \right]}{\partial q} = \sum_i \varepsilon_i e^{-\beta \varepsilon_i} \quad (3)$$

where the differentiation is carried out at *constant volume* since the energies ε_i depend upon the volume. Hence,

$$\bar{\varepsilon} = \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_V = - \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad (4)$$

Therefore, from Eqs. 1 and 4 for a system containing N particles,

$$U = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad (5)$$

Since $\beta = 1/kT$ and $Nk = nR$ (where n is the number of moles), we have

$$U = -nR \left(\frac{\partial \ln q}{\partial (1/kT)} \right)_V$$

Or
$$U = nRT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (6)$$

Molar Heat Capacity, C_v : For one mole of a system ($n = 1$), differentiation of U with respect to T at constant V , yields the molar heat capacity C_v . Hence,

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V = R \frac{\partial}{\partial T} \left[T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \right] = \frac{R}{T^2} \left[\frac{\partial^2 \ln q}{\partial (1/T)^2 V} \right] \quad (7)$$

Entropy, S : If the particles are considered *indistinguishable*, then the thermodynamic probability for the system, must be divided by $N!$ to yield the new thermodynamic probability of the **Boltzmann** distribution as

$$W = \prod_i g_i^{n_i} / n_i! \quad (8)$$

Using the **Boltzmann** equation for entropy, viz.,

$$S = k \ln W \quad (9)$$

We have,
$$S = k \left(\sum_i n_i \ln g_i - \sum_i \ln N! \right) \quad (10)$$

Using the Stirling approximation, viz.,

$$\ln n_i! = n_i \ln n_i - n_i \quad (11)$$

We obtain
$$S = k \sum_i n_i \ln(g_i / n_i) + kN \quad (12)$$

Since,
$$\ln(g_i / n_i) = \ln(q / N) + \varepsilon_i / kT$$

Substituting in Eq. 12, we have

$$S = k \sum_i n_i \ln q / N + \sum_i n_i \varepsilon_i / kT + kN = kN \ln q / N + U / T + kN \quad (13)$$

For n moles of the system, $kN = nR$. Also, using the expression for U given by Eq. 6, we have

$$S = nR [\ln q / N + T(\partial \ln q / \partial T)_V + 1] \quad (14)$$

Helmholtz Function or Work Function, A: $A = U - TS$

Hence, after substituting for U from Eq. 6 and for S from Eq. 14,

We have
$$A = nRT^2(\partial \ln q / \partial T)_V - nRT [\ln q / N + (\partial \ln q / \partial T)_V + 1]$$

$$A = -nRT [\ln q / N + 1] \quad (15)$$

Since $nR = Nk$, we can write Eq. 15 as

$$A = -kT [\ln q^N - (N \ln N - N)] = -kT \ln(q^N / N!) \quad (16)$$

$$A = -kT \ln Q \quad (17)$$

Where Q is the **molar** partition function, i.e., the partition function for one mole, viz., for Avogadro's number of particles and q is the **molecular** partition function, viz., the partition function for a single molecule.

Pressure, P: By definition, pressure is given by

$$P = - \left(\frac{\partial A}{\partial V} \right)_T \quad (18)$$

Differentiating Eq. 16 with respect to V at constant T , we have

$$\left(\frac{\partial A}{\partial V}\right)_T = -nRT \left(\frac{\partial \ln q}{\partial V}\right)_T \quad (19)$$

$$\therefore P = -nRT \left(\frac{\partial \ln q}{\partial V}\right)_T \quad (20)$$

Gibbs Function, G: The Gibbs free energy defined as

$$G = H - TS = (U + PV) - TS = A + PV$$

Substituting Eq. 15 for **A** and Eq. 20 for **P**, we obtain

$$G = -nRT \left[\ln \frac{q}{N} + 1 - V \left(\frac{\partial \ln q}{\partial V}\right)_T \right] \quad (21)$$

Enthalpy, H: Enthalpy is defined as $H = U + PV$

Substituting Eq. 6 for **U** and Eq. 20 for **P**, we have

$$H = nRT \left[\left(\frac{\partial \ln q}{\partial \ln T}\right)_V + \left(\frac{\partial \ln q}{\partial \ln V}\right)_T \right] \quad (22)$$

The chemical potential

In equilibrium, a system is in steady state. Thus, a simple chemical reaction in equilibrium, of the form



has to have as many molecules going from **A** → **B** as from **B** → **A** in equilibrium. Another way to say this is that there should be no change in free energy for a reacting molecule, or that the total chemical potential (change in free energy per molecule) is zero

$$\mu_A = \mu_B \quad (2)$$

in equilibrium. The equilibrium condition can be related to the free energy for the different ensembles by

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{\partial E}{\partial N}\right)_{S,V} \quad (3)$$

For gas phase reactions in the Canonical ensemble, where $A = -kT \ln Q$, and $Q = q^N / N!$ the chemical potential is

$$\mu = \left(\frac{\partial A}{\partial N}\right) = -kT \frac{\partial}{\partial N} \ln \left(\frac{q^N}{N!}\right) \quad (4)$$

using Stirling's approximation, $\ln N! = N \ln N - N$. This gives a simple relation for reacting gas particles, for which the system partition function $Q = Q_A Q_B$ is the product of the partition function for each species. In this case, the condition for equilibrium

$$\begin{aligned}
 -kT \frac{Q}{N_A} &= -kT \frac{Q}{N_B} \\
 \ln \left(\frac{q_A}{N_A} \right) &= \ln \left(\frac{q_B}{N_B} \right) \\
 \left(\frac{q_A}{N_A} \right) &= \left(\frac{q_B}{N_B} \right) \tag{5}
 \end{aligned}$$

where N_A and N_B are the number of **A** and **B** molecules respectively

The equilibrium constant

The equilibrium condition can be written as a constant with respect to N because q_A and q_B are both single particle partition functions with no N dependence

$$K_N = \frac{N_B}{N_A} = \frac{q_B}{q_A} \tag{6}$$

The equilibrium constant can also be written in terms of concentrations, which are independent of volume. Substituting the density $\rho = N/V$

$$K_C = \frac{\rho_B}{\rho_A} = \frac{q_B/V}{q_A/V} = \frac{q_B}{q_A} \tag{7}$$

The single particle partition function q is equal to the volume times a function of T , so that q/V is independent of volume, which makes K_C also a constant with respect to volume. For simple reactions, given by Eq. 7, these two constants are equal, $K_N = K_C$.

We can also find an equilibrium pressure constant, using the ideal gas relation $PV = NkT$,

$$K_P = \frac{P_B}{P_A} = \frac{N_B kT/V}{N_A kT/V} = \frac{N_B}{N_A} \tag{8}$$

which again reduces to K_N and K_C .

1.6. Thermodynamic Properties of Ideal Gas

An **ideal gas** is a theoretical gas composed of a set of randomly moving, non-interacting point particles. The ideal gas concept is useful because it obeys the ideal gas law, a simplified equation of state, and is amenable to analysis under statistical mechanics. One mole of an ideal gas has a volume of 22.41 L at STP.

At normal conditions such as standard temperature and pressure, most real gases behave qualitatively like an ideal gas. Many gases such as nitrogen, oxygen, hydrogen, noble gases, and some heavier gases like carbon dioxide can be treated like ideal gases within reasonable tolerances. Generally, a gas behaves more like an ideal gas at higher temperature and lower pressure, as the work which is against intermolecular forces becomes less significant compared with the particles' kinetic energy, and the size of the molecules becomes less significant compared to the empty space between them.

The ideal gas model tends to fail at lower temperatures or higher pressures, when intermolecular forces and molecular size become important. It also fails for most heavy gases, such as many refrigerants, and for gases with strong intermolecular forces, notably water vapor. At low pressures, the volume of a real gas is often considerably greater than that of an ideal gas. At low temperatures, the pressure of a real gas is often considerably less than that of an ideal gas. At some point of low temperature and high pressure, real gases undergo a phase transition, such as to a liquid or a solid. The model of an ideal gas, however, does not describe or allow phase transitions. These must be modelled by more complex equations of state.

The ideal gas model has been explored in both the Newtonian dynamics (as in "kinetic theory") and in quantum mechanics (as a "gas in a box"). The ideal gas model has also been used to model the behaviour of electrons in a metal (in the Drude model and the free electron model), and it is one of the most important models in statistical mechanics.

One of them is the well known ideal gas law derived from Boyle's law (at constant T and n); Charles's law (at constant P and n); and Avogadro's law (at constant T and P).

$$PV = nRT$$

The other equation of state of an ideal gas must express **Joule's law**, that the internal energy of a fixed mass of ideal gas is a function only of its temperature. For the present purposes it is convenient to postulate an exemplary version of this law by writing:

$$U = c_v nRT$$

In order to switch from macroscopic quantities (left hand side of the following equation) to microscopic ones (right hand side), we use

$$nR = Nk_B$$

Where, N is the number of gas particles; k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$).

The probability distribution of particles by velocity or energy is given by the Maxwell speed distribution.

The ideal gas law is an extension of experimentally discovered gas laws. Real fluids at low density and high temperature approximate the behavior of a classical ideal gas. However, at lower temperatures or a higher density, a real fluid deviates strongly from the behavior of an ideal gas, particularly as it condenses from a gas into a liquid or as it deposits from a gas into a solid. This deviation is expressed as a compressibility factor.

Specific Heat Capacity

The heat capacity at constant volume, including an ideal gas is:

$$c_v = \frac{1}{nR} T \left(\frac{\partial S}{\partial T} \right)_v = \frac{1}{nR} \left(\frac{\partial U}{\partial T} \right)_v$$

where S is the entropy. This is the dimensionless heat capacity at constant volume, which is generally a function of temperature due to intermolecular forces. For moderate temperatures, the constant for a monatomic gas is $c_v = 3/2$ while for a diatomic gas it is $c_v = 5/2$. It is seen that macroscopic measurements on heat capacity provide information on the microscopic structure of the molecules.

The heat capacity at constant pressure of $1/R$ mole of ideal gas is:

$$c_p = \frac{1}{nR} T \left(\frac{\partial S}{\partial T} \right)_p = \frac{1}{nR} \left(\frac{\partial H}{\partial T} \right)_p = c_v + 1$$

where $H = U + pV$ is the enthalpy of the gas.

Sometimes, a distinction is made between an ideal gas, where c_v and c_p could vary with temperature, and a perfect gas, for which this is not the case.

The ratio of the constant volume and constant pressure heat capacity is

$$\Upsilon = \frac{c_p}{c_v} \quad \text{for air which is a mixture it is 1.4.}$$

Entropy

The expression for the entropy of an ideal gas. Since the entropy is an exact differential, using the chain rule, the change in entropy when going from a reference state 0 to some other state with entropy S may be written as ΔS where:

$$\Delta S = c_v Nk \ln \left(\frac{T}{T_o} \right) + Nk \ln \left(\frac{V}{V_o} \right)$$

which implies that the entropy may be expressed as:

$$S = Nk \ln \left(\frac{VT^{c_v}}{f(N)} \right)$$

Differentiating this with respect to a , setting a equal to unity, and then solving the differential equation yields $f(N)$:

$$f(N) = \Phi N$$

Where Φ which may vary for different gases, but will be independent of the thermodynamic state of the gas. It will have the dimensions of VT^{c_v} / N . Substituting into the equation for the entropy:

$$\frac{S}{Nk} = \ln \left(\frac{VT^{c_v}}{N\Phi} \right)$$

and using the expression for the internal energy of an ideal gas, the entropy may be written:

$$\frac{S}{Nk} = \ln \left[\frac{V}{N} \left(\frac{U}{c_v kN} \right)^{c_v} \frac{1}{\Phi} \right]$$

Since this is an expression for entropy in terms of U , V , and N , it is a fundamental equation from which all other properties of the ideal gas may be derived.

Thermodynamics potential

The chemical potential of the ideal gas is calculated from the corresponding equation of state

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}$$

where G is the Gibbs free energy and is equal to $U + PV - TS$ so that:

$$\mu(T, N, V) = kT \left(c_p - \ln \left(\frac{VT^{c_v}}{N\Phi} \right) \right)$$

The thermodynamic potentials for an ideal gas can now be written as functions of T , V , and N as:

$$\begin{aligned} U &= c_v NkT \\ A &= U - TS = \mu N - NkT \\ H &= U + PV = c_p NkT \\ G &= U + PV - TS = \mu N \end{aligned}$$

where, as before, $c_p = c_v + 1$. The most informative way of writing the potentials is in terms of their natural variables, since each of these equations can be used to derive all of the other thermodynamic variables of the system. In terms of their natural variables, the thermodynamic potentials of a single-species ideal gas are:

$$U(S, V, N) = c_v Nk \left(\frac{N\Phi}{V} e^{S/Nk} \right)^{1/c_v}$$

$$A(T, V, N) = NkT \left(c_p - \ln \left(\frac{VT^{c_v}}{N\Phi} \right) \right)$$

$$H(S, P, N) = c_p Nk \left(\frac{P\Phi}{k} e^{S/Nk} \right)^{1/c_p}$$

$$G(T, P, N) = NkT \left(c_p - \ln \left(\frac{kT^{c_p}}{P\Phi} \right) \right)$$

In statistical mechanics, the relationship between the Helmholtz free energy and the partition function is fundamental, and is used to calculate the thermodynamic properties of matter

Surface Chemistry

Topic to be covered:

2. Interfacial Structure

2.1. Surface Tension and Surface Free Energy

2.2. Methods of Surface Tension Measurement

2.3. Nature and Thermodynamics of Liquid-Gas Interface

2.4. The Surface Tension of Solutions

2.5. Surfaces of Solids

2.6. Adsorption at the Solid Solution Interface

Introduction

Surface chemistry can be roughly defined as the study of chemical reactions at interfaces. It is closely related to surface engineering, which aims at modifying the chemical composition of a surface by incorporation of selected elements or functional groups that produce various desired effects or improvements in the properties of the surface or interface. Surface chemistry also overlaps with electrochemistry. Surface science is of particular importance to the field of heterogeneous catalysis.

In this chapter we will discuss the physical chemistry of surfaces in a broad sense. Although an obvious enough point, it is perhaps worth noting that in reality we will always be dealing with the interface between two phases (liquid-gas, solid-liquid and solid-gas) and that, in general, the properties of an interface will be affected by physical or chemical changes in either of the two phases involved.

2. Interfacial Structure

A phase defined as a part of a system that was "homogeneous throughout." Such a definition implies that the matter deep in the interior of a phase is subject to exactly the same conditions as the matter at the exterior which forms the surface. An interface is a surface forming a common boundary among two different phases of matter, such as an insoluble solid and a liquid, two immiscible liquids, a liquid and an insoluble gas or a liquid and vacuum. The importance of the interface depends on the type of system: the bigger the quotient area/volume, the more effect the surface phenomena will have. This is clearly impossible in any case, since the molecules (or

ions) in the interior are surrounded on all sides by the uniform field of force of neighbor molecules (or ions) of the same substance. The molecules at the surface were bounded on one side by neighbors of the same kind but on the other side by an entirely different sort of environment.

Consider, for example, the surface of a liquid in contact with its vapor, shown in figure below. A molecule in the interior of the liquid is in a uniform field of force. A molecule at the surface is subject to a net attraction toward the bulk of the liquid, which is not compensated by an equal attraction from the more highly dispersed vapor molecules. Thus all liquid surfaces, in the absence of other forces, tend to contract to the minimum area. For example, freely suspended volumes of liquid assume a spherical shape, since the sphere has the minimum surface-to-volume ratio.

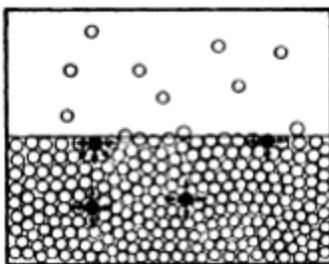


Figure: Liquid-vapor interfaces.

In order to extend the area of an interface like that in figure that is to bring molecules from the interior into the surface, works must be done against the cohesive forces in the liquid. It follows that the surface portions of the liquid have a higher free energy than the bulk liquid. This extra surface free energy is more usually described by saying that there is a *surface tension*, acting parallel to the surface, which opposes any attempt to extend the interface.

2.1. Surface Tension and Surface Free Energy

Although referred to as a free energy per unit area, surface tension may equally well be thought of as a force per unit length. Two serve to illustrate these viewpoints. Consider, first, a soap film stretched over a wire frame, one end of which is movable (Fig.). Experimentally one observes that a force is acting on the movable member in the direction opposite to that of the arrow in the diagram. If the value of the force per unit length is denoted by γ , then the work done in extending the movable member a distance dx is

$$\text{Work} = \gamma dx = \gamma dA \quad (1)$$

Where $dA = ldx$ is the change in area. In the second formulation, γ appears to be energy per unit area.

A second illustration involves the soap bubble. We will choose to think of γ in terms of energy per unit area. In the absence of gravitational or other fields, a soap bubble is spherical, as this is the shape of minimum surface area for an enclosed volume. A soap bubble of radius r has a total surface free energy of $4\pi r^2\gamma$ and, if the radius were to decrease by dr , then the change in surface free energy would be $8\pi r\gamma dr$. Since shrinking decreases the surface energy, the tendency to do so must be balanced by a pressure difference across the film



Figure: A soap film stretched across a wire frame with one movable side.

ΔP such that the work against this pressure $\Delta P 4\pi r^2 dr$ is just equal to the decrease in surface free energy. Thus

$$\Delta P 4\pi r^2 dr = 8\pi r\gamma dr \quad (2)$$

Or

$$\Delta P = 2\gamma/r \quad (3)$$

One thus arrives at the important conclusion that the smaller the bubble, the greater the pressure of the air inside relative to that outside.

The forgoing examples illustrate the point that equilibrium surfaces may be treated using either the mechanical concept of surface tension or the mathematically equivalent concept of surface free energy. A similar duality of viewpoint can be argued on a molecular scale so that the decision as to whether *surface tension* or *surface free energy* is the more fundamental concept becomes somewhat a matter of individual taste. The term surface tension is the older of the two; it goes back to early ideas that the surface of a liquid had some kind of contractile “skin”. *Surface free energy* implies only that work is required to bring molecules from the interior of the phase to the surface. Table given below shows surface tension of some liquids.

Surface tension of liquids at 20 °C

Liquid	$\gamma/(10^{-3} \text{ N/m})$	Liquid	$\gamma/(10^{-3} \text{ N/m})$
Acetone	23.70	Ethyl ether	17.01
Benzene	28.85	<i>n</i> -Hexane	18.43
Carbon tetrachloride	26.95	Methyl alcohol	22.61
Ethyl acetate	23.9	Toluene	28.5

2.2. Methods of Surface Tension Measurement

(i) Capillary-rise Method

A capillary tube of radius r is vertically inserted into a liquid. The liquid rises to a height h and forms a concave meniscus. The surface tension (γ) acting along the inner circumference of the tube exactly supports the weight of the liquid column.

By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is θ , the vertical component of surface tension is $\gamma \cos \theta$. The total surface tension along the circular contact line of meniscus is $2\pi r$ times. Therefore,

$$\text{Upward force} = 2\pi r \gamma \cos \theta$$

where r is the radius of the capillary. For most liquids, θ is essentially zero, and $\cos \theta = 1$. Then the upward force reduces to $2\pi r \gamma$.

The downward force on the liquid column is due to its weight which is *mass* \times *gravity*. Thus,

$$\text{Downward force} = h\pi r^2 dg$$

where d is the density of the liquid.

But

$$\text{Upward force} = \text{Downward force}$$

or

$$2\pi r \gamma = h\pi r^2 dg$$

$$\gamma = hrdg/2$$

In order to know the value of γ , the value of h is found with the help of a travelling microscope and density (d) with a pycnometer.

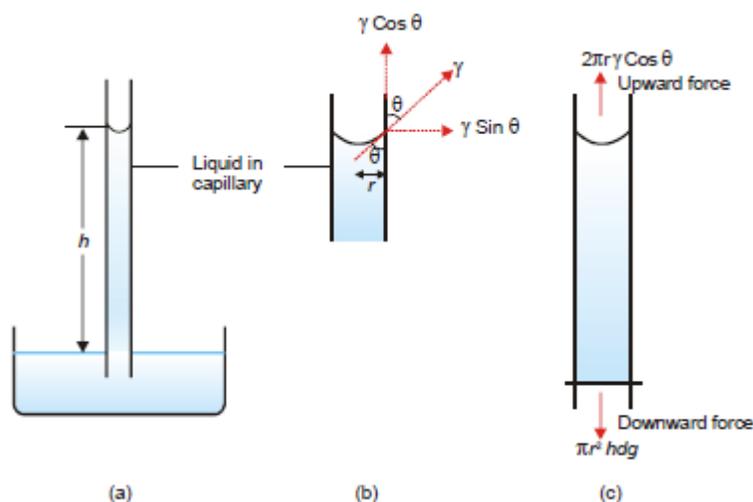


Figure: (a) Rise of liquid in a capillary tube; (b) Surface tension (γ) acts along tangent to meniscus and its vertical component is $\gamma \cos \theta$; (c) Upward force $2\pi r \gamma \cos \theta$ counter balances the downward force due to weight of liquid column, $\pi r^2 h d g$.

PROBLEM 1. A capillary tube of internal diameter 0.21 mm is dipped into a liquid whose density is 0.79 g cm^{-3} . The liquid rises in this capillary to a height of 6.30 cm. Calculate the surface tension of the liquid. ($g = 980 \text{ cm sec}^{-2}$).

SOLUTION

We know:

$$\gamma = h r d g / 2$$

Where, h = height of liquid in capillary in centimeters; r = radius of capillary in centimeters; d = density of liquid in g cm^{-3} ; g = acceleration due to gravity in cm sec^{-2}

Substituting the values from the above example, $h = 6.30 \text{ cm}$

$$r = 0.21/2 \times 1/10 = 0.0105 \text{ cm}$$

$$d = 0.79 \text{ g.cm}^{-3}$$

$$g = 980 \text{ cm.sec}^{-2}$$

Substituting these in above eq.

$$\gamma = (6.30 \times 0.0105 \times 0.79 \times 980) / 2$$

$$\gamma = 25.6 \text{ dynes cm}^{-1}$$

(ii) Drop Formation Method

A drop of liquid is allowed to form at the lower end of a capillary tube. The drop is supported by the upward force of surface tension acting at the outer circumference of the tube. The weight of the drop (mg) pulls it downward. When the two forces are balanced, the drop breaks. Thus at the point of breaking,

$$m g = 2 \pi r \gamma \quad (1)$$

where m = mass of the drop; g = acceleration due to gravity; r = outer radius of the tube

Statistical Thermodynamics and Surface Chemistry

The apparatus employed is a glass pipette with a capillary at the lower part. This is called a **Stalagmometer** or **Drop pipette**. It is cleaned, dried and filled with the experimental liquid, say upto mark A. Then the surface tension is determined by one of the two methods given below.

(a) **Drop-weight Method.** About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus weight of one drop is found. The drop-pipette is again cleaned and dried. It is filled with a second reference liquid (say water) and weight of one drop determined as before.

Then from equation (1)

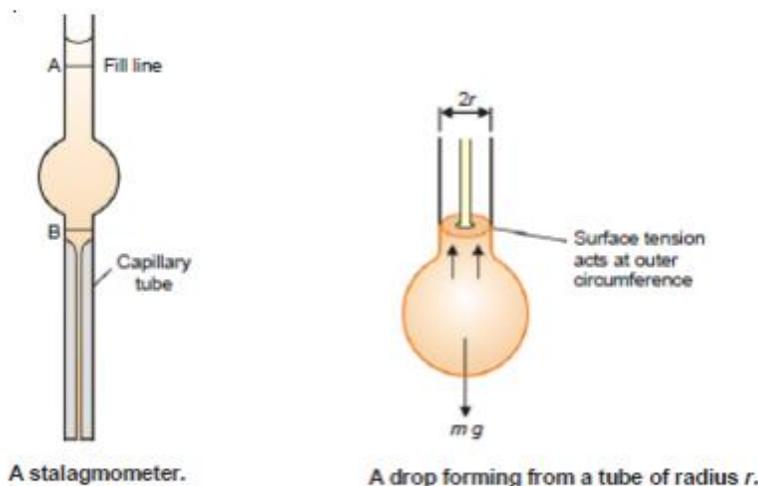
$$m_1 g = 2 \pi r \gamma_1 \quad (2)$$

$$m_2 g = 2 \pi r \gamma_2 \quad (3)$$

Dividing (2) by (3)

$$\gamma_1/\gamma_2 = m_1/m_2$$

Knowing the surface tension of reference liquid from Tables, that of the liquid under study can be found.



(b) **Drop-number Method.** The drop-pipette is filled upto the mark A with the experimental liquid (No.1). The number of drops is counted as the meniscus travels from A to B. Similarly, the pipette is filled with the reference liquid (No.2) as the meniscus passes from A to B. Let n_1 and n_2 be the number of drops produced by the same volume V of the two liquids. Thus,

$$\text{The volume of one drop of liquid 1} = V/n_1$$

$$\text{The mass of one drop of liquid 1} = (V/n_1)d_1$$

where d_1 is the density of liquid 1.

Similarly,

$$\text{The mass of one drop of liquid 2} = (V/n_2)d_2$$

Then from equation (4)

$$\gamma_1/\gamma_2 = (V/n_1)d_1/(V/n_2)d_2 = n_2d_1/n_1d_2$$

The value of d_1 is determined with a pycnometer. Knowing d_2 and γ_2 from reference tables, γ_1 can be calculated.

Problem: In the determination of surface tension of a liquid by the drop-number method, it gives 55 drops while water gave 25 drops for the same volume. The densities of the liquid and water are 0.996 and 0.800 g/cm³ respectively. Find the surface tension of the liquid if that of water is 72 dynes/cm.

Solution:

We know that

$$\gamma_1/\gamma_2 = n_2 d_1 / n_1 d_2 \quad (1)$$

Where γ_1 = Surface tension of liquid; γ_2 = Surface tension of water; n_1 = number of drops of liquid; n_2 = number of drops of water.

Therefore,

$$\gamma_2 = 72 \text{ dynes cm}^{-1}, n_1 = 55, n_2 = 25, d_1 = 0.996 \text{ g cm}^{-3}, d_2 = 0.800 \text{ g cm}^{-3}$$

Using equation (1),

$$\gamma_1 = 72 \times (0.996 \times 25) / (0.800 \times 55) = 40.7 \text{ dynes cm}^{-1}$$

Therefore, the surface tension of the given liquid is 40.7 dynes cm⁻¹

(iii) Ring-detachment Method

In this method the force required to detach a platinum ring (du Nouy ring) from the liquid surface is measured. **This force (F) is exactly equal to the downward pull due to surface tension γ acting along the circumference of the ring.** Twice the length of the circumference ($2 \times 2\pi r$) is taken since the liquid is in contact with both the inside and the outside of ring. Thus,

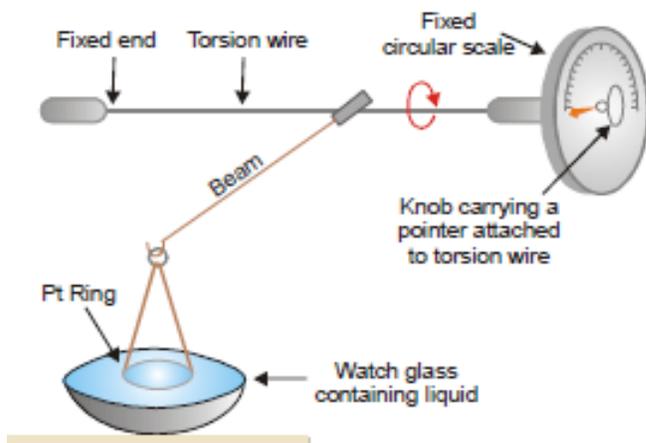
$$F = 4 \pi r \gamma$$

or

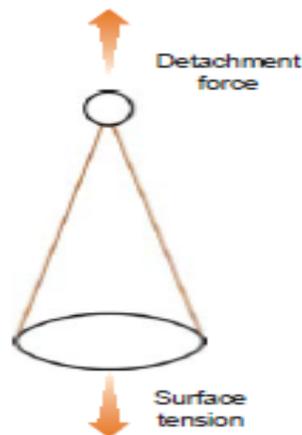
$$\gamma = F/4\pi r$$

where r is the radius of the ring.

The apparatus employed is called the **du Nouy Tensiometer**. Its essential parts are shown in Fig. One end of the torsion wire is fixed while the other is attached to a knob carrying a pointer. The pointer moves on a fixed scale. The scale is previously calibrated by taking different weights on the beam and noting the scale reading when it is lifted from the horizontal position. The liquid whose surface tension is to be determined is placed in a watch glass so that the Pt ring just touches its surface. The knob of the torsion wire is then slowly turned till the ring is just detached from the surface. The reading shown by the pointer on the scale gives the force F . The surface tension is then calculated from equation (1).



du Nouy Tensiometer



du Nouy ring with a suspending hook.

2.3. Nature and Thermodynamics of Liquid-Gas Interface

The surface tension is a definite and accurately measurable property of the interface between liquid phases. Moreover, its value is very rapidly established in pure substances of ordinary viscosity; dynamic methods indicate that a normal surface tension is established within a millisecond and probably sooner. Thus it is appropriate to discuss the thermodynamic basic for surface tension.

Surface Thermodynamic Quantities for a pure Substance

A hypothetical system consisting of some liquid that fills a box having a sliding cover; the material of the cover is such that the interfacial tension between it and the liquid is zero. If the cover is slid back so as to uncover an amount of surface dA , the work required to do so will be γdA . This is reversible work at constant pressure and temperature and thus gives the increase in free energy of the system.

$$dG = \gamma dA \quad (1)$$

The total free energy of the system is then made up of the molar free energy times the total number of moles of the liquid plus G^s , the surface free energy per unit area, times the total surface area. Thus

$$G^s = \gamma = \left(\frac{dG}{dA} \right)_{T,P} \quad (2)$$

Because this process is a reversible one, the heat associated with it gives the is *surface entropy*

$$dq = T dS = TS^s dA \quad (3)$$

where S^s is the surface entropy per square centimeter of surface.

Because $(dG/dT)_p = -S$, it follows that

$$\left(\frac{dG^s}{dA}\right)_p = -S^s \quad (4)$$

Or, in conjunction with Eq. 1,

$$\frac{d\gamma}{dT} = -S^s \quad (5)$$

Finally, the total surface enthalpy per square centimeter H^s is

$$H^s = G^s + TS^s \quad (6)$$

Often, and as a good approximation, H^s and the surface energy E^s are not distinguished, so Eq.6 can be seen in the form

$$E^s = G^s + TS^s \quad (7)$$

Or

$$E^s = \gamma - T d\gamma/dT \quad (8)$$

The total surface energy E^s generally is larger than the surface free energy. It is frequently the more informative of the two quantities, or at least it is more easily related to molecular models.

The surface specific heat C^s (distinction between C_p^s and C_v^s is rarely made), is an additional quantity to be mentioned at this point. It is given by

$$C^s = dE^s/dT \quad (9)$$

The surface tension of most liquid decreases with increasing temperature in a nearly linear fashion. The near-linearity has stimulated many suggestions as to algebraic forms that give exact linearity. An old and well-known relationship is

$$\gamma V^{2/3} = k (T_c - T) \quad (10)$$

Where V is the molar volume. One does expect the surface tension to go to zero at the critical temperature, but the interface seems to become diffuse at a slightly lower temperature replaced T_c in Eq. 10 by $(T_c - \delta)$. In either form, the constant k is about the same for most liquids and has a value of about 2.1 ergs/K.

$$\gamma = \gamma^o \left(1 - \frac{T}{T_c}\right)^n \quad (11)$$

Where n is 11/9 for many organic liquids but may be closer to unity for metals.

2.4. The Surface Tension of Solutions

The principal point of interest to be discussed in this section is the manner in which the surface tension of a binary system varies with composition. The effects of other variables such as pressure and temperature are similar to those for pure substances, and the more elaborate treatment for two-component system is not considered here.

A fairly simple treatment is useful for the case of ideal or nearly ideal solutions. An abbreviated derivation begins with the free energy of a species

$$G_i = kT \ln a_i \quad (1)$$

Where a_i is the absolute activity, $a_i = N_i g_i$, where N_i is the mole fraction of species I (unity for pure liquids), and g_i derives from the partition function Q_i . For a pure liquid 1, the surface tension may be written as

$$\gamma_1 \sigma_1 = -kT \ln a_1 / a_1^s \quad (2)$$

Or

$$\exp(-\gamma_1 \sigma_1 / kT) = g_1 / g_1^s \quad (3)$$

where the surface is viewed as a two-dimensional phase of molecular state corresponding to g_1^s and σ_1 is the molecular area. Thus, the work of bringing a molecule into the surface is expressed as a ΔG using Eq. 1.

The same relations are then applied to each component of a solution

$$\exp(-\gamma \sigma_1 / kT) = N_1 g_1 / N_1^s g_1^s \quad (4)$$

$$\exp(-\gamma \sigma_2 / kT) = N_2 g_2 / N_2^s g_2^s \quad (5)$$

where N^s denotes the mole fraction in the surface phase. Equation 4 and 5 may be solved for N_1^s and N_2^s , respectively, and substituted into the requirement that $N_1^s + N_2^s = 1$. If it is assumed that $\sigma = \sigma_1 = \sigma_2$, one then obtains

$$\exp(-\gamma \sigma / kT) = N_1 g_1 / g_1^s + N_2 g_2 / g_2^s \quad (6)$$

and, in combination with Eq. 3,

$$\exp(-\gamma \sigma / kT) = N_1 \exp(-\gamma_1 \sigma / kT) + N_2 \exp(-\gamma_2 \sigma / kT) \quad (7)$$

Hildebrand and Scott give an expansion of Eq. 7 for $\sigma_1 \neq \sigma_2$.

Guggenheim extended his treatment to the case of regular solution, that is, solutions for which

$$RT \ln f_1 = -\alpha N_2^2 \quad RT \ln f_2 = -\alpha N_1^2 \quad (8)$$

where f denotes the activity coefficient. A very simple relationship for such regular solutions comes from Prigogine and Defay:

$$\gamma = \gamma_1 N_1 + \gamma_2 N_2 - \beta N_1 N_2 \quad (9)$$

where β is a semi-empirical constant.

2.5. Surfaces of Solids

A *solid*, by definition, is a portion of matter that is rigid and resists stress. Although the surface of a solid must, in principle, be characterized by surface free energy, it is evident that the usual methods of capillarity are not very useful since they depend on measurements of equilibrium surface properties given Laplace's equation. Since a solid deforms in an elastic manner, its shape will be determined more by its past history than by surface tension forces.

Surface growth

A simple picture of a perfect crystal surface is as a tray of oranges in a grocery store (Fig. 1). A gas molecule that collides with the surface can be imagined as a table-tennis ball bouncing erratically over the oranges. The molecule loses energy as it bounces under the influence of intermolecular forces, but it is likely to escape from the surface before it has lost so much kinetic energy that it has become trapped. The same is true, to some extent, of an ionic crystal in contact with a solution. There is little energy advantage for an ion in solution to discard some of its solvating molecules and stick at an exposed position on a flat surface.

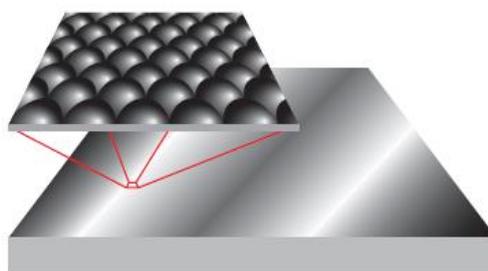


Fig. 1: A schematic diagram of the flat surface of a solid.

The picture changes when the surface has defects, for then there are ridges of incomplete layers of atoms or ions. A typical type of surface defect is a **step** between two otherwise flat layers of atoms called **terraces** (Fig. 2). A step defect might itself have defects, including kinks. When an atom settles on a terrace it migrates across it under the influence of the intermolecular potential, and might come to a step or a corner formed by a kink. Instead of interacting with a single

terrace atom, the molecule now interacts with several, and the interaction may be strong enough to trap it. Likewise, when ions deposit from solution, the loss of the solvation interaction is offset by a strong Coulombic interaction between the arriving ions and several ions at the surface defect.

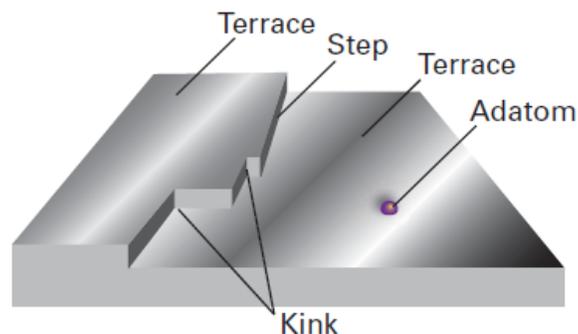


Fig. 2: Some of the kinds of defects that may occur on otherwise perfect terraces. Defects play an important role in surface growth and catalysis.

The rapidity of growth depends on the crystal plane concerned and—perhaps surprisingly—the slowest growing faces dominate the appearance of the crystal. This feature is explained in Fig. 3, where we see that although the horizontal face grows forward most rapidly, it grows itself out of existence and the more slowly growing faces survive.

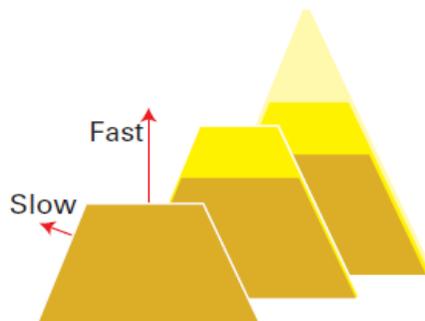


Fig. 3: The slower-growing faces of a crystal dominate its final external appearance. Three successive stages of the growth are shown.

Surface Composition and structure

Under normal conditions, a surface exposed to a gas is constantly bombarded with molecules and a freshly prepared surface is covered very quickly. Just how quickly can be estimated by using the kinetic theory of gases and the following expression for the **collision flux**, Z_w , the number of hits on a region of a surface during an interval divided by the area of the region and the duration of the interval:

$$Z_w = \frac{P}{(2\pi mk_b T)^{1/2}} \quad (1)$$

where m is the mass of the molecules. For air at 1 atm and 25°C the collision flux is $3 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}$.

Because 1 m^2 of metal surface consists of about 10^{19} atoms, each atom is struck about 10^8 times each second. Even if only a few collisions leave a molecule adsorbed to the surface, the time for which a freshly prepared surface remains clean is very short. There are various techniques which can be applied to measure the chemical composition of solid surface.

Surface Tension and Surface Free Energy

Unlike the situation with liquids, in the case of a solid, the surface tension is not necessarily equal to the surface stress. As Gibbs pointed out the surface tension is the work spent in forming unit area of surface (and may alternatively be called the surface free energy, while the surface stress involves the work spent in strengthening the surface. It is helpful to imagine that the process of forming a fresh surface of a monoatomic substance is divided into two steps: first, the solid or liquid is cleaved so as to expose a new surface, keeping the atoms fixed in the atoms in the same positions that they occupied when in the bulk phase; second, the atoms in the surface region are allowed to rearrange to their final equilibrium positions. In the case of the liquid, these two steps occur as one, but with solids the second step may occur only slowly because of the immobility of the surface region. Thus, with a solid it may be possible to stretch or to compress the surface region without changing the number of atoms in it, only their distances apart.

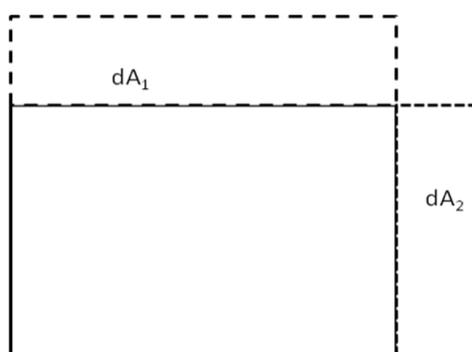


Fig. 4: Displacement in solid surface.

Surface free energy and surface stress were treated as equivalent, and both were discussed in terms of the energy to form unit additional surface. It is now desirable to consider an independent, more mechanical definition of surface stress. If a surface is cut by a plane normal to

it, then, in order that the atoms on either side of the cut remain in equilibrium, it will be necessary to apply some external force to them. The total such force per unit length is the surface stress, and half the sum of the two surface stresses along mutually perpendicular cuts is equal to the surface tension. In the case of a liquid or isotropic solid the two surface stresses are equal, but for a non-isotropic solid or crystal, this will not be true. In such a case the partial surface stresses or stretching tensions may be denoted as τ_1 and τ_2 .

For an anisotropic solid, if the area is increased in two directions by dA_1 and dA_2 , as illustrated in fig. 4. then the total increase in free energy is given by the reversible work against the surface stresses, that is

$$\tau_1 = G^s + A_1 dG^s / dA_1 \text{ and } \tau_2 = G^s + A_2 dG^s / dA_2 \quad (2)$$

where G^s is the free energy per unit area. If the solid is isotropic Eq. 2 reduces to

$$\tau_1 = \frac{d(AG^s)}{dA} = G^s + \frac{AdG^s}{dA} \quad (3)$$

For liquids, the last terms in Eq. 3 is zero, so that $\tau = G^s$ (or $\tau = \gamma$, since we will use G^s and γ interchangeably); the same would be true of a solid if the change in area dA were to occur in such a way that an equilibrium surface configuration was always maintained. Thus the stretching of a wire under reversible conditions would imply that interior atoms would move into the surface as needed so that the increased surface area was not accompanied by any change in specific surface properties. If, however, the stretching were done under conditions such that full equilibrium did not prevail, a surface stress would be present whose value would differ from γ by an amount that could be time-dependent and would depend on the term $\frac{AdG^s}{dA}$.

Adsorption

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called **adsorption**. The substance that deposits at the surface is called **Adsorbate** and the solid on whose surface the deposition occurs is called the **Adsorbent**.

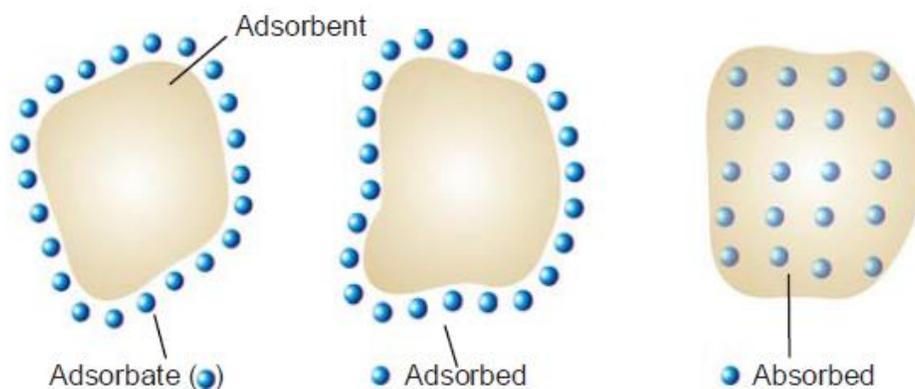


Fig. 5: Adsorption versus absorption illustration.

Adsorption versus Absorption

The term ‘adsorption’ must be carefully distinguished from another like-sounding term ‘absorption’. **While adsorption implies deposition at the surface only, absorption implies penetration into the body of the solid.** For illustration a chalk crayon when dipped in ink adsorbs the latter and on breaking it is found to be white from within. On the other hand, water is absorbed by a sponge and is distributed throughout the sponge uniformly.

Both adsorption and absorption often take place side by side. It is thus difficult to distinguish between the two processes experimentally. Mc Bain introduced the general term **Sorption** which includes both *the adsorption and absorption*.

Physisorption and Chemisorptions

Molecules and atoms can attach to surfaces in two ways, although there is no clear frontier between the two types of adsorption. In **physisorption** (an abbreviation of ‘physical adsorption’), there is a van der Waals interaction between the adsorbate and the substrate (for example, a dispersion or a dipolar interaction of the kind responsible for the condensation of vapors to liquids). The energy released when a molecule is physisorbed is of the same order of magnitude as the enthalpy of condensation. Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion, and a molecule bouncing across the surface will gradually lose its energy and finally adsorb to it in the process called **accommodation**. The enthalpy of physisorption can be measured by monitoring the rise in temperature of a sample of

known heat capacity, and typical values are in the region of -20 kJ mol^{-1} (Table 1). This small enthalpy change is insufficient to lead to bond breaking, so a physisorbed molecule retains its identity but might be distorted. Enthalpies of physisorption may also be measured by observing the temperature dependence of the parameters that occur in the adsorption isotherm.

Table 1: Maximum observed enthalpies of physisorption, $\Delta_{ads}H_{ads}^o / (\text{kJmol}^{-1})$

CH ₄	-21
CO	-25
H ₂	-84
H ₂ O	-59
N ₂	-21
NH ₃	-38
O ₂	-21

In **chemisorption** (an abbreviation of ‘chemical adsorption’), the molecules (or atoms) adsorb to the surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the substrate. The enthalpy of chemisorption is much more negative than that for physisorption, and typical values are in the region of -200 kJ mol^{-1} (Table 2). The distance between the surface and the closest adsorbate atom is also typically shorter for chemisorption than for physisorption. A chemisorbed molecule may be torn apart at the demand of the unsatisfied valencies of the surface atoms and the existence of molecular fragments on the surface as a result of chemisorption is one reason why solid surfaces catalyse reactions.

Table 2: Enthalpies of chemisorption, $\Delta_{ads}H_{ads}^o / (\text{kJmol}^{-1})$

Adsorbate	Adsorbent (substrate)			
	Cr	Fe	Ni	Pt
C ₂ H ₄	-427	-285	-243	
CO		-192		
H ₂	-188	-134		
NH ₃		-188	-155	
O ₂				-293

COMPARISON OF PHYSICAL ADSORPTION AND CHEMISORPTION

Physical adsorption	Chemisorption
<ol style="list-style-type: none"> 1. Caused by intermolecular van der Waal's forces. 2. Depends on nature of gas. Easily liquefiable gases are adsorbed readily. 3. Heat of adsorption is small (about 5 kcal mol⁻¹). 4. Reversible. 5. Occurs rapidly at low temperature; decreases with increasing temperature. 6. Increase of pressure increases adsorption; decrease of pressure causes desorption. 7. Forms multimolecular layers on adsorbent surface. 	<ol style="list-style-type: none"> 1. Caused by chemical bond formation. 2. Much more specific than physical adsorption. 3. Heat of adsorption is large (20–100 kcal mol⁻¹). 4. Irreversible. 5. Increases with increase of temperature. 6. Change of pressure has no such effects. 7. Forms unimolecular layer.

The extent of adsorption

The attachment of molecules to a surface is called **adsorption**. The substance that adsorbs is the **adsorbate** and the underlying material that we are concerned with in this section is the **adsorbent** or **substrate**. The reverse of adsorption is **desorption**.

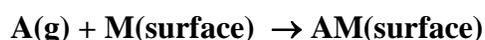
The extent of surface coverage is normally expressed as the **fractional coverage**, θ (theta):

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}} \quad (1)$$

The fractional coverage can be inferred from the volume of adsorbate adsorbed by $\theta = V/V^\infty$, where V^∞ is the volume of adsorbate corresponding to complete monolayer coverage. In each case, the volumes in the definition of θ are those of the free gas measured under the same conditions of temperature and pressure, not the volume the adsorbed gas occupies when attached to the surface. The **rate of adsorption** is the rate of change of surface coverage and is measured by observing the change of fractional coverage with time.

Adsorption isotherms

The free gas **A** and the adsorbed gas are in a dynamic equilibrium of the form



and the fractional coverage of the surface depends on the pressure of the overlying gas. The enthalpy change associated with the forward reaction (per mole of adsorbed species) is the **enthalpy of adsorption**, $\Delta_{\text{ads}}H$. The variation of θ with pressure at a chosen temperature is called the **adsorption isotherm**.

The simplest physically plausible adsorption isotherm is based on three assumptions:

1. Adsorption cannot proceed beyond monolayer coverage.
2. All sites are equivalent and the surface is uniform (that is, the surface is perfectly flat on a microscopic scale).
3. There are no interactions between adsorbed molecules, so the ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

Assumptions 2 and 3 imply, respectively, that the enthalpy of adsorption is the same for all sites and is independent of the extent of surface coverage. The relation between the fractional coverage θ and the partial pressure of A, p , that results from these three assumptions is the

Langmuir isotherm:

$$\theta = \frac{Kp}{1 + Kp} \quad K = \frac{k_a}{k_b} \quad (2)$$

where k_a and k_b are, respectively, the rate constants for adsorption and desorption. This expression is plotted for various values of K (which has the dimensions of 1/pressure) in Fig. 6. We see that as the partial pressure of A increases, the fractional coverage increases towards 1. Half the surface is covered when $p = 1/K$. At low pressures (in the sense that $Kp \ll 1$), the denominator can be replaced by 1, and $\theta = Kp$. Under these conditions, the surface coverage increases linearly with pressure. At high pressure (in the sense that $Kp \gg 1$), the 1 in the denominator can be neglected, the Kp cancel, and $\theta = 1$. Now the surface is saturated.

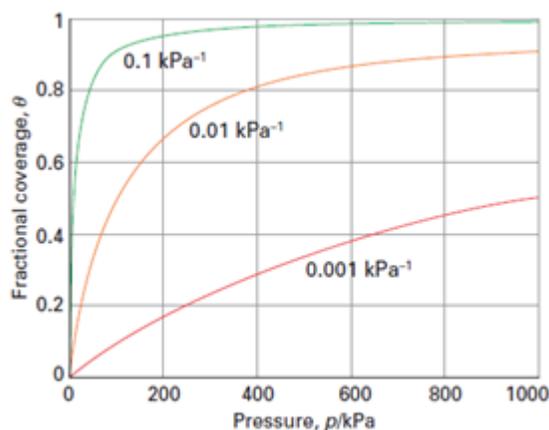


Fig. 6: Langmuir isotherm for nondissociative adsorption for different values of K .

A further point is that because K is essentially an equilibrium constant, then its temperature dependence is given by the van't Hoff equation :

$$\ln K = \ln K' - \frac{\Delta_{ads}H}{R} \left(\frac{1}{T} - \frac{1}{T'} \right) \quad (3)$$

It follows that if we plot $\ln K$ against $1/T$, then the slope of the graph is equal to $-\Delta_{\text{ads}}H/R$, where $\Delta_{\text{ads}}H$ is the standard enthalpy of adsorption. However, because this quantity might vary with the extent of surface coverage either because the adsorbate molecules interact with each other or because adsorption occurs at a sequence of different sites, care must be taken to measure K at the same value of the fractional coverage. The resulting value of $\Delta_{\text{ads}}H$ is called the **isosteric enthalpy of adsorption**. The variation of $\Delta_{\text{ads}}H$ with θ allows us to explore the validity of the assumptions on which the Langmuir isotherm is based. There are two modifications of the Langmuir isotherm that should be noted. Suppose the substrate dissociates on adsorption, as in



The resulting isotherm is

$$\theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}} \quad (4)$$

The second modification we need to consider deals with a mixture of two gases A and B that compete for the same sites on the surface. To show that if A and B both follow Langmuir isotherms, and adsorb without dissociation, then

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}, \quad \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B} \quad (5)$$

where K_J (with $J = A$ or B) is the ratio of adsorption and desorption rate constants for species J , p_J is its partial pressure in the gas phase, and θ_J is the fraction of total sites occupied by J . Coadsorption of this kind is important in catalysis and we use these isotherms later.

The rates of surface processes

Figure 7, shows how the potential energy of a molecule varies with its distance above the adsorption site. As the molecule approaches the surface its potential energy decreases as it becomes physisorbed into the **precursor state** for chemisorption. Dissociation into fragments often takes place as a molecule moves into its chemisorbed state, and after an initial increase of energy as the bonds stretch there is a sharp decrease as the adsorbate–substrate bonds reaches their full strength. Even if the molecule does not fragment, there is likely to be an initial increase of potential energy as the bonds adjust when the molecule approaches the surface.

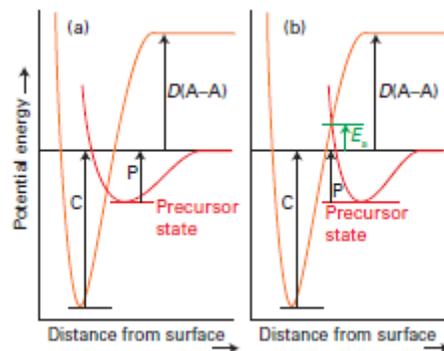


Fig. 7: The potential energy profiles for the dissociative chemisorption of an A_2 molecule. In each case, P is the enthalpy of (nondissociative) physisorption and C that for chemisorption (at $T = 0$). The relative locations of the curves determine whether the chemisorption is (a) not activated or (b) activated.

In most cases, therefore, we can expect there to be a potential energy barrier separating the precursor and chemisorbed states. This barrier, though, might be low and might not rise above the energy of a distant, stationary molecule (as in Fig. 7a). In this case, chemisorption is not an activated process and can be expected to be rapid. Many gas adsorptions on clean metals appear to be nonactivated. In some cases the barrier rises above the zero axis (as in Fig 7b); such chemisorptions are activated and slower than the nonactivated kind. An example is the adsorption of H_2 on copper, which has an activation energy in the region of $20\text{--}40\text{ kJ mol}^{-1}$.

One point that emerges from this discussion is that rates are not good criteria for distinguishing between physisorption and chemisorption. Chemisorption can be fast if the activation energy is small or zero; but it may be slow if the activation energy is large. Physisorption is usually fast, but it can appear to be slow if adsorption is taking place on a porous medium.

The rate at which a surface is covered by adsorbate depends on the ability of the substrate to dissipate the energy of the incoming molecule as thermal motion as it crashes on to the surface. If the energy is not dissipated quickly, the molecule migrates over the surface until a vibration expels it into the overlying gas or it reaches an edge. The proportion of collisions with the surface that successfully lead to adsorption is called the **sticking probability**, s :

$$s = \frac{\text{rate of adsorption of particles by the surface}}{\text{rate of collision of particles with the surface}} \quad (6)$$

The denominator can be calculated from kinetic theory, and the numerator can be measured by observing the rate of change of pressure. Values of s vary widely. For example, at room temperature CO has s in the range $0.1\text{--}1.0$ for several d-metal surfaces, suggesting that almost

every collision sticks, but for N_2 on rhenium $s < 10^{-2}$, indicating that more than a hundred collisions are needed before one molecule sticks successfully.

Desorption is always an activated process because the molecules have to be lifted from the foot of a potential well. A physisorbed molecule vibrates in its shallow potential well, and might shake itself off the surface after a short time. The temperature dependence of the first-order rate of departure can be expected to be Arrhenius-like,

$$k_d = Ae^{-E_d/RT} \quad (7)$$

where A is a pre-exponential factor and the activation energy for desorption, E_d , is likely to be comparable to the enthalpy of physisorption. In the discussion of half-lives of first-order reactions is $t_{1/2} = (\ln 2)/k$; so for desorption, the half-life for remaining on the surface has a temperature dependence given by

$$t_{1/2} = \frac{\ln 2}{k_d} = \tau_o e^{E_d/RT}, \quad \tau_o = \frac{\ln 2}{A} \quad (8)$$

(Note the positive sign in the exponent: the half-life *decreases* as the temperature is raised.) If we suppose that $1/\tau_o$ is approximately the same as the vibrational frequency of the weak molecule–surface bond (about 10^{12} Hz) and $E_d \approx 25 \text{ kJ mol}^{-1}$, then residence half-lives of around 10 ns are predicted at room temperature. Lifetimes close to 1 s are obtained only by lowering the temperature to about 100 K. For chemisorption, with $E_d = 100 \text{ kJ mol}^{-1}$ and guessing that $\tau_o = 10^{-14}$ s (because the adsorbate–substrate bond is quite stiff), we expect a residence half-life of about 3×10^3 s (about an hour) at room temperature, decreasing to 1 s at about 350 K.

One way to measure the desorption activation energy is to monitor the rate of increase in pressure when the sample is maintained at a series of temperatures and then to attempt to make an Arrhenius plot. A more sophisticated technique is **temperature programmed desorption** (TPD) or **thermal desorption spectroscopy** (TDS). The basic observation is a surge in desorption rate (as monitored by a mass spectrometer) when the temperature is raised linearly to the temperature at which desorption occurs rapidly; but once desorption has occurred there is no more adsorbate to escape from the surface, so the desorption flux falls again as the temperature continues to rise. The TPD spectrum, the plot of desorption flux against temperature, therefore shows a peak, the location of which depends on desorption activation energy. There are three maxima in the example shown in Fig. 8, indicating the presence of three adsorption sites with different activation energies.

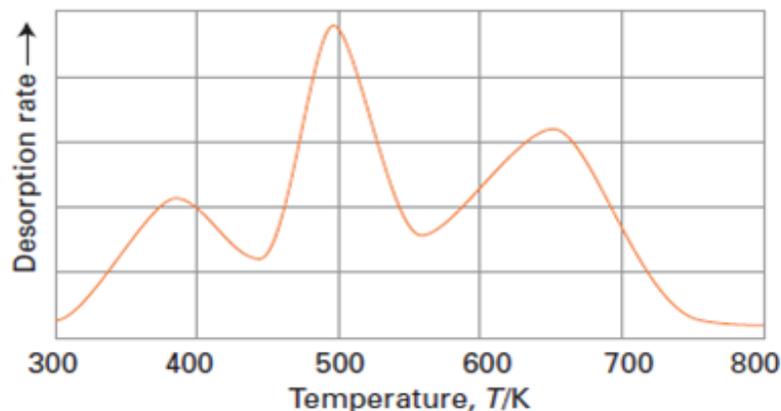


Fig. 8: The flash desorption spectrum of H_2 on the face of tungsten.

Catalytic activity at surfaces

A catalyst acts by providing an alternative reaction path with lower activation energy. A catalyst does not disturb the final equilibrium composition of the system, only the rate at which that equilibrium is approached. In this section we shall consider **heterogeneous catalysis**, in which the catalyst and the reagents are in different phases. A common example is a solid introduced as a heterogeneous catalyst into a gas-phase reaction. Many industrial processes make use of heterogeneous catalysts, which include platinum, rhodium, zeolites, and various metal oxides, but increasingly attention is turning to homogeneous catalysts, partly because they are easier to cool. However, their use typically requires additional separation steps, and such catalysts are generally immobilized on a support, in which case they become heterogeneous. In general, heterogeneous catalysts are highly selective and to find an appropriate catalyst each reaction must be investigated individually.

Computational procedures are beginning to be a fruitful source of prediction of catalytic activity. A metal acts as a heterogeneous catalyst for certain gas-phase reactions by providing a surface to which a reactant can attach by chemisorption. For example, hydrogen molecules may attach as atoms to a nickel surface and these atoms react much more readily with another species (such as an alkene) than the original molecules. The chemisorption step therefore results in a reaction pathway with lower activation energy than in the absence of the catalyst. Note that chemisorption is normally required for catalytic activity: physisorption might precede chemisorption but is not itself sufficient.

Mechanisms of heterogeneous catalysis

Heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction. Often this modification takes the form of a fragmentation of the reactant molecules. The **catalyst ensemble** is the minimum arrangement of atoms at the surface active site that can be used to model the action of the catalyst. It may be determined, for instance, by diluting the active metal with a chemically inert metal and observing the catalytic activity of the resulting alloy. In this way it has been found, for instance, that as many as 12 neighboring Ni atoms are needed for the cleavage of the C—C bond in the conversion of ethane to methane.

The decomposition of phosphine (PH₃) on tungsten is first-order at low pressures and zeroth-order at high pressures. To account for these observations, we write down a plausible rate law in terms of an adsorption isotherm and explore its form in the limits of high and low pressure. If the rate is supposed to be proportional to the surface coverage and we suppose that θ is given by the Langmuir isotherm, we would write

$$\text{Rate} = k_r \theta = \frac{k_r K p}{1 + K p} \quad (9)$$

where p is the pressure of phosphine and k_r is a rate constant. When the pressure is so low that $Kp \ll 1$, we can neglect Kp in the denominator and obtain

$$\text{Rate} = k_r K p \quad (10)$$

and the decomposition is first-order. When $Kp \gg 1$, we can neglect the 1 in the denominator, whereupon the Kp terms cancel and we are left with

$$\text{Rate} = k_r \quad (11)$$

and the decomposition is zeroth-order. Many heterogeneous reactions are first-order, which indicates that the rate-determining stage is the adsorption process.

In the **Langmuir–Hinshelwood mechanism** (LH mechanism) of surface-catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms adsorbed on the surface. We therefore expect the rate law to be overall second order in the extent of surface coverage:



Insertion of the appropriate isotherms for A and B then gives the reaction rate in terms of the partial pressures of the reactants. For example, if A and B follow the adsorption isotherms given in eqn 4, then the rate law can be expected to be

$$Rate = \frac{k_r K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \quad (12)$$

The parameters K in the isotherms and the rate constant k_r are all temperature dependent, so the overall temperature dependence of the rate may be strongly non-Arrhenius, in the sense that the reaction rate is unlikely to be proportional to $e^{-E_a/RT}$. The LH mechanism is dominant for the catalytic oxidation of CO to CO₂ on the surface of platinum.

In the **Eley–Rideal mechanism** (ER mechanism) of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface. We can therefore expect the rate of formation of product to be proportional to the partial pressure, p_B , of the nonadsorbed gas B and the extent of surface coverage, θ_A , of the adsorbed gas A. It follows that the rate law should be



The rate constant, k_r , might be much larger than for the uncatalysed gas-phase reaction because the reaction on the surface has a low activation energy and the adsorption itself is often not activated. If we know the adsorption isotherm for A, we can express the rate law in terms of its partial pressure, p_A . For example, if the adsorption of A follows a Langmuir isotherm in the pressure range of interest, then the rate law would be

$$Rate = \frac{k_r K p_A p_B}{1 + K p_A} \quad (13)$$

If **A** were a diatomic molecule that adsorbed as atoms, then we would substitute the isotherm given in eqn 4 instead. According to eqn 13, when the partial pressure of **A** is high (in the sense $K p_A \gg 1$) there is almost complete surface coverage, and the rate law is

$$Rate = \frac{k_r K p_A p_B}{K p_A} = k_r p_B \quad (14)$$

Now the rate-determining step is the collision of **B** with the adsorbed fragments. When the pressure of **A** is low ($K p_A \ll 1$), perhaps because of its reaction, the rate law becomes

$$Rate \approx \frac{k_r K p_A p_B}{1} = k_r K p_A p_B \quad (15)$$

Now the extent of surface coverage is rate determining. Almost all thermal surface-catalysed reactions are thought to take place by the LH mechanism, but a number of reactions with an ER mechanism have also been identified from molecular beam investigations.

2.6. Adsorption at the Solid Solution Interface

Adsorption of a solute from a solution onto a solid adsorbent is more difficult to treat theoretically than the corresponding adsorption of gases on solids. It appears however that in this case, too, like the gas-solid adsorption, a monomolecular layer is formed. The solvating power of the solvent inhibits the formation of a multilayer.

For adsorption from solutions, a commonly used isotherm is the Freundlich adsorption isotherm. If x is the mass of the solute adsorbed on mass m of adsorbent and c is the concentration of the solute in the solution, then the Freundlich adsorption isotherm is expressed as

$$x/m = a = kc^n \quad (1)$$

where k and n are empirical constants. Taking logs,

$$\ln a = \ln k + n \ln c \quad (2)$$

This logarithmic form is convenient to use. If we plot $\ln a$ versus $\ln c$, the plot would be a straight line with slope equal to n and intercept equal to $\ln k$.

The Gibbs Adsorption Isotherm for Adsorption from solutions

The concentration of a solute at the surface of a solution is, in general, markedly different from that in the bulk. If the surface tension of the solute is lower than that of the liquid, it tends to accumulate at the surface of the liquid thereby decreasing the surface tension (or the surface free energy per unit area) of the liquid. A quantitative treatment of the thermodynamics of adsorption of a solute at the surface of a liquid was given in 1878 by J. W. Gibbs, the greatest 19th century American mathematical physicist.

For a system containing two components, the Gibbs free energy can be written as

$$G = n_1\mu_1 + n_2\mu_2 \quad (3)$$

Where n_1 and n_2 are the amounts (number of moles), μ_1 and μ_2 are the chemical potentials (*i.e.*, partial molar Gibbs free energies) of the two components, respectively. Since we are dealing with the adsorption of one of the components on the surface which results in changing the surface free energy, Eq.3 is modified to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma \quad (4)$$

where, γ is the *surface energy* which is numerically the same as the surface tension and σ is the *surface area*. The complete differential of Eq. 4 is written as

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma \quad (5)$$

We see that free energy G now depends upon five independent variables, viz., T, P, n_1, n_2 and σ .

Thus,

$$G = f(T, P, n_1, n_2, \sigma) \quad (6)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \sigma} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \sigma} dP + \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, \sigma} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, \sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma}\right)_{P, T, n_2, n_2} d\sigma \quad (7)$$

According to thermodynamics, the partial derivatives

$$-\left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \sigma}, \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \sigma}, \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, \sigma}, \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, \sigma} \text{ and } \left(\frac{\partial G}{\partial \sigma}\right)_{P, T, n_2, n_2}$$

Eq. 7 are, respectively, equal to S, V, μ_1, μ_2 and γ .

Hence,
$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \quad (8)$$

At constant temperature ($dT = 0$) and at constant pressure ($dP = 0$), Eq. 8 reduces to

$$(dG)_{T, P} = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \quad (9)$$

From, Eqs. 5 and 9

$$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0 \quad (10)$$

The corresponding expression for the bulk of the liquid is

$$n_1^o d\mu_1 + n_2^o d\mu_2 = 0 \quad (11)$$

Where n_1^o and n_2^o are the amounts (number of moles) of the liquid and the solute, respectively, in the bulk phase.

Since the system is in equilibrium, the chemical potential of each component in the bulk and the surface phase must be the same. The system, on being disturbed, attains a new equilibrium so that the changes in the chemical potentials must be identical in both the phases, *i.e.*, $d\mu_1$ and $d\mu_2$ in **Eqs. 10** and **11** must be identical. Elimination of $d\mu_2$ from these equations gives

$$n_1 \left[-\left(\frac{n_2^o}{n_1^o}\right) d\mu_2 \right] + n_2 d\mu_2 + \sigma d\gamma = 0$$

Or
$$(n_2 - n_1 n_2^o / n_1^o) d\mu_2 + \sigma d\gamma = 0$$

$$\text{Or} \quad -\frac{d\gamma}{d\mu_2} = \frac{n_2 - (n_1 n_2^o / n_1^o)}{\sigma} \quad (12)$$

The quantity within parenthesis of Eq. 12 gives the amount n_2^o of solute 2 associated with the amount n_1^o of liquid 1 in the *bulk* phase. On the other hand, n_2 is the amount of the solute associated with the amount n_1 of the liquid at the *surface*. Thus, the numerator on the right hand side of Eq. 12 gives the *excess amount of the solute* present in the surface of the solute per unit area of the surface, designated as Γ_2 , *i.e.*, $[n_2 - (n_1 n_2^o / n_1^o)] / \sigma = \Gamma_2$. Thus, from Eq. 12,

$$\Gamma_2 = -\frac{d\gamma}{d\mu_2} \quad (13)$$

The chemical potential of solute 2 is given by

$$\mu_2 = \mu_2^*(l) + RT \ln a_2 \quad (14)$$

where $\mu_2^*(l)$ is the chemical potential of the pure solute in the liquid phase. Hence,

$$d\mu_2 = RT d \ln a_2 \quad [\because d\mu_2^*(l) = 0] \quad (15)$$

Substituting for $d\mu_2$ in Eq. 13, we obtain

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln a_2} \right)_T = -\frac{a_2}{RT} \left(\frac{\partial \gamma}{\partial a_2} \right)_T \quad (16)$$

When the solution is very dilute, it behaves ideally so that the activity a_2 of the solute can be replaced by its concentration c_2 . Thus,

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln c_2} \right)_T = -\frac{c_2}{RT} \left(\frac{\partial \gamma}{\partial c_2} \right)_T \quad (17)$$

Eq. 17, is called **Gibbs adsorption isotherm**. Knowing concentration-dependence of γ , Γ_2 can be calculated. For a solute that lowers the surface tension, the surface excess concentration Γ_2 is *positive* and for a solute that raises the surface tension, Γ_2 is *negative*.