HOKKAIDO UNIVERSITY

Title	NOTES ON HORIUTI'S METHOD OF STATISTICAL-MECHANICAL CALCULATIONS Part . HORIUTI's Statistical-Mechanical Functions
Author(s)	NAKAMURA, Takashi
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 15(2), 127-171
Issue Date	1967-12
Doc URL	http://hdl.handle.net/2115/24832
Type	bulletin (article)
File Information	15(2)_P127-171.pdf

Instructions for use

NOTES ON HORIUTI'S METHOD OF STATISTICAL-MECHANICAL CALCULATIONS

Part I. HORIUTI's Statistical-Mechanical Functions

By

Takashi NAKAMURA[*]

(Received September 28, 1967)

Abstract

HORIUTI has developed "a method of treating equilibrium and chemical reaction (rate) by introducing a set of conjugate statistical-mechanical functions defined as the factor of multiplication of the Zustandsumme (= partition function) caused by increasing a certain constituent of the assembly of interest or by imposing a microscopic constraint upon the elementary state of the constituent" [quoted from his article, J. Research Inst. Catalysis, Hokkaido University, 1, 8 (1948)], and has applied it to calculations of adsorption equilibria and of rates of heterogeneous reactions. The present notes, which are based on a series of lectures given by the author at the Research Institute for Catalysis, Hokkaido University in 1965-1966, are devoted to the exposition of HORIUTI's method with the purpose of filling in a gap which seems to exist between his papers and what is found in the current textbooks of statistical mechanics. In order to elucidate the significance of HORIUTI's statistical-mechanical functions and certain related concepts, a simple spin system and the sitewise (= localized) adsorption of a one-component gas are discussed at considerable length in Part I. The discussion of a few examples of equilibrium calculations and the treatment of chemical reaction rates along the same lines are left for Parts II and III.

§ 1. Introduction

HORIUTI has done a number of statistical-mechanical calculations relating to adsorbed phase, most of which are concerned with the effects of the interactions between adsorbed atoms (molecules) on thermodynamic properties of an adsorbed phase. He has also applied his method of statistical-mechanical calculations to the derivation of absolute rate expressions for chemical reactions taking place in adsorbed phases, namely heterogeneous reactions. Although his theory is of much interest and importance, a considerable number of students seem to find it difficult to familiarize themselves with HORIUTI's theory for the reason that the way of theoretical development and also the mathematical notation used in his papers are quite different from those they find in the

---

*) Research Institute for Catalysis, Hokkaido University, Sapporo, Japan.

Takashi NAKAMURA

current textbooks on statistical mechanics. I do not think however that the difference is as big as the students are likely to think; there is nothing basically different or particularly unusual in his theory. The present notes have been written in the hope that they will help students to find the connection between HORIUTI's theory and what is found in the textbooks. Here it is not attempted to discuss all the important aspects*) of HORIUTI's statistical-mechanical method; these notes are intended simply as a guide to his papers.

T. L. HILL's "Introduction to Statistical Thermodynamics" (1960) is of established reputation as an up-to-date, introductory textbook of statistical mechanics. Throughout the present notes, therefore, his book will be used as the general reference.

§ 2.   Thermodynamical Consideration of Chemical Equilibrium

In these notes we shall have a few occasions to discuss, as an illustration, the equilibrium of the chemical reaction,

$$A + B \rightleftharpoons 2C , \qquad (2.1)$$

taking place in a fluid mixture of three components A, B and C. The pressure, volume and temperature of this mixture will be denoted by p, V and T, respectively. The equilibrium of (2.1), although a very simple one, furnishes a good example showing important features of the thermodynamical or statistical-mechanical theory of chemical equilibrium.

Perhaps any discussion of chemical equilibrium should start with a thermodynamical consideration. In fact, classical thermodynamics has long been, and will continue to be, a frame of reference in the theory of macroscopic systems in equilibrium. The well-known, thermodynamical condition for equilibrium of a system kept at constant temperature and pressure is that the GIBBS free energy G of the system is minimum. In the case of chemical equilibrium it is customary to express this condition as

$$\Delta G = 0 . \qquad (2.2)$$

Let us first suppose that the above mixture is a perfect gas mixture (DENBIGH,[1] p. 112). In this particular case the whole story will be a very simple one. For one thing, the "additivity" of thermodynamic functions holds for this mixture; for example, the GIBBS free energy G of the mixture is additive in the sense that

---

*) For instance, I shall not argue about his theoretical analyses of various experimental results.

$$G = n_A g_A + n_B g_B + n_C g_C . \tag{2.3}$$

On the right hand side of (2.3), n_A is the number of moles of A in the mixture, g_A is the molar GIBBS free energy of *pure* A at temperature T and pressure p_A, where p_A is the partial pressure of A in the mixture; the remaining symbols are defined in a similar fashion. The expression for ΔG to be used in (2.2) is likewise simple; corresponding to the stoichiometry of (2.1), it is written as

$$\Delta G = 2g_C - g_A - g_B . \tag{2.4}$$

Also we can make use of the well-known relation between the pressure and free energy of a perfect gas, namely,

$$g_A = g_A^0 + RT \ln p_A \quad \text{etc.,} \tag{2.5}$$

where g_A^0 is a function only of temperature. Combining (2.2) with (2.4) and (2.5), we get an important relation which holds when the reaction (2.1) is in equilibrium:

$$p_C^2 / p_A p_B = \exp(-\Delta G^0 / RT) , \tag{2.6}$$

where ΔG^0 is defined by

$$\Delta G^0 = 2g_C^0 - g_A^0 - g_B^0 . \tag{2.7}$$

It follows from (2.7) that the right hand side of (2.6) is constant at a constant temperature; hence it is called the equilibrium constant of the reaction (2.1) at temperature T and denoted by K_p. In other words, the partial pressure quotient on the left hand side of (2.6) is equal to the equilibrium constant K_p.

Expressions such as (2.4) or (2.6) is elementary and well-known. It is to be remembered however that their application is limited to perfect gas mixtures. Let us therefore turn to the case in which the above mixture is not "perfect"; in other words it may be a mixture of imperfect gases or may be a liquid mixture (solution). Although the condition (2.2) for equilibrium always remains true (of course, under the condition of constant pressure and temperature), the additivity relation (2.3) now ceases to be true. A very general relation however holds instead of (2.3); namely (*cf.* DENBIGH,[1] p. 99),

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C , \tag{2.8}$$

where the chemical potentials, μ_A etc. appear in place of the molar Gibbs free energies, g_A etc. in (2.3). Also the left hand side of (2.2), namely ΔG, now ought to be computed by using the expression,

$$\Delta G = 2\mu_C - \mu_A - \mu_B , \tag{2.9}$$

(DENBIGH,[1] Chapter 4) rather than the relation (2.4) which is appropriate to perfect gas mixtures. Eqs. (2.8) and (2.9) might look as simple as (2.3) and (2.4), but their contents are in actual fact much more complicated. First of all, the chemical potential μ_A of A depends on the nature and amounts of B and C coexisting in the mixture, whereas the molar GIBBS free energy g_A of pure A evidently does not. Interpreted in molecular terms, the coexisting B and C affect the chemical potentital of A through the interactions between the molecules B and A, and between C and A. A similar thing can be said of μ_B and μ_C. In short the above complication has its origin in the molecular interactions (= interactions among molecules). We shall consider this point in more detail later in Part II, where the same problem will be discussed in statistical-mechanical language.

It is instructive to consider an imperfect gas mixture in particular. We know that an imperfect gas reduces to a perfect gas in the low density limit (namely $p \to 0$); as a gas is rarefied, the molecular interactions are reduced in effect. In this connection we are reminded of the concept of activity (fugacity) and activity coefficient (fugacity coefficient) for an imperfect gas. The activity coefficient γ_J of the component J (J = A, B or C) is defined by

$$\gamma_J = p_J^{-1} \exp\left[(\mu_J - \mu_J^0)/RT\right],\tag{2.10}$$

where μ_J^0 is the standard chemical potential of J, which is a function only of temperature (DENBIGH,[1] p. 123), and $\gamma_J \to 1$ in the low density limit. In place of (2.6) and (2.7), the following relations (2.11) and (2.12) result from (2.2), (2.9) and (2.10):

$$\frac{p_C^2}{p_A p_B} = \left(\frac{\gamma_C^2}{\gamma_A \gamma_B}\right)^{-1} \exp\left(-\frac{\Delta G^0}{RT}\right),\tag{2.11}$$

where ΔG^0 is defined by

$$\Delta G^0 = 2\mu_C^0 - \mu_A^0 - \mu_B^0.\tag{2.12}$$

The standard change of free energy ΔG^0 in (2.11) as well as that in (2.6) is a function only of temperature. However, on account of the activity coefficient quotient $(\gamma_C^2/\gamma_A \gamma_B)$, the right hand side of (2.11) is not constant at a constant temperature, unlike that of (2.6). The activity coefficient γ_A of the component A depends on the nature and amounts of the partner components B and C; much the same can be said of the activity coefficients γ_B and γ_C. In this sense the concept of the equilibrium constant K_p is not applicable to an imperfect gas mixture. Only in the low density limit, where the gas imperfection vanishes, will the chemcical potentials, μ_A etc, become numerically equal to the

molar GIBBS free energies, g_A etc.; then (2.8) and (2.9) will reduce to (2.3) and (2.4), the activity coefficient quotient to unity and the equality (2.11) to the equality (2.6). We shall come back to the molecular (statistical-mechanical) interpretation of the activity coefficients γ_J in Part II.

It remains to say something about the case of liquid solutions. Empirically we know that there exists a certain class of liquid solutions, called ideal solutions, for which the chemical potential of every component is related to its mole fraction x_J by the simple relation,

$$\mu_J = \mu_J^* + RT \ln x_J , \qquad (2.13)$$

where μ_J^* is a fucntion of temperature and pressure only (DENBIGH,[1] Chapter 8). The expression (2.13) is reminiscent of (2.5). In fact, from (2.2), (2.9) and (2.13) we obtain

$$\frac{x_C^2}{x_A x_B} = \exp\left(-\frac{\Delta G^*}{RT}\right), \qquad (2.14)$$

where ΔG^* is given by

$$\Delta G^* = 2\mu_C^* - \mu_A^* - \mu_B^* .$$

The relation (2.14) is very similar to (2.6); the right hand side of (2.14) is a constant at constant temperature and pressure. In other words, the right hand side of (2.14) is the equilibrium constant. It should be remembered however that (2.14) is again of limited applicability since it is based on the special relation (2.13). Solutions for which (2.13) holds over the whole range of composition are very exceptional. In this connection the concept of activity coefficient is often very useful also in the theory of liquid solutions. In any event, the theory of chemical equilibrium in liquid solution is much more complicated than that in gas. In liquid, whose density is much higher than that of gas, the molecular interactions have a decisive influence; were it not for the molecular interactions, there would exist no liquid at all.

In his important papers published in 1935–36 EYRING has shown that the statistical-mechanical calculation of chemical reaction rates is essentially that of the equilibrium constant between activated complex and reactants of the reaction (GLASSTONE *et al.*,[3] Chapter IV). This means that the theory of absolute reaction rate of EYRING *et al.* has a great deal in common with the statistical-mechanical theory of chemical equilibrium. In formulating his theory, EYRING started with what is to be regarded as the statistical mechanics of perfect gases; consequently his rate expressions are, strictly speaking, applicable only to reactions in perfect gas mixtures. On the basis of the close similarity between the theory of reaction rate and that of chemical equilibrium, he claimed

Takashi NAKAMURA

however that their applicability could at once be extended to reactions in imperfect gases, liquid solutions, adsorbed phase, etc. by giving adequately modified interpretations to the partition functions involved in them and by introducing, when necessary, activity cefficients into them in much the same way that the coefficients γ_J have been introduced into equilibrium expressions such as (2.11) (see GLASSTONE *et al.*,[3] Chapters VII and VIII). In so doing, it seems to me, he had to rely on a sort of plausibility argument and/or certain particular models. Most ingeneous as his theory of absolute reaction rate was, the question therefore remained: how can the whole theory of absolute reaction rate be founded on the basis of the general theory of statistical mechanics? One of HORIUTI's efforts has been to answer this question; we shall come back to this point in Part III.

§ 3. Canonical Distribution

The central subject matter of Parts I and II of the present notes is the statistical mechanical treatment of chemical (or adsorption) equilibrium. In Sections 3–6 I shall however make a somewhat lengthy excursion and discuss the statistical mechanics of a simple spin system. The reason is: (1) this spin problem is of particular importance in its own right, that is, as the basis of the theory of magnetism; (2) there is a close relationship (*cf.* Section 7 and Appendix D) between the statistical mechanics of a spin system and that of adsorbed phase, the latter being the central subject of HORIUTI's theory; (3) a detailed discussion of such a spin system is of much pedagogical value for introducing some important concepts or principles of statistical mechanics (see below).

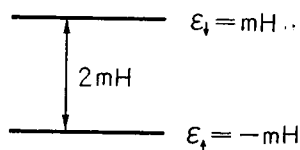Our *spin system* consists of N identical spins, each having spin 1/2 and a magnetic moment m (*cf.* HILL,[4] Section 12.4). Further we suppose that the system is placed in a uniform external magnetic field, and that the spins (=magnetic moments) are attached to N *sites* which in turn form a rigid lattice. Let these sites be numbered $1, 2, \cdots,$ N. As is well-known each of the spins has two quantum states, ↑ and ↓, which signify the spin being parallel and antiparallel, respectively, to the external field. In other words, the spin is a "two-level molecule" having the two energy levels,

$\varepsilon_\uparrow = -mH$

$2mH$

$\varepsilon_\downarrow = mH$

Fig. 1.

$$\varepsilon_\uparrow = -mH \quad \text{for the ↑ state,} \tag{3.1}$$

and

$$\varepsilon_\downarrow = mH \quad \text{for the ↓ state,} \tag{3.2}$$

where H is the strength of the magnetic field. (See Fig. 1.) Any elementary account of the theory of paramagnetism, ferromagnetism, antiferromagnetism, ESR or NMR starts with this kind of simple spin system.

First we assume that the interactions among the spins are so weak as to be negligible in the statistical calculation of spin distribution. This assumption suffices to calculate the spin distribution in paramagnetic substances. Then each spin is regarded as practically *independent*; in fact, on this basis can we speak of the "private" energy (3.1) or (3.2) of each spin and calculate the probability $p_\uparrow$ or $p_\downarrow$ of any spin in the system being in the $\uparrow$ or $\downarrow$ state by the BOLTZMANN distribution law,

$$p_\uparrow = q^{-1} \exp(-\varepsilon_\uparrow/kT), \quad p_\downarrow = q^{-1} \exp(-\varepsilon_\downarrow/kT), \tag{3.3}$$

where T is the temperature of the spin system[*] and q is the partition function of the spin,

$$q = \exp(-\varepsilon_\uparrow/kT) + \exp(-\varepsilon_\downarrow/kT). \tag{3.4}$$

Let $\langle N_\uparrow \rangle$ be the mean number of $\uparrow$-spins (that is, spins in the $\uparrow$ state) and let $\langle N_\downarrow \rangle$ be that of $\downarrow$-spins. These numbers are given by

$$\langle N_\uparrow \rangle = Np_\uparrow = \frac{N}{q} \exp\left(-\frac{\varepsilon_\uparrow}{kT}\right), \quad \langle N_\downarrow \rangle = Np_\downarrow = \frac{N}{q} \exp\left(-\frac{\varepsilon_\downarrow}{kT}\right),$$

hence it follows that

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = \frac{p_\downarrow}{p_\uparrow} = \frac{\exp(-\varepsilon_\downarrow/kT)}{\exp(-\varepsilon_\uparrow/kT)}, \tag{3.5}$$

$$\langle N_\uparrow \rangle + \langle N_\downarrow \rangle = N.$$

The temperature or field dependence of the paramagnetism of this system is readily calculated from (3.5); that is, the mean total magnetic moment M of the system is given by

$$M = m\langle N_\uparrow \rangle + (-m)\langle N_\downarrow \rangle = (mN/q)\left[\exp(-\varepsilon_\uparrow/kT) - \exp(-\varepsilon_\downarrow/kT)\right]$$

Using (3.1), (3.2) and (3.4), we thus have the well-known result (HILL,[4] Section 12.4; WANNIER,[11] Section 15.1),

$$M = mN \tanh(mH/kT), \tag{3.6}$$

---

[*] Here we suppose that our spin system is a macroscopic one, that is, $N \sim 10^{20}$ or more. What is termed a *system* in the present notes has been called an *assembly* by FOWLER.[2] HORIUTI and RUSHBROOKE have followed FOWLER. My usage of the term "system" is in agreement with that in thermodynamics and that employed in many papers or textbooks on statistical mechanics (of course, except those by FOWLER, RUSHBROOKE and HORIUTI). See in this connection RUSHBROOKE,[10a] p. 4.

which is the quantum mechanical version of the LANGEVIN formula.

So far the discussion has been quite elementary, since we have neglected the interactions among spins. Now let us see how the interactions among spins change everything. We shall start with the simplest possible case. Imagine the hypothetical situation in which there is an appreciable interaction between a *pair* of spins in the system, say the spins on the neighboring lattice sites 1 and 2, which we shall call spins 1 and 2 for short, but the interaction between the pair and the remaining $N-2$ spins is so weak as to be negligible (Fig. 2). Since spin 1 (or 2) is no longer independent, the probability $p_{1\uparrow}$ or $p_{1\downarrow}$ ($p_{2\uparrow}$ or $p_{2\downarrow}$) of its being $\uparrow$ or $\downarrow$ can not be computed by using (3.3). In this case it is
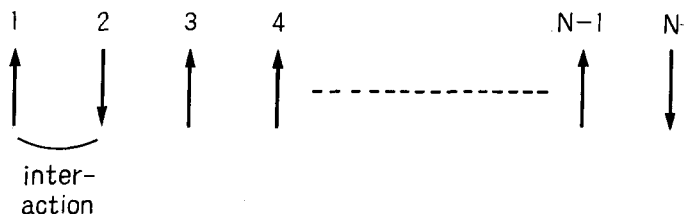

Fig. 2.

appropriate to speak of the energy of the pair (see below) but *not* of the "private" energy of spin 1 (or spin 2). We therefore take the spin pair, rather than individual spins, as the *statistical unit* to which the BOLTZMANN distribution law similar to (3.3) is applied, because the pair has been assumed to be practically independent of the remaining $N-2$ spins. The number of quantum states of this pair is four; they are $\uparrow\uparrow$, $\downarrow\uparrow$, $\uparrow\downarrow$ and $\downarrow\downarrow$. (The symbol $\downarrow\uparrow$, for instance, means that spins 1 and 2 are $\downarrow$ and $\uparrow$, respectively.) We assume that the energies of these states of the pair are given by

$$\varepsilon(\uparrow\uparrow) = 2\varepsilon_\uparrow - J,$$
$$\varepsilon(\downarrow\uparrow) = \varepsilon(\uparrow\downarrow) = \varepsilon_\uparrow + \varepsilon_\downarrow + J, \qquad (3.7)$$
$$\varepsilon(\downarrow\downarrow) = 2\varepsilon_\downarrow - J,$$

where J is a positive constant (*cf.* HILL,[4] p. 250) and $\varepsilon_\uparrow$ and $\varepsilon_\downarrow$ are given by (3.1) and (3.2). Eqs. (3.7) indicate that there is negative interaction energy $-J$ between parallel spins ($\uparrow\uparrow$ or $\downarrow\downarrow$) and a positive interaction energy J between antiparallel spins ($\downarrow\uparrow$ or $\uparrow\downarrow$). In other words, the interaction tends to stabilize the parallel pair and to destabilize the antiparallel pair; if, for instance, spin 2 is $\uparrow$, spin 1 is tempted to be $\uparrow$ rather than $\downarrow$. This type of interaction between electronic spins is known to be the origin of ferromagnetism (WANNIER,[11] Chapter 15). Anyway the probability $P(\uparrow\uparrow)$ of the pair being

in the ↑↑ state is, according to the BOLTZMANN distribution law, given by

$$P(\uparrow\uparrow) = (q_{\text{pair}})^{-1} \exp\left[-\varepsilon(\uparrow\uparrow)/kT\right] . \tag{3.8}$$

In (3.8), q_{pair} is the partition function of the pair defined by

$$q_{\text{pair}} = \sum_{j} \exp\left[-\varepsilon(j)/kT\right] , \tag{3.9}$$

where the summation $\sum_{j}$ runs over all the four states (that is, $j = \uparrow\uparrow$, $\downarrow\uparrow$, $\uparrow\downarrow$ and $\downarrow\downarrow$). The other probabilities $P(\downarrow\uparrow)$, $P(\uparrow\downarrow)$ and $P(\downarrow\downarrow)$ are obtained in much the same way. Now the above-mentioned probability $p_{1\uparrow}$ of spin 1 being ↑ is readily calculated. The elementary theory of probability shows us that $p_{1\uparrow}$ is given by

$$p_{1\uparrow} = P(\uparrow\uparrow) + P(\uparrow\downarrow) , \tag{3.10}$$

since spin 1 is ↑ when and only when the pair is in the ↑↑ or ↑↓ state. Similary,

$$p_{1\downarrow} = P(\downarrow\uparrow) + P(\downarrow\downarrow) , \tag{3.11}$$

$$p_{2\uparrow} = P(\uparrow\uparrow) + P(\downarrow\uparrow) , \quad p_{2\downarrow} = P(\uparrow\downarrow) + P(\downarrow\downarrow) . \tag{3.12}$$

Now it is very easy to prove, using Eqs. (3.7)–(3.12), that in the limit of $J \rightarrow 0$ (vanishing interaction),

$$q_{\text{pair}} = q^{2} , \tag{3.13}$$

$$p_{1\downarrow} = p_{2\downarrow} = p_{\downarrow} , \quad p_{1\uparrow} = p_{2\uparrow} = p_{\uparrow} , \tag{3.14}$$

$$P(\uparrow\uparrow) = p_{\uparrow}^{2} , \quad P(\downarrow\uparrow) = P(\uparrow\downarrow) = p_{\uparrow}p_{\downarrow} , \quad P(\downarrow\downarrow) = p_{\downarrow}^{2} , \tag{3.15}$$

where $p_{\downarrow}$, $p_{\uparrow}$ and q are given by (3.3) and (3.4). Take, for instance, one of the above relations, $P(\downarrow\uparrow) = p_{\downarrow}p_{\uparrow}$. It indicates that the probability $P(\downarrow\uparrow)$ for the pair is written as the product of the probabilities $p_{\downarrow}$ and $p_{\uparrow}$ for individual spins. This is what we expect since, in the absence of the interaction (that is, $J = 0$), the orientation of spin 1 and that of spin 2 are independent events (in other words, there is no *correlation* between them).

We have just considered the statistical mechanics of two interacting spins. The treatment can be readily extended to the case of three (or more) interacting spins. However what we are really interested in is the problem of N *interacting spins*, where N is the number of the spins constituting a macroscopic spin system (see the footnote on p. 133). In (3.8) we have applied the BOLTZMANN distribution law to a spin pair rather than to a single spin. Can we apply anything like the BOLTZMANN law to the whole system of N spins? The answer is, 'yes''; according to the general theory of statistical mechanics

(DENBIGH,[1] Section 11.9), the probability $P(I)$ of the system being in its I-th quantum state having energy $E(I)$ is given by

$$P(I) = \frac{1}{Q} \exp\left[-E(I)/kT\right],$$
(3. 16)

provided that the system is an isothermal system with constant volume, that is, it is in contact with environment (or more precisely, a heat bath) of temperature T and its volume is kept constant. In (3.16), Q is the partition function of the system given by

$$Q = \sum_I \exp\left[-E(I)/kT\right],$$
(3. 17)

where the summation runs over all the quantum states of the system. The distribution given by (3.16), appropriate for an isothermal system with constant volume, is called *canonical distribution* (DENBIGH,[1] Chapter 11; HILL,[4] Chapter 1). Indeed the relation (3.16) is of fundamental importance in statistical mechanics. Using the distribution (3.16) we can calculate the mean values (canonical ensemble averages) of various physical quantities of the system.

Our spin system may be regarded as a two-component system consisting of ↑-spins and ↓-spins. The transition of a spin between the ↑ and ↓ states may be regarded as an isomerization reaction, namely

↑-spin $\rightleftharpoons$ ↓-spin
(3. 18)

Suppose that when the system is in the I-th quantum state, its "composition" is given by $N_\uparrow(I)$ and $N_\downarrow(I)$, which stand for the number of ↑-spins and that of ↓-spins respctively. Evidently,

$$N_\uparrow(I) + N_\downarrow(I) = N.$$

Then the mean values of these numbers are given by

$$\langle N_\uparrow \rangle = \sum_I N_\uparrow(I)P(I), \quad \langle N_\downarrow \rangle = \sum_I N_\downarrow(I)P(I).$$
(3. 19)

Now our task is to extend the above two-spin calculation, centering around (3.8), (3.9), etc., to the N-spin case. To do this we start with the basic formula (3.16) and the expression (3.25) below for the energy levels of the N-spin system. The problem we are going to deal with is known as the ISING *problem*, which is treated in many textbooks on statistical mechanics. (See, for example, HILL,[4] Chapter 14 and WANNIER,[11] Chapters 15 and 16.) Eq. (3.25) implies that each spin has only two quantum states, ↑ and ↓, and that there is an interaction energy $\pm J$ between each nearest-neighbor pair of spins (HILL,[4] p. 250; WANNIER,[11] Section 15.4). A close study of the statistical-mechanical

treatment of this sort of spin system, whose energy levels are given by the simple, transparent expression (3.25), indeed has the pedagogical advantage that good insight into the effect of the interactions on a statistical distribution is obtained relatively easily from it. (See Part II.) Since we are going to deal with very many spins, it is convenient to introduce a new variable s_j which can take on just two values, -1 and $+1$; more specifically $s_j = -1$ or $+1$ signifies that spin j is $\downarrow$ or $\uparrow$ respectively. It is found that the number of quantum states of the N-spin system is 2^N, and these states are described by a set of N variables, $(s_1, s_2, \cdots, s_N)$. In order to illustrate this, let us consider the rather trivial case $N=2$. As we have seen above, there are 2^2 quantum states, $\uparrow\uparrow$, $\downarrow\uparrow$, $\uparrow\downarrow$ and $\downarrow\downarrow$, which are described by $(s_1, s_2)=(1,1)$, $(-1,1)$, $(1,-1)$ and $(-1,-1)$, respectively. In terms of the s_j variables the energy expressions (3.7) for two interacting spins are unified into the single equation,

$$\varepsilon(s_1 s_2) = -s_1 mH - s_2 mH - s_1 s_2 J \,, \tag{3.20}$$

and (3.9) is rewritten as

$$q_{\mathrm{pair}} = \sum_{s_1} \sum_{s_2} \exp\left[-\varepsilon(s_1 s_2)/kT\right] \,.$$

Returning to the N-spin case, we observe that the quantum number I in (3.16) and (3.17) can be replaced by the set of N variables $(s_1, s_2, \cdots, s_N)$; thus (3.16), (3.17) and (3.19) are rewritten as

$$P(s_1 s_2 \cdots s_N) = \frac{1}{Q} \exp\left[-E(s_1 s_2 \cdots s_N)/kT\right] \,, \tag{3.21}$$

$$Q = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} \exp\left[-E(s_1 s_2 \cdots s_N)/kT\right] \,, \tag{3.22}$$

$$\langle N_\uparrow \rangle = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} N_\uparrow(s_1 s_2 \cdots s_N) P(s_1 s_2 \cdots s_N) \,, \tag{3.23}$$

$$\langle N_\downarrow \rangle = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} N_\downarrow(s_1 s_2 \cdots s_N) P(s_1 s_2 \cdots s_N) \,, \tag{3.24}$$

The energy of our N-spin system is assumed to be given by an expression similar to (3.7) or (3.20):

$$E(s_1 s_2 \cdots s_N) = -\sum_{j=1}^{N} s_j mH - \sum_{(j,k)} s_j s_k J \,, \tag{3.25}$$

where the summation $\sum_{(j,k)}$ runs over all nearest-neighbor pairs of spins. Eq. (3.25) implies therefore that there is an interaction energy $\pm J$ (see the discussion following (3.7)) between nearest-neighbor spins while second-neighbor, and higher, interactions are negligible. I shall not delve into a detailed discussion of the energy expression (3.25), which is usually called the ISING *model*

expression, because its derivation is a business of quantum mechanics (cf. WANNIER,[11] Chapter 15) rather than that of statistical mechanics.

The important probability $P(s_1 s_2 \cdots s_N)$ is a function of the N variables, $s_1, s_2, \cdots, s_N$, each of them assuming one of two discrete values, -1 and 1. We shall be much interested in the probability that a certain spin, say spin 1, in the spin system be in the $\uparrow$ or $\downarrow$ state. As is shown below this probability can be derived from $P(s_1 s_2 \cdots s_N)$ in essentially the same way that the probabilities $p_{1\uparrow}$ and $p_{1\downarrow}$ have been calculated from $P(j)$ $(j = \uparrow\uparrow, \downarrow\uparrow, \uparrow\downarrow$ and $\downarrow\downarrow)$ by means of (3.10)–(3.11). To do this we introduce the following function of the t variables $s_1 s_2 \cdots s_t$ $(t < N)$:

$$P^{(t)}(s_1 s_2 \cdots s_t) \equiv \sum_{s_{t+1}} \sum_{s_{t+2}} \cdots \sum_{s_N} P(s_1 s_2 \cdots s_N). \tag{3.26}$$

This function $P^{(t)}(s_1 s_2 \cdots s_t)$ is very much like the *specific distribution function* extensively used in the distribution function theory of fluids (HILL A,[5] p. 182). In (3.26) the N-spin distribution function P on the right hand side is "reduced" to the t-spin distribution function $P^{(t)}$ on the left hand side by the $(N-t)$-fold summation $\sum_{s_{t+1}} \sum_{s_{t+2}} \cdots \sum_{s_N}$. The significance of the "reduced distribution function" $P^{(t)}$ can be best understood by considering $P^{(1)}(s_1)$ and $P^{(2)}(s_1 s_2)$ as typical examples. Evidently $P^{(1)}(1)$ is the probability of spin 1 being $\uparrow$; in other words, $P^{(1)}(1)$ is the same thing as $p_{1\uparrow}$ in (3.10). Similarly $P^{(1)}(-1)$ is the same thing as $p_{1\downarrow}$ in (3.11). $P^{(2)}(1, -1)$ is the probability that spin 1 is $\uparrow$ and spin 2 is $\downarrow$ at the same time.

It immediately follows from the definitions (3.21)–(3.22) and (3.26) that the following relations hold when the interactions among spins are absent $(J = 0)$:

$$Q = \left[\sum_{s_1} \exp(s_1 mH/kT) \right]^N = q^N, \tag{3.27}$$

$$P^{(1)}(s_1) = q^{-1} \exp(s_1 mH/kT), \tag{3.28}$$

$$P^{(2)}(s_1 s_2) = q^{-2} \exp(s_1 mH/kT) \exp(s_2 mH/kT) = P^{(1)}(s_1) P^{(1)}(s_2), \tag{3.29}$$

$$P^{(t)}(s_1 s_2 \cdots s_t) = \prod_{j=1}^{t} q^{-1} \exp(s_j mH/kT) = \prod_{j=1}^{t} P^{(1)}(s_j), \tag{3.30}$$

$$P(s_1 s_2 \cdots s_N) = \prod_{j=1}^{N} q^{-1} \exp(s_j mH/kT) = \prod_{j=1}^{N} P^{(1)}(s_j), \tag{3.31}$$

where q is defined by (3.4). These equations are to be regarded as the extension of (3.13)–(3.15) to the N-spin case.

Provided that all the N spins are equivalent, the important ratio $\langle N_\downarrow \rangle / \langle N_\uparrow \rangle$

is expressed in terms of the probability $P^{(1)}(s_1)$ of spin 1 being $\uparrow$ or $\downarrow$ (see Appendix A) as

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = \frac{P^{(1)}(-1)}{P^{(1)}(1)} . \tag{3.32}$$

When the interactions among the spins are absent, the relation (3.32), by virtue of (3.28), reduces to

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = \frac{\exp(-mH/kT)}{\exp(mH/kT)} = \exp\left[-(\varepsilon_\downarrow - \varepsilon_\uparrow)/kT\right], \tag{3.33}$$

which is nothing but the simple BOLTZMANN distribution law (3.5).

So far our discussion has been just that of well-known, elementary probability relations; it might seem formal and rather empty of any real content. In Part II, I shall however show that the right hand side of the general relation (3.32) is rewritten as follows:

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = \frac{\exp\left[-(\varepsilon_\downarrow + w_\downarrow)/kT\right]}{\exp\left[-(\varepsilon_\uparrow + w_\uparrow)/kT\right]} . \tag{3.34}$$

This expression bears a formal resemblance to (3.33), but the quantities $w_\downarrow$ and $w_\uparrow$ occurring on the right hand side of (3.34) are of very complicated nature. They arise from the interactions among spins and have the properties of free energy. Hence they are temperature dependent whereas $\varepsilon_\downarrow$ and $\varepsilon_\uparrow$ are, of course, not. In passing we note that (3.34) is rewritten as

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = \frac{\exp(-w_\downarrow/kT)}{\exp(-w_\uparrow/kT)} \exp\left[-(\varepsilon_\downarrow - \varepsilon_\uparrow)/kT\right]. \tag{3.35}$$

It is interesting to compare the relations (3.33) and (3.35) for the "reaction" (3.18) with the earlier relations (2.6) and (2.11) for the reaction (2.1); the factor $\exp(-w_\downarrow/kT)/\exp(-w_\uparrow/kT)$ on the right hand side of (3.35) becomes unity in the limit $J \to 0$ (vanishing interactions) and is indeed reminiscent of the activity coefficient quotient $\gamma_A \gamma_B/\gamma_C^2$ occurring in (2.11). I shall discuss this point more sharply in Part II.

§ 4. Constraints on System and Partition Functions

In Section 3 I have defined the partition function Q of the spin system by (3.17), where the sum is taken over all the 2^N quantum states of the system. According to the general theory of statistical mechanics (HILL,[4])

Takashi NAKAMURA

Chapter 1; DENBIGH,[1] Chapter 11) the HELMHOLTZ *free energy*[*] F of the system is related to the partition function Q by

$$F = -kT \ln Q .\tag{4.1}$$

In this section we shall define three other partition functions, $Q^{(1)}(s_1)$, Q_n and $Q_n^{(1)}(s_1)$, and consider their significance.[**] Let us begin with $Q^{(1)}(s_1)$, where s_1 is the variable we have introduced in Section 3; hence it takes on two values, -1 and 1. First let s_1 be -1. We pick out, from the above 2^N states, only those states in which s_1 is -1 (that is, those states in which spin 1 is ↓), and construct the partition function $Q^{(1)}(-1)$ as

$$Q^{(1)}(-1) = \sum_I^{s_1=-1} \exp\left[-E(I)/kT\right] ,\tag{4.2}$$

where the superscript $s_1 = -1$ on $\sum_I$ indicates that the sum is taken over only those states in which s_1 is -1. The number of such states is 2^{N-1}, which fact is most easily seen from (4.6) below. Thus $Q^{(1)}(-1)$ defined by (4.2) is what might be termed a "partial-sum-over-states" as against Q which is defined by (3.17) and called a *sum-over-states (Zustandsumme)*. In Section 3 we have considered the probability $P^{(1)}(-1)$ of spin 1 being ↓, which is equal to the probability of the system being in any of the 2^{N-1} states with $s_1 = -1$. Since $P(I)$ given by (3.16) is the probability of the system being in the I-th state, the probability $P^{(1)}(-1)$ is expressed as

$$P^{(1)}(-1) = \sum_I^{s_1=-1} P(I) = Q^{(1)}(-1)/Q .\tag{4.3}$$

Much the same applies to the case $s_1 = 1$, and therefore we write

$$Q^{(1)}(1) = \sum_I^{s_1=1} \exp\left[-E(I)/kT\right] ,\tag{4.4}$$

$$P^{(1)}(1) = Q^{(1)}(1)/Q .\tag{4.5}$$

In passing it is to be noted that the relations (4.2) and (4.4) are conveniently rewritten in terms of the set of variables $s_1, s_2, \cdots, s_N$ as

---

*) In the present notes, the HELMHOLTZ and GIBBS free energies are denoted by F and G, respectively, which conforms to the IUPAP (and IUPAC) recommendation but deviates from HILL[4][5] and the practice of American chemists. In magnetic problems such as the one we are dealing with, some authors prefer to give different names to the free energy F given by (4.1), where the partition function Q is defined by (3.22), and there is a good reason for this. However the discussion of this matter is beyond the scope of the present notes. (HILL A,[5] Section 41; WANNIER,[11] Sections 8.2 and 15.4)

**) The definitions of these partition functions can be best understood by considering the special case $N=3$, which is described in Appendix B.

$$Q^{(1)}(s_1) = \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} \exp\left[-E(s_1 s_2 \cdots s_N)/kT\right]. \tag{4.6}$$

Notice that the summation on the right hand side of (4.6) is $(N-1)$-fold (that is, we do not sum with respect to s_1), whereas that on the right hand side of (3.22) is N-fold. Comparing the above expression (4.6) for $Q^{(1)}(s_1)$ with (3.22), (3.26) and (3.21) we readily see that

$$\left.\begin{aligned}
Q &= \sum_{s_1} Q^{(1)}(s_1) = Q^{(1)}(1) + Q^{(1)}(-1), \\
P^{(1)}(s_1) &= \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} P(s_1 s_2 \cdots s_N) = Q^{(1)}(s_1)/Q, \\
P^{(1)}(1) &+ P^{(1)}(-1) = 1.
\end{aligned}\right\} \tag{4.7}$$

The second equation coincides with (4.3) and (4.5), and the third is what it should be.

Next we define the partition function Q_n $(0 \leq n \leq N)$ by

$$Q_n = \sum_{I} {}_n \exp\left[-E(I)/kT\right], \tag{4.8}$$

where the subscript n attached to $\sum_{I}$ implies that the sum is taken over those states which satisfy the condition $N_\downarrow(I) = n$, that is, the condition that the number of $\downarrow$-spins is n. The number of such states is $N!/n!(N-n)!$, since there are $N!/n!(N-n)!$, ways of choosing n sites for $\downarrow$-spins from the N sites. Now let P_n be the probability of the spin distribution being $(n, N-n)$, that is, the probability that the number of $\downarrow$-spins in the system is n (thus the number of $\uparrow$-spins is $N-n$); P_n is obtained from $P(I)$ in much the same way that $P^{(1)}(-1)$ has been obtained from $P(I)$ by means of (4.3):

$$P_n = \sum_{I} {}_n P(I) = Q_n/Q. \tag{4.9}$$

We easily find that the summation $\sum_{I}$ is equivalent to the double summation $\sum_{n=0}^{N} \sum_{I} {}_n$ and therefore the second equation of (3.19), for example, is rewritten as

$$\langle N_\downarrow \rangle = \sum_{n=0}^{N} \sum_{I} {}_n N_\downarrow(I) P(I) = \sum_{n=0}^{N} n \sum_{I} {}_n P(I) = \sum_{n=0}^{N} n P_n. \tag{4.10}$$

Finally the partition function $Q_n^{(1)}(\pm 1)$ is defined by

$$Q_n^{(1)}(\pm 1) = \sum_{I} {}_n^{s_1 = \pm 1} \exp\left[-E(I)/kT\right]. \tag{4.11}$$

The super- and subscripts, $s_1 = \pm 1$ and n, attached to $\sum_{I}$ on the right hand side of (4.11) have the same meaning as in (4.2), (4.4) and (4.8); therefore the sum runs over only those states which satisfy the conditions, $s_1 = \pm 1$ and $N_\downarrow(I) = n$, simultaneously. The number of the states satisfying both the

conditions, $s_1 = 1$ and $N_{\downarrow}(I) = n$ is $(N-1)!/n!\,(N-n-1)!$; the number of the states satisfying both $s_1 = -1$ and $N_{\downarrow}(I) = n$ is $(N-1)!/(n-1)!\,(N-n)!$. It should be noted that relations analogous to (4.7) hold; namely,

$$Q = \sum_{n=0}^{N} Q_n, \qquad \sum_{n=0}^{N} P_n = 1,$$

$$Q_n = Q_n^{(1)}(+1) + Q_n^{(1)}(-1),$$

$$Q^{(1)}(\pm 1) = \sum_{n=0}^{N} Q_n^{(1)}(\pm 1).$$

Now we define, in analogy with (4.1), the following quantities:

$$F^{(1)}(\pm 1) = -kT \ln Q^{(1)}(\pm 1), \tag{4.12}$$

$$F_n = -kT \ln Q_n, \tag{4.13}$$

$$F_n^{(1)}(\pm 1) = -kT \ln Q_n^{(1)}(\pm 1).$$

In the following we shall consider the physical significance of these quantities. We have calculated the partition function of the spin system by (3.17), which is based on the fact that all the 2^N quantum states are available to the system. Let us imagine a certain *constraint* which limits the number of available (*accessible*) states. (*cf.* HILL,[4] Section 2.3). For example, let the constraint be such that spin 1 is locked in the $\downarrow$ state. When this constraint is imposed on the system, only the 2^{N-1} states with $s_1 = -1$ are available to the system (that is, the remaining 2^{N-1} states with $s_1 = 1$ are *inaccessible* states), and therefore its partition function and free energy are respectively given by $Q^{(1)}(-1)$ and $F^{(1)}(-1)$ instead of Q and F. Thus[*]

$$F^{(1)}(-1) - F = -kT \ln\left[Q^{(1)}(-1)/Q\right] = -kT \ln P^{(1)}(-1) \quad (4.14)$$

is the *free energy increment* due to the addition of this constraint to the system. Using the language of thermodynamics one may call the free energy increment (4.14) the isothermal reversible work, or *reversible work* for short, required to lock spin 1 in the $\downarrow$ state. (*Cf.* HILL,[4] p. 307).

If, on the other hand, the system is subjected to a constraint such that the number of $\downarrow$-spins in the system is held fixed, say at n, then the states available to the system are those appearing in the summation $\sum_n$ on the right hand side of (4.8). Hence we see that Q_n and F_n are the partition function and free energy of the spin system whose "composition" (see Section 3) is

---

[*] Phrased in HORIUTI's way, the partition function ratio $Q^{(1)}(-1)/Q$ in (4.14) is the factor of multiplication of the partition function Q caused by imposing the above constraint upon the state of spin 1. See Section 6 and HORIUTI,[7] p. 8.

fixed by the constraint. Finally the meaning of $Q_n^{(1)}(s_1)$ or $F_n^{(1)}(s_1)$ should be evident from the above discussion.

The constraints considered in this section are "fictitious" ones. Any experimental (macroscopic) method of imposing these constraints on the system does not have to exist. For example, we know of no method of locking spin 1 in the ↓ state because of the "microscopically detailed nature" (see HORIUTI,[7] p. 16) of this constraint. The terms, *constraint* and *reversible work*, in this section are used simply to give convenient "physical" interpretations to certain mathematical relations.

§ 5. Most Probable Distribution and Minimum Free Energy

The probability P_n is that of the spin distribution being $(n, N-n)$; in other words, it determines the fluctuation in the "composition" (Section 3) of the spin system. Since the spin system we are dealing with is a macroscopic system, this kind of fluctuation is actually very small so that we can completely ignore it. Consequently we can assume that the *most probable distribution* practically determines the equilibrium properties of the spin system; in other words, the value which n (= the number of ↓-spins) assumes in equilibrium can be regarded as equal to n^*, where n^* is the most probable value of n, that is, the value of n which maximizes Q_n and therefore P_n. (See HILL,[4] Sections 2.1 and 10.3; MAYER-MAYER,[10] Section 3e.) Thus Q_{n^*} and P_{n^*} are respectively the maximum values of Q_n and P_n. According to (4.13), Q_{n^*} in turn corresponds to F_{n^*}, which is the *minimum value of the free energy* F_n. Since the spin system we are working with is macroscopic, this number n^* as well as N can be assumed to be very large numbers, say 10^{20} or more. Consequently: (1) Taking $\ln Q_n$ to be a smooth function of a continuous variable n $(0 \leq n \leq N)$, we can determine the most probable distribution $(n^*, N-n^*)$ from the condition,

$$\left(\frac{\partial}{\partial n} \ln Q_n \right)_{n=n^*} = 0 \quad \text{or} \quad \left(\frac{\partial F_n}{\partial n} \right)_{n=n^*} = 0 , \tag{5.1}$$

where the suffix $n=n^*$ implies that we set n equal to n^* after the differentiation; (2) since $n^* \gg 1$, the above derivative of $\ln Q$ is expressed as

$$\left(\frac{\partial}{\partial n} \ln Q_n \right)_{n=n^*} = \ln Q_{n^*+1} - \ln Q_{n^*} = \ln (Q_{n^*+1}/Q_{n^*})$$
$$= -\ln \lambda(n^*) \tag{5.2}$$

(HILL,[4] p. 307; KIRKWOOD,[9] p. 302) where $\lambda(n)$ is defined by

$$\lambda(n) = Q_n/Q_{n+1} . \tag{5.3}$$

Hence the condition (5.1) for the most probable distribution or for minimum free energy is now expressed as

$$\ln \lambda(n^*) = 0 \,,$$

that is,

$$Q_{n^*}/Q_{n^*+1} = \lambda(n^*) = 1 \,. \tag{5.4}$$

To determine the equilibrium point of a chemical reaction or an adsorption process we shall later have recourse to relations very similar to (5.4). (See Section 7 and Part II.)

I have already mentioned that the fluctuation of n around the most probable value n^* is extremely small. In other words the probabilities P_n of all distributions which are appreciably different from the most probable one $(n^*, N-n^*)$ are extremely small. For this reason, (4.10) is rewritten as

$$\langle N_\downarrow \rangle = \sum_{n=0}^{N} n P_n = \sum_{n=0}^{N} n^* P_n = n^* \sum_{n=0}^{N} P_n = n^* \,.$$

A similar relation for $\langle N_\uparrow \rangle$ is immediately obtained, and it is thus shown that

$$\langle N_\downarrow \rangle = n^* \quad \text{and} \quad \langle N_\uparrow \rangle = N-n^* \,, \tag{5.5}$$

which imply that the mean values coincide with the corresponding most probable values.

According to (4.3) and (4.5) we can write

$$P^{(1)}(\pm 1) = Q^{(1)}(\pm 1)/Q \,, \tag{5.6}$$

that is,

$$P^{(1)}(\pm 1) = \frac{\sum_{I}^{s_1 = \pm 1} \exp[-E(I)/kT]}{\sum_{I} \exp[-E(I)/kT]} \,. \tag{5.7}$$

In calculating the right hand side of (5.7), we shall resort to the maximum term method (HILL,[4] pp. 10 and 251). In other words, in the sums in the numerator and denominator on the right hand side of (5.7), we shall ignore all terms except those corresponding to the most probable distribution $(n^*, N-n^*)$. This is quite justified since all the equilibrium properties of the system are, as I have said above, expressed by the properties of the most probable distribution. (See also MAYER-MAYER,[10] Section 3e.) In terms of the symbols defined in connection with (4.11), the probability $P^{(1)}(\pm 1)$ is thus expressed as

$$P^{(1)}(\pm 1) = \frac{\sum_{I}^{s_1 = \pm 1} \exp[-E(I)/kT]}{\sum_{I} n^* \exp[-E(I)/kT]} = \frac{Q_{n^*}^{(1)}(\pm 1)}{Q_{n^*}} \,, \tag{5.8}$$

which relation implies that the ratio $Q^{(1)}(\pm1)/Q$ on the right hand side of (5.6) can be replaced by a similar ratio, $Q_{n^*}^{(1)}(\pm1)/Q_{n^*}$, appropriate to the most probable distribution.

§6. HORIUTI's Statistical Mechnical Functions

In Sections 3–5 I have discussed a few important relations between probabilities and partition functions, and between partition functions and free energies. From (3.32), (5.6) and (4.12) we have

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = \frac{P^{(1)}(-1)}{P^{(1)}(1)} = \exp(-W/kT), \qquad (6.1)$$

where W is the free energy change given by

$$W = -kT \ln Q^{(1)}(-1)/Q^{(1)}(1) = F^{(1)}(-1) - F^{(1)}(1), \qquad (6.2)$$

As I have stated in Section 4, W may be interpreted as the reversible work required to convert, on site 1, a ↑-spin into a ↓-spin. Comparing (6.1) with (3.34) we find

$$W = (\varepsilon_\downarrow + w_\downarrow) - (\varepsilon_\uparrow + w_\uparrow), \qquad (6.3)$$

which in the limit $J \to 0$ (the absence of the interactions) becomes

$$W = \varepsilon_\downarrow - \varepsilon_\uparrow . \qquad (6.4)$$

The right hand side of (6.4) is the separation $\Delta\varepsilon$ of the two energy levels $\varepsilon_\downarrow$ and $\varepsilon_\uparrow$ (Fig. 1). In (5.8) we have observed that the probability $P^{(1)}(\pm1)$ can be expressed also in terms of the partition functions $Q_{n^*}^{(1)}(\pm1)$ appropriate to the most probable distribution. Insofar as n^* is a very large number, the difference between n^* and n^*+1 can be regarded as extremely small; hence the numerical value of the ratio $Q_{n^*}^{(1)}(\pm1)/Q_{n^*}$ in (5.8) is practically unaffected by changing the suffix n^* attached to Q into n^*+1. Thus we have

$$P^{(1)}(\pm1) = Q_{n^*}^{(1)}(\pm1)/Q_{n^*} = Q_{n^*+1}^{(1)}(\pm1)/Q_{n^*+1} . \qquad (6.5)$$

It follows from (6.1) and (5.8) that

$$W = -kT \ln Q_{n^*}^{(1)}(-1)/Q_{n^*}^{(1)}(1) = F_{n^*}^{(1)}(-1) - F_{n^*}^{(1)}(1) . \qquad (6.6)$$

Now we are in a position to consider the connection between HORIUTI's theory and what we have discussed in the preceding sections, and to see how things are expressed in HORIUTI's language. Throughout the rest of this section, we shall use his notation by adapting it for our spin problem. In Table 1 a set of new symbols we are going to use are listed and correlated

Takashi NAKAMURA

with those in the preceding sections.[*] First note that the partition functions Q_n and Q_{n+1} are now denoted by ΩC and ΩC^+; that is,[**] the spin system consisting of n ↓-spins and $N-n$ ↑-spins is called C and that consisting of $n+1$ ↓-spins and $N-n-1$ ↑-spins is called C^+, and the corresponding partition functions are denoted by ΩC and ΩC^+. In Section 4 we have considered a constraint relevant to the state of the spin on site 1 (namely, spin 1), and in this connection the partition functions $Q^{(1)}(\pm 1)$ and $Q_n^{(1)}(\pm 1)$ have been defined. In the new system of symbols, the imposition of this constraint on the systems C and C^+ is represented by the suffix $\sigma(\downarrow)$ or $\sigma(\uparrow)$, which means that the spin on site σ ($\equiv$ site 1) is ↓ or ↑. Thus (see Table 1) the partition functions $Q_n^{(1)}(-1)$, $Q_n^{(1)}(1)$ and $Q_{n+1}^{(1)}(-1)$ are now denoted by $\Omega C_{\sigma(\downarrow)}$, $\Omega C_{\sigma(\uparrow)}$ and $\Omega C_{\sigma(\downarrow)}^+$ respectively. Table 1 also lists the statistical-mechanical functions p^+, q_σ^+, $\Theta_{\sigma(\downarrow)}$ and $\Theta_{\sigma(\uparrow)}$ defined as the ratios of the above partition functions. They are the spin problem version of HORIUTI's "conjugate statistical mechanical functions defined respectively as the factor of multiplication of the partition function caused by increasing a certain constituent of the assembly (= system) of interest or by imposing a microscopic constraint upon the elementary state of the constituent" (HORIUTI,[7] p. 8; see also the footnote on p. 142 of the present notes).[***] It is readily seen that the function p^+ is nothing but the reciprocal of $\lambda(n)$ defined by (5.3) and there exists the following interrelation:

$$\frac{\Theta_{\sigma(\downarrow)}}{\Theta_{\sigma(\uparrow)}} = \frac{q_\sigma^+}{p^+} \qquad (6.7)$$

The functions $\Theta_{\sigma(\downarrow)}$ and $\Theta_{\sigma(\uparrow)}$ are functions of the variable n. In the following we shall be interested in the important case $n = n^*$. Then, by virtue of (6.5), we have

$$\Theta_{\sigma(\downarrow)} = Q_{n+1}^{(1)}(-1)/Q_{n+1} = Q_{n^*+1}^{(1)}(-1)/Q_{n^*+1} = P^{(1)}(-1), \qquad (6.8)$$

$$\Theta_{\sigma(\uparrow)} = Q_n^{(1)}(1)/Q_n = Q_{n^*}^{(1)}(1)/Q_{n^*} = P^{(1)}(1). \qquad (6.9)$$

In other words, with the understanding that n is set equal to its most probable value n^*, $\Theta_{\sigma(\downarrow)}$ and $\Theta_{\sigma(\uparrow)}$ in Table 1 are respectively identified with the probabilities $P^{(1)}(-1)$ and $P^{(1)}(1)$ introduced earlier. Thus it follows from (3.32), (6.1) and (6.7) that

---

[*] See also Appendix B.

[**] The superscript $+$ on C will appear on other symbols in the following, and is to be understood to mean a change such that the spin system loses one ↑-spin and gains one ↓-spin instead, namely, the change in the spin distribuion, $(n, N-n) \to (n+1, N-n-1)$.

[***] For example, the function p^+ is "the factor of multiplication of the partition function ΩC caused by the change represented by the superscript $+$."

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = \frac{P^{(1)}(-1)}{P^{(1)}(1)} = \frac{\Theta_{\sigma(\downarrow)}}{\Theta_{\sigma(\uparrow)}} = \frac{q_\sigma^+}{p^+} , \qquad (6.10)$$

$$W = -kT \ln q_\sigma^+ + kT \ln p^+ . \qquad (6.11)$$

As we shall see in Section 7 and Part II, a relation which is essentially the same as (6.7) or (6.10) is used as an important basic relation in HORIUTI's statistical-mechanical calculations. Since the functions q_σ^+ and p^+ are defined as partition function ratios, both $-kT \ln q_\sigma^+$ and $-kT \ln p^+$ may be interpreted as free energy increment or reversible work (*cf.* Section 4 and Appendix B). Remembering the relation (5.4) which is expressed as

$$p^+ = 1 , \qquad \text{when} \quad n = n^* , \qquad (6.12)$$

we find however that $-kT \ln p^+$ vanishes when $n = n^*$. Thus (6.11) implies that $-kT \ln q_\sigma^+$ equals the reversible work W required to convert, on site σ, a $\uparrow$-spin into a $\downarrow$-spin.

TABLE 1.

"New"	Sections 4-5
ΩC	Q_n
ΩC^+	Q_{n+1}
$p^+ = \Omega C^+ / \Omega C$	$1/\lambda(n) = Q_{n+1}/Q_n$
$\Omega C_{\sigma(\downarrow)}$	$Q_n^{(1)}(-1)$
$\Omega C_{\sigma(\uparrow)}$	$Q_n^{(1)}(1)$
$\Omega C_{\sigma(\downarrow)}^+$	$Q_{n+1}^{(1)}(-1)$
$q_\sigma^+ = \Omega C_{\sigma(\downarrow)}^+ / \Omega C_{\sigma(\uparrow)}$	$Q_{n+1}^{(1)}(-1)/Q_n^{(1)}(1)$
$\Theta_{\sigma(\downarrow)} = \Omega C_{\sigma(\downarrow)}^+ / \Omega C^+$	$Q_{n+1}^{(1)}(-1)/Q_{n+1}$
$\Theta_{\sigma(\uparrow)} = \Omega C_{\sigma(\uparrow)} / \Omega C$	$Q_n^{(1)}(1)/Q_n$

One may easily verify that the following relations hold in the limit $J \to 0$ (that is, the absence of the interactions):

$$\Omega C = Q_n = \frac{N!}{n!(N-n)!} (e^{mH/kT})^N (e^{-\Delta\epsilon/kT})^n , \qquad (6.13)$$

$$\Omega C^+ = Q_{n+1} = \frac{N!}{(n+1)!(N-n-1)!} (e^{mH/kT})^N (e^{-\Delta\epsilon/kT})^{n+1} , \qquad (6.14)$$

$$p^+ = \frac{\Omega C^+}{\Omega C} = \frac{1}{\lambda(n)} = \frac{N-n}{n+1} e^{-\Delta\epsilon/kT} , \qquad (6.15)$$

$$\Omega C_{\sigma(\downarrow)} = Q_n^{(1)}(-1) = \frac{(N-1)!}{(n-1)!(N-n)!} (e^{mH/kT})^N (e^{-\Delta\epsilon/kT})^n , \qquad (6.16)$$

Takashi NAKAMURA

$$\mathfrak{Q}C_{\sigma(\uparrow)} = Q_n^{(1)}(1) = \frac{(N-1)!}{n!(N-n-1)!}(e^{mH/kT})^N(e^{-\Delta\epsilon/kT})^n, \qquad (6.17)$$

$$\mathfrak{Q}C_{\sigma(\downarrow)}^+ = Q_{n+1}^{(1)}(-1) = \frac{(N-1)!}{n!(N-n-1)!}(e^{mH/kT})^N(e^{-\Delta\epsilon/kT})^{n+1}, \qquad (6.18)$$

$$q_\sigma^+ = \frac{\mathfrak{Q}C_{\sigma(\downarrow)}^+}{\mathfrak{Q}C_{\sigma(\uparrow)}} = \frac{Q_{n+1}^{(1)}(-1)}{Q_n^{(1)}(1)} = e^{-\Delta\epsilon/kT}, \qquad (6.19)$$

$$\Theta_{\sigma(\downarrow)} = \frac{\mathfrak{Q}C_{\sigma(\downarrow)}^+}{\mathfrak{Q}C^+} = \frac{n+1}{N}, \qquad (6.20)$$

$$\Theta_{\sigma(\uparrow)} = \frac{\mathfrak{Q}C_{\sigma(\uparrow)}}{\mathfrak{Q}C} = \frac{N-n}{N}, \qquad (6.21)$$

where $\Delta\epsilon = \epsilon_\downarrow - \epsilon_\uparrow = 2mH$ (Fig. 1).   Combining (6.15) with (5.4) or (6.12) we find[*]

$$e^{-\Delta\epsilon/kT} = n^*/(N-n^*), \qquad (6.22)$$

that is,

$$n^* = N\frac{e^{-\Delta\epsilon/kT}}{1+e^{-\Delta\epsilon/kT}}. \qquad (6.23)$$

Also it follows from (6.10)–(6.12) and (6.19) that

$$\frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = q_\sigma^+ = e^{-\Delta\epsilon/kT}$$

and

$$W = \Delta\epsilon,$$

which are in agreement with (3.33) and (6.4).

§ 7. Adsorption Equilibrium

In Section 4 we have seen that the probability of n $\downarrow$-spins being found in the spin system is expressed, in terms of the partition functions, as

$$P_n = Q_n/Q, \qquad (7.1)$$

where Q_n is the partition function of the spin system with fixed "composition" (cf. p. 142) and is related to Q by

$$Q = \sum_{n=0}^{N} Q_n. \qquad (7.2)$$

---

[*] Remember that unity is completely negligible as compared with n^*.

It is well-known that the statistical-mechanical theory of the spin system described in the preceding sections parallels very closely that of localized adsorptions (= sitewise or immobile adsorption). Therefore many of the statistical-mechanical expressions for the spin system obtained so far are readily transcribed into those for the adsorption problem.

Suppose that we place a solid adsorbent and a one-component gas consisting of N molecules in a container having a fixed volume V and immersed in a heat bath at temperature T (Fig. 3), and that a portion of the gas is adsorbed on the adsorbent surface. In the following we shall be concerned with this system consisting of the gas phase, adsorbed phase and adsorbent, and shall refer to it as the system AG.
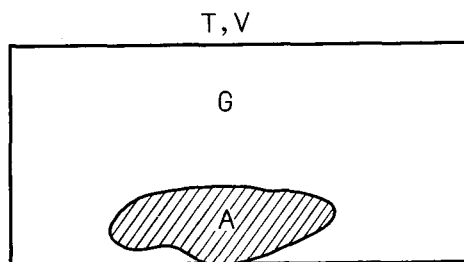

Fig. 3. System AG

Let $Q(n, m)$ be the partition function of the system AG in the situation where n molecules are adsorbed on the adsorbent and m molecules remain in the gas phase. Although the total number of the molecules $N (= n+m)$ in AG is constant, the number n and therefore the number $m (= N-n)$ actually fluctuate, just as the number of $\downarrow$-spins n does in the above spin system. Hence the partition function of AG is written as

$$Q = \sum_{n=0}^{M} Q(n, N-n), \tag{7.3}$$

where M is the largest possible number of adsorbed molecules. In other words, we assume that there are M adsorption sites on the adsorbent surface and each site is capable of adsorbing one molecule at a time. The probability of the number of adsorbed molecules being n is given by

$$P_n = Q(n, N-n)/Q. \tag{7.4}$$

The above equations (7.3) and (7.4) are much the same as (7.2) and (7.1) of the spin problem. From (7.3) and (7.4) we can calculate the mean value $\langle n \rangle$ of the number of adsorbed molecules:

Takashi NAKAMURA

$$\langle n \rangle = \sum_{n=0}^{M} n P_n = \sum_{n=0}^{M} n Q(n, N-n)/Q . \qquad (7.5)$$

However, as far as the system AG is macroscopic (hence N and M are very large numbers), the fluctuation in n eventually turns out to be extremely small. Thus we find the important relation,

the equilibrium value of $n = n^* = \langle n \rangle , \qquad (7.6)$

which is just the kind of thing we have already seen in Section 5. See also MAYER-MAYER,[10] Section 3e or HILL,[4] Chapter 2. The surface coverage (fraction of sites occupied) θ in the equilibrium state is thus given by

$$\theta = n^*/M = \langle n \rangle /M . \qquad (7.7)$$

In analogy with (5.1) or (5.4), the most probable value n^* is determined from the condition,

$$\left(\frac{\partial}{\partial n} \ln P_n \right)_{n=n^*} = 0 , \quad \text{that is,} \quad \left[\frac{\partial}{\partial n} \ln Q(n, N-n) \right]_{n=n^*} = 0 , \quad (7.8)$$

or

$$\lambda(n^*) = 1 , \qquad (7.9)$$

where $\lambda(n)$ is defined by

$$\lambda(n) = Q(n, N-n)/Q(n+1, N-n-1) .$$

In the following the conditions (7.8) and (7.9) will be rewritten in a more familiar form.

The derivative on the left hand side of (7.8) is brought into the form,

$$\frac{\partial}{\partial n} \ln Q(n, N-n) = \frac{\partial}{\partial n} \ln Q(n, m) + \frac{\partial m}{\partial n} \frac{\partial}{\partial m} \ln Q(n, m)$$

$$= \frac{\partial}{\partial n} \ln Q(n, m) - \frac{\partial}{\partial m} \ln Q(n, m) ,$$

with the understanding that m is set equal to $N-n$ after differentiation. In analogy with (5.2), we can write

$$\frac{\partial}{\partial n} \ln Q(n, m) = -\ln \lambda_A(n, m) , \quad \frac{\partial}{\partial m} \ln Q(n, m) = -\ln \lambda_G(n, m) ,$$

where $\lambda_A(n, m)$ and $\lambda_G(n, m)$ are defined by

$$\lambda_A(n, m) = \frac{Q(n, m)}{Q(n+1, m)} , \quad \lambda_G(n, m) = \frac{Q(n, m)}{Q(n, m+1)} . \qquad (7.10)$$

Therefore (7.8) becomes

$$\left[\frac{\partial}{\partial n}\ln Q(n, m)\right]_{m=N-n^*}^{n=n^*} = \left[\frac{\partial}{\partial m}\ln Q(n, m)\right]_{m=N-n^*}^{n=n^*}, \qquad (7.11)$$

or

$$-\ln \lambda_A(n^*, N-n^*) = -\ln \lambda_G(n^*, N-n^*). \qquad (7.12)$$

Let us remember the relation between partition function and HELMHOLTZ free energy (Section 4). We immediately find that $F(n, m)$ defined by

$$F(n, m) = -kT\ln Q(n, m) \qquad (7.13)$$

is the HELMHOLTZ free energy of the system AG under the condition that there are n molecules in the adsorbed phase and m molecules in the gas phase. Therefore $\mu_A(n, m)$ and $\mu_G(n, m)$ defined by the following equations are the chemical potentials of the adsorbed phase and that of the gas phase, respectively:

$$\mu_A(n, m) = N_0 \frac{\partial}{\partial n} F(n, m) = -RT\frac{\partial}{\partial n}\ln Q(n, m) = RT\ln \lambda_A(n, m), \quad (7.14)$$

$$\mu_G(n, m) = N_0 \frac{\partial}{\partial m} F(n, m) = -RT\frac{\partial}{\partial m}\ln Q(n, m) = RT\ln \lambda_G(n, m), \quad (7.15)$$

where N_0 is the AVOGADRO number. It is to be understood that in (7.14) we differentiate with respect to the number of adsorbed molecules n holding m, T and V fixed. Much the same applies to the partial differentiation with respect to the number of gaseous molecules m in (7.15). In books or papers on statistical mechanics another definition of chemical potential, which differs from that in (7.14) or (7.15) by a factor of N_0, is very often used (for example, HILL,[4] Eq. 1.36 and p. 26); in that case (7.14) and (7.15) should read

$$\mu_A(n, m) = \frac{\partial}{\partial n} F(n, m) = kT\ln \lambda_A(n, m),$$

$$\mu_G(n, m) = \frac{\partial}{\partial m} F(n, m) = kT\ln \lambda_G(n, m).$$

However the definition employed in (7.14) or (7.15) agrees with common thermodynamic practice and also with that used in Section 2. It turns out from (7.14) and (7.15) that $\lambda_A(n, m)$ and $\lambda_G(n, m)$ defined by (7.10) are the *absolute activity* of the adsorbed phase and that of the gas phase, respectively. Thus our conclusion is: The condition (7.11) or (7.12) is equivalent to saying that the chemical potential (or absolute activity) of the adsorbed phase is equal to that of the gas phase, that is,

$$\mu_A(n^*, N-n^*) = \mu_G(n^*, N-n^*), \qquad (7.16)$$

Takashi NAKAMURA

$$\lambda_A(n^*, N-n^*) = \lambda_G(n^*, N-n^*) . \tag{7.17}$$

To shorten the notation the values of the variables, n^* and $N-n^*$, attached to μ or λ will often be suppressed in the following, then (7.16) and (7.17) read

$$\mu_A = \mu_G , \tag{7.18}$$

$$\lambda_A = \lambda_G . \tag{7.19}$$

Now we are ready to see how HORIUTI formulates his statistical-mechanical theory of localized adsorption. He starts with a set of statistical-mechanical functions which are very similar to those we have encountered in Table 1. The partition functions $Q(n, m)$, $Q(n+1, m)$ and $Q(n, m+1)$ appearing in (7.10) are now denoted by ΩC, ΩC^δ and $\Omega C^{\delta'}$, respectively, where the superscript δ represents the addition of one adsorbed molecule δ to the system (that is, to increase the number of adsorbed molecules from n to $n+1$) and the superscript δ' indicates the addition of one gas molecule δ' (that is, to increase m by one). HORIUTI's p-functions are defined as shown in Table 2, from which we at once find that the functions p^δ and $p^{\delta'}$ are just the reciprocals of the absolute activities λ_A and λ_G, and the condition for the adsorption equilibrium (7.17) or (7.19) is equivalent to the equation,

$$p^\delta = p^{\delta'} . \tag{7.20}$$

(*Cf.* HORIUTI,[7] Eq. 6.1 and p. 36; HORIUTI-NAKAMURA,[8] Eq. II.11).

TABLE 2.

Horiuti	Eq. (7.10)
ΩC	$Q(n, m)$
ΩC^δ	$Q(n+1, m)$
$\Omega C^{\delta'}$	$Q(n, m+1)$
$p^\delta = \dfrac{\Omega C^\delta}{\Omega C}$	$[\lambda_A(n, m)]^{-1} = \dfrac{Q(n+1, m)}{Q(n, m)}$
$p^{\delta'} = \dfrac{\Omega C^{\delta'}}{\Omega C}$	$[\lambda_G(n, m)]^{-1} = \dfrac{Q(n, m+1)}{Q(n, m)}$

It remains to introduce a few more functions, namely,

$$\Omega C_{\sigma(0)}, \ \Omega C_{\sigma(\delta)}, \ \Omega C^\delta_{\sigma(0)}, \ \Omega C'_{\sigma(\delta)}, \ q^\delta_\sigma, \ \Theta_{\sigma(0)}, \ \Theta_{\sigma(\delta)} , \tag{7.21}$$

and also the following interrelations among them:

$$q^\delta_\sigma = \Omega C^\delta_{\sigma(\delta)}/\Omega C_{\sigma(0)} , \tag{7.22}$$

---

*) Phrased in HORIUTI's way (*cf.* p. 146), the superscript δ or δ' represents "to increase a certain constituent of the assembly (= system)."

Method of Statistical-Mechanical Calculations

$$\Theta_{\sigma(\delta)} = \mathfrak{Q}C_{\sigma(\delta)}^{\delta}/\mathfrak{Q}C^{\delta}, \qquad \Theta_{\sigma(0)} = \mathfrak{Q}C_{\sigma(0)}/\mathfrak{Q}C, \qquad (7.23)$$

$$\Theta_{\sigma(\delta)}/\Theta_{\sigma(0)} = q_{\sigma}^{\lambda}/p^{\delta}. \qquad (7.24)$$

The analogs of the functions (7.21) and the relations (7.22)–(7.24) have already appeared in Section 6. First we are going to define the first four functions in (7.21), in terms of which the remaining three functions in (7.21) are defined by (7.22) and (7.23); the relation (7.24) immediately follows from the definitions (7.22) and (7.23). In Section 6 we have been concerned with a particular site, called σ, of the lattice of spins, and have calculated the probability of the spin on σ being ↑ or ↓. Here we proceed in a similar way to calculate the probability that a particular site, also called σ, on the adsorbent surface is occupied by an adsorbed molecule.

We start with the partition function of the system AG,

$$\mathfrak{Q}C = Q(n, m) = \sum_{J} \exp\left[-E(n, m; J)/kT\right], \qquad (7.25)$$

where $E(n, m; J)$ is the energy of the J-th quantum state of AG, the symbols n and m in the parentheses specifying that n molecules are adsorbed and m molecules are in the gas phase. In defining the partition function $\mathfrak{Q}C_{\sigma(0)}$ we come back to the concept of constraints we have introduced in Section 4. (See also HORIUTI,[7] Sections 2 and 3.) Suppose the system AG is subjected to a constraint such that the site σ is kept vacant; the partition function of AG in this particular situation is denoted by $\mathfrak{Q}C_{\sigma(0)}$. In short $\mathfrak{Q}C_{\sigma(0)}$ is the partition function of AG in the situation in which the site σ is vacant. Similarly $\mathfrak{Q}C_{\sigma(\delta)}$ is that in the situation in which the site σ is occupied by an adsorbed molecule, called δ. Referring back to the expression (7.25) we may express the foregoing somewhat differently. The partition functions $\mathfrak{Q}C_{\sigma(0)}$ and $\mathfrak{Q}C_{\sigma(\delta)}$ are defined as "partial" sum-over-states (see Section 4), which are related to the sum-over-states $\mathfrak{Q}C$ by

$$\mathfrak{Q}C_{\sigma(0)} + \mathfrak{Q}C_{\sigma(\delta)} = \mathfrak{Q}C. \qquad (7.26)$$

The sum in (7.25) is supposed to run over all the quantum states of AG. However, when this sum is taken over only those states in which the site σ is vacant, $\mathfrak{Q}C_{\sigma(0)}$ is obtained; on the other hand, when the sum is over those states in which σ is occupied by an adsorbed molecule, $\mathfrak{Q}C_{\sigma(\delta)}$ results.[*] Consequently the relation (7.26) holds. In analogy with (7.25) we can write

$$\mathfrak{Q}C^{\delta} = Q(n+1, m) = \sum_{J} \exp\left[-E(n+1, m; J)/kT\right]. \qquad (7.27)$$

---

[*] The "partial" summation to be carried out here is illustrated by a few examples given in Appendix E, where more explicit mathematical expressions for the functions in (7.21) are given.

Takashi NAKAMURA

The sum in (7.27) is divided up into two partial sums in much the same way as above, and we obtain the partition functions $\Omega C_{\sigma(0)}^{\delta}$ and $\Omega C_{\sigma(\delta)}^{\delta}$, which of course satisfy the relation,

$$\Omega C_{\sigma(0)}^{\delta} + \Omega C_{\sigma(\delta)}^{\delta} = \Omega C^{\delta} \,. \tag{7.28}$$

Since, in practice, the number of adsorbed molecules n is very large, we have

$$\frac{\Omega C_{\sigma(\delta)}}{\Omega C} = \frac{\Omega C_{\sigma(\delta)}^{\delta}}{\Omega C^{\delta}} = \Theta_{\sigma(\delta)} \,, \tag{7.29}$$

in analogy with (6.5) (cf. HORIUTI,[7] Eq. 4.2). In Section 4 we have seen that a statistical-mechanical probability is expressed*) as the ratio of a partial sum-over-states to a sum-over-states. In the present case, the partition function ratios $\Omega C_{\sigma(0)}/\Omega C$ ($= \Theta_{\sigma(0)}$) and $\Omega C_{\sigma(\delta)}/\Omega C$ ($= \Theta_{\sigma(\delta)}$) in (7.29) are found to be the probability of the site σ being vacant and the probability of σ being occupied by an absorbed molecule, respectively, in the situation where there are n absorbed molecules on the adsorbent. In the following we shall be concerned with the case where n equals its most probable value n^*, that is, the case where the adsorption equilibrium has been attained between the adsorbed phase and the gas phase. If all the M sites are equivalent (that is, M sites are of the same kind), the probability, $\Theta_{\sigma(\delta)}$, of the site σ being occupied is related to $\langle n \rangle$ by**)

$$M\Theta_{\sigma(\delta)} = \langle n \rangle \,.$$

Hence using (7.7) we have

$$\Theta_{\sigma(\delta)} = \theta \,, \qquad \Theta_{\sigma(0)} = 1 - \theta \,. \tag{7.30}$$

Since the relation (7.20) holds in the state of adsorption equilibrium, the relation (7.24) becomes

$$\frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(0)}} = \frac{q_{\sigma}^{\delta}}{p^{\delta'}} = q_{\sigma}^{\delta}\lambda_{G} = q_{\sigma}^{\delta} \exp\left(\mu_{G}/RT\right) \,. \tag{7.31}$$

In the special case where (7.30) holds, the above relation reads

$$\frac{\theta}{1 - \theta} = q_{\sigma}^{\delta}\lambda_{G} = q_{\sigma}^{\delta}\frac{m}{r} \,, \tag{7.32}$$

where Eq. (C.5) of Appendix C has been used. This equation (7.32) is essentially identical with HORIUTI,[7] Eq. 17.3.

Let Λ represent any of p^{δ}, q_{σ}^{δ}, $\Theta_{\sigma(0)}$ and $\Theta_{\sigma(\delta)}$. Then Λ is the ratio of a partition function to another partition function. For the reason we have already

---

*) Cf. Eqs. (4.3), (4.5), (4.9) and (5.8).

**) The proof is easy. Cf. the relation (7.47) below, which is proved in Appendix A.

considered in Section 4, the quantity $-kT \ln \varLambda$ is the free energy increase relevant to or the reversible work required for a certain process. (*Cf.* also HORIUTI, Section 7.) When $\varLambda \equiv p^\delta$, for instance, $-kT \ln \varLambda$ is the free energy increase due to the addition of an adsorbed molecule to the system AG or, in other words, the chemical potential of the adsorbed phase divided by the AVOGADRO number N_0 (see above). Another example is $-kT \ln q_\sigma^\delta$, which equals

$$-kT \ln \mathfrak{Q}C_{\sigma(\delta)}^\delta - (-kT \ln \mathfrak{Q}C_{\sigma(0)}) . \tag{7.33}$$

The first or second term of (7.33) represents the free energy of the system AG in the particular situations specified by the sub- and superscipts, δ, $\sigma(\delta)$ and $\sigma(0)$, attached to $\mathfrak{Q}C$. Thus HORIUTI calls $-kT \ln q_\sigma^\delta$ or (7.33) "the reversible work required to bring up the molecule δ from its standard (=reference) state to the preliminarily evacuated site σ" (see HORIUTI,[7] Section 7).

The system AG consists of the adsorbent solid and a large number of adsorbed and gaseous molecules. Therefore such a thing as the energy level $E(n, m; J)$ of AG appearing in (7.25) necessarily has very complicated contents. In order that the above theoretical formulation of the adsorption problem is of much practical value, certain approximations or simplifying assumptions relating to $E(n, m; J)$ have to be introduced, which is done in Appendix C. In the rest of this section we are going to take a look at some of important results which follow from the simplified energy expression, Eq. (C.9) of Appendix C.

Specializing to the case where the M sites are equivalent, we find that the partition function $\mathfrak{Q}C$ is written as

$$\mathfrak{Q}C = Q(n, m) = R_m Z_0 z^n I^{(n)} , \tag{7.34}$$

where R_m, Z_0, z and $I^{(n)}$ are the partition functions for the gas phase, the adsorbent, an adsorbed molecule and the interaction energy among adsorbed molecules, respectively, their precise definitions being given in Appendixes C and E. Hence the Helmholtz free energy of AG is given by

$$F(n, m) = -kT \ln \mathfrak{Q}C = -kT \ln Q(n, m) = F_m^{(G)} + F^{(s)} + (F_n^{(a)} + F_n^{(I)}) , \tag{7.35}$$

where $F_m^{(G)}$, $F^{(s)}$, and $(F_n^{(a)} + F_n^{(I)})$ are the contributions of the gas phase, adsorbent, and adsorbed phase, respectively, to the free energy $F(n, m)$. These F's are defined by

$$F_m^{(G)} = -kT \ln R_m , \qquad F^{(s)} = -kT \ln Z_0 , \tag{7.36}$$

---

*) Accordingly he gives a particulary lengthy name to the function q_σ^δ itself: namely, "the Boltzmann factor of the reversible work required to bring up the molecule δ from its standard state to the preliminarily evacuated site σ."

Takashi NAKAMURA

$$F_n^{(a)} = -kT \ln \frac{M!}{(M-n)!\, n!} - nkT \ln z , \qquad (7.37)$$

$$F_n^{(I)} = -kT \ln \frac{(M-n)!\, n!}{M!} I^{(n)} . \qquad (7.38)$$

The $I^{(n)}$ is often called the *configurational partition function*. Notice that as shown in Appendix E, in the absence of interactions between adsorbed molecules $I^{(n)}$ equals $M!/(M-n)!n!$ and consequently $F_n^{(I)}$ vanishes. In other words, $F_n^{(a)}$ is the free energy of the adsorbed phase in the absence of the interactions.[*] Also it is shown in Appendix E that the p^δ and q_σ^δ functions are expressed as

$$p^\delta = z(I^{(n+1)}/I^{(n)}) , \qquad q_\sigma^\delta = z(I_{\sigma(\delta)}^{(n+1)}/I_{\sigma(0)}^{(n)}) , \qquad (7.39)$$

where the quotients in the parentheses are the parts of p^δ and q_σ^δ which depend on the interaction energy among adsorbed molecules. In the absence of the interactions they take on the following values:

$$I^{(n+1)}/I^{(n)} = (M-n)/(n+1) , \qquad I_{\sigma(\delta)}^{(n+1)}/I_{\sigma(0)}^{(n)} = 1 . \qquad (7.40)$$

From the second equation of (7.39) we have

$$-kT \ln q_\sigma^\delta = -kT \ln z + w_n , \qquad (7.41)$$

where

$$w_n = -kT \ln (I_{\sigma(\delta)}^{(n+1)}/I_{\sigma(0)}^{(n)}) .$$

In other words, the free energy increase (or reversible work) $-kT \ln q_\sigma^\delta$ splits into two parts, $-kT \ln z$ and w_n. According to (7.40) the second part w_n vanishes in the absence of the interactions; thus HORIUTI calls w_n the "free energy of repulsion" in some of his papers.[**]

It is also shown in Appendix E that the statistical-mechanical functions for the spin system discussed in Section 6 are expressed in much the same way as (7.34) and (7.39):

$$\Omega C = Q_n = y^N x^n I^{(n)} \qquad (7.42)$$

$$p^+ = x(I^{(n+1)}/I^{(n)}) , \qquad q_\sigma^+ = x(I_{\sigma(\downarrow)}^{(n+1)}/I_{\sigma(\uparrow)}^{(n)}) , \qquad (7.43)$$

where y and x are defined by[***]

$$y = e^{mH/kT} , \qquad (7.44)$$

---

[*] The above division of the free energy of the adsorbed phase into $F_n^{(a)}$ and $F_n^{(I)}$ is in line with FOWLER and GUGGENHEIM. See FOWLER-GUGGENHEIM,[2] pp. 429–430.

[**] In most cases he has treated adsorbed phases in which *repulsive* interactions exist between adsorbed molecules (atoms). Hence the name, free energy of *repulsion*.

[***] See Fig. 1.

$$x = y^{-2} = e^{-2mH/kT} = e^{-4\iota/kT} = \exp\left[-(\varepsilon_\downarrow - \varepsilon_\uparrow)/kT\right]. \tag{7.45}$$

The I-functions (configurational partition functions) appearing in (7.42) and (7.43) are very similar to those in (7.34) and (7.39) and depend on the spin-spin interaction energy J. Finally let us remember some of the relations we have obtained in Section 6. The relation (6.7) in the spin problem is the counterpart of (7.24) in the adsorption problem. Since the relation (6.12) holds in the equilibrium state $(n = n^*)$, the relation (6.7) reads

$$\frac{\Theta_{\sigma(\downarrow)}}{\Theta_{\sigma(\uparrow)}} = q_\sigma^+ . \tag{7.46}$$

Using (5.5), (6.8), (6.9) and the relation proved in Appendix A, we have

$$N\Theta_{\sigma(\downarrow)} = NP^{(1)}(-1) = \langle N_\downarrow \rangle = n^* , \tag{7.47}$$

$$N\Theta_{\sigma(\uparrow)} = NP^{(1)}(1) = \langle N_\uparrow \rangle = N - n^* . \tag{7.48}$$

Thus (7.46) becomes

$$\frac{n^*}{N - n^*} = \frac{\langle N_\downarrow \rangle}{\langle N_\uparrow \rangle} = q_\sigma^+ , \tag{7.49}$$

which is to be compared with (7.32).

The calculation of equilibrium amount of adsorption θ or the equilibrium number of $\downarrow$-spins n^* requires the evaluation of the function q_σ^λ in (7.32) or q_σ^+ in (7.49). In the absence of the interactions between adsorbed molecules or between spins,

$$q_\sigma^\lambda = z , \qquad q_\sigma^+ = x = \exp\left[-(\varepsilon_\downarrow - \varepsilon_\uparrow)/kT\right] ;$$

hence we have

$$\frac{\theta}{1 - \theta} = \frac{m}{V_G} \frac{z}{r^0} , \tag{7.50}$$

$$\frac{n^*}{N - n^*} = \exp\left[-(\varepsilon_\downarrow - \varepsilon_\uparrow)/kT\right] , \tag{7.51}$$

where $r^0 = r/V_G$ and V_G is the volume of the gas phase (in other words, r^0 is the partition function of the gas molecule per unit volume). Since the ratio z/r^0 is independnt of the amount of adsorption θ and the density of the gas m/V_G (see Appendix C for the definitions of z and r), the right hand side of (7.50) is proportional to the gas density m/V_G; that is, (7.50) is essentially the LANGMUIR *adsorption isotherm*. As we have seen in Section 3, (7.51) is nothing but the BOLTZMANN distribution law; that is, (7.51) gives the field and

Takashi NAKAMURA

temperature dependence of *paramagnetism* expressed by (3.6). In the presence of the interactions we are confronted with a big difficulty, which is related to the treatment of the I-functions in (7.34), (7.39), (7.42) and (7.43). This is the problem of n interacting molecules or spins on lattice sites, and n is a very large number—10^{15} or more. This kind of "n-body problem" is known as the problem of *lattice statistics*, which is very important in connection with the theories of ferromagnetism (antiferromagnetism), phase transition, etc. In 1940's and 1950's a great deal of important work was done in the area of lattice statistics by theoretical physicists (KRAMERS, WANNIER and ONSAGER—to name just a few), but the discussion of these sophisticated theories (WANNIER,[11] Chapter 16; HILL A,[5] Chapter 7) is beyond the scope of the present notes. Two approximate methods, the BRAGG-WILLIAMS approximation and the BETHE-PEIERLS approximation, can be applied to the treatment of the above I-functions. They are rather rough approximations, in which the above n-body problem is reduced essentially to one-body calculation (the BRAGG-WILLIAMS approximation) or to several-body calculation (the BETHE-PEIERLS approximation); however they are found very useful in many important cases. This matter will be discussed in full in Part II.

Acknowledgement

Note added in proof.

(1) S. G. BRUSH has recently published a very interesting and informative article, in which he describes the history, current status and significance of the theories of lattice statistics. [S. G. BRUSH, "History of the LENZ-ISING model," Rev. Mod. Phys., **39**, 883 (1967).]

(2) I thank Mr. Chao-Feang LIN for a few useful comments on the manuscript.

Appendix A

Here the proof of the relation (3.32) is given. Let us start with the relation (3.23) and notice that the number of ↑-spins $N_\uparrow(s_1 s_2 \cdots s_N)$ is expressed as

$$N_\uparrow(s_1 s_2 \cdots s_N) = \sum_{j=1}^{N} f_\uparrow(s_j), \qquad (A.1)$$

where $f_\uparrow(s_j)$ is a function of s_j such that

$$f_\uparrow (s_j) = \begin{cases} 1 & \text{when} \quad s_j = 1 \\ 0 & \text{when} \quad s_j = -1 \,. \end{cases} \tag{A.2}$$

Substitution of (A.1) into (3.23) yields

$$\langle N_\uparrow \rangle = \sum_{j=1}^{N} \Big[\sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} f_\uparrow (s_j) P(s_1 s_2 \cdots s_N) \Big] \,. \tag{A.3}$$

So far as the N spins are equivalent (see p. 138), the quantity in the brackets on the right hand side of (A.3) actually does not depend on j, and therefore (A.3) is rewritten as

$$\langle N_\uparrow \rangle = N \Big[\sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} f_\uparrow (s_1) P(s_1 s_2 \cdots s_N) \Big] \,. \tag{A.4}$$

It follows from the definitions (3.26) and (A.2) that the right hand side of (A.4) is nothing but $NP^{(1)}(1)$. We can show in a similar way that $\langle N_\downarrow \rangle = NP^{(1)}(-1)$. Thus (3.32) is proved.

Appendix B

The construction of the partition functions appearing in Sections 4 and 6 are illustrated by considering the trivial case $N=3$ (3-spin system). We suppose that the three spins are arranged on equilateral-triangular lattice sites as shown in Fig. B1. There are 2^3 quantum states of this spin system, which are labeled with $I=1,2,\cdots,8$ and listed in Table B1. It follows at once that

$$Q^{(1)}(-1) = \sum_{I=1}^{4} e^{-E(I)/kT} \,, \qquad Q^{(1)}(1) = \sum_{I=5}^{8} e^{-E(I)/kT} \,,$$

$$Q = Q^{(1)}(-1) + Q^{(1)}(1) \,.$$

Next we consider the partition function $Q_n(\equiv \mathfrak{Q}C)$ and a few related functions introduced in Sections 4 and 6. Let $n=2$, for instance; then

$$\mathfrak{Q}C = Q_2 = e^{-E(2)/kT} + e^{-E(3)/kT} + e^{-E(5)/kT} = 3e^{-mH/kT}e^{-J/kT} \,,$$

$$\mathfrak{Q}C^+ = Q_3 = e^{-E(1)/kT} = e^{-3mH/kT}e^{3J/kT} \,,$$

$$\mathfrak{Q}C_{\sigma(\downarrow)} = Q_2^{(1)}(-1) = e^{-E(2)/kT} + e^{-E(3)/kT} = 2e^{-mH/kT}e^{-J/kT} \,,$$

$$\mathfrak{Q}C_{\sigma(\uparrow)} = Q_2^{(1)}(1) = e^{-E(5)/kT} = e^{-mH/kT}e^{-J/kT} \,,$$

$$\mathfrak{Q}C_{\sigma(\downarrow)}^+ = Q_3^{(1)}(-1) = e^{-E(1)/kT} = e^{-3mH/kT}e^{3J/kT} \,,$$

$$p^+ = Q_3/Q_2 = \frac{1}{3} e^{-2mH/kT}e^{4J/kT} \,,$$

$$q_\sigma^+ = Q_3^{(1)}(-1)/Q_2^{(1)}(1) = e^{-2mH/kT}e^{4J/kT} \,.$$

When $J=0$, these results are in agreement with (6.13)–(6.19). As stated in

Takashi NAKAMURA

the text, both

$$-kT \ln p^+ = 2mH - 4J + kT \ln 3 \tag{B.1}$$

and

$$-kT \ln q_\sigma^+ = 2mH - 4J \tag{B.2}$$

may be called a reversible work required to cause the change + (see the footnote on p. 146). It is left to the students to explain the difference kT $\ln 3$ between (B.2) and (B.1). Finally one word of caution is necessary: Some of the relations derived in Sections 5 and 6 rely on the supposition that N is a very large number, and therefore they do not apply to the present case, $N=3$. For small N the fluctuation is very large.
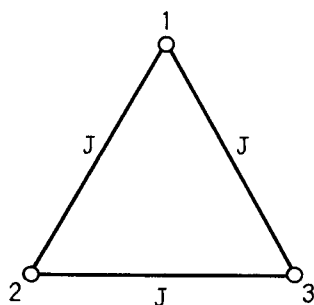
TABLE B 1.

Fig. B 1.

I	spin state			n	s_1	$E(I)$
	1	2	3			
1	↓	↓	↓	3	−1	$3mH-3J$
2	↓	↓	↑	2	−1	$mH+J$
3	↓	↑	↓	2	−1	$mH+J$
4	↓	↑	↑	1	−1	$-mH+J$
5	↑	↓	↓	2	1	$mH+J$
6	↑	↓	↑	1	1	$-mH+J$
7	↑	↑	↓	1	1	$-mH+J$
8	↑	↑	↑	0	1	$-3mH-3J$

Appendix C

In this Appendix we shall go further with the calculation of the partition function $Q(n, m)$, which plays a pivotal role in the statistical-mechanical theory of the adsorbed phase developed in Section 7. Suppose that the system AG is divided into two *subsystems*, namely the gas phase part G and the part A consisting of the adsorbent and adsorbed phase. In the statistical-mechanical calculation the mechanical coupling between the subsystems A and G may be regarded as very weak, which fact has the following consequence. The energy $E(n, m; J)$ of the system AG (*cf.* Fig. 3) splits into two parts:

$$E(n, m; J) = E_A(n: J') + E_G(m; J''),$$

where the first and second terms on the right hand side are the energy of A and that of G. Thus the partition function $Q(n, m)$ is written as the product of the two partition functions, Z_n for the subsystem A and R_m for the sub-

system G (HILL,[4] p. 61); that is,

$$
\begin{aligned}
Q(n, m) &= \sum_J \exp\left[-E(n, m; J)/kT\right] \\
&= \sum_{J'} \sum_{J''} \exp\left[-E_A(n; J')/kT\right] \exp\left[-E_G(m; J'')/kT\right] \\
&= Z_n R_m,
\end{aligned} \tag{C.1}
$$

where

$$
Z_n = \sum_{J'} \exp\left[-E_A(n; J')/kT\right],
$$

$$
R_m = \sum_{J''} \exp\left[-E_G(m; J'')/kT\right].
$$

Now the expression (7.10) for the absolute activity of G becomes

$$
\lambda_G(n, m) = \frac{Z_n R_m}{Z_n R_{m+1}} = \frac{R_m}{R_{m+1}}, \tag{C.2}
$$

which indicates that λ_G and therefore μ_G actually do not depend on n. Therefore we shall write $\lambda_G(m)$ for $\lambda_G(n, m)$. Much the same applies to λ_A:

$$
\lambda_A(n, m) = \frac{Z_n R_m}{Z_{n+1} R_m} = \frac{Z_n}{Z_{n+1}}. \tag{C.3}
$$

When the gas phase G can be regarded as a perfect gas, the partition function R_m can be expressed as

$$
R_m = r^m / m! \tag{C.4}
$$

(*cf.* HILL,[4] Eq. 8.3). In (C.4), r is the partition function for a single gas molecule and is written as

$$
r = r_{int} V_G (2\pi M k T)^{\frac{3}{2}} / h^3,
$$

where V_G is the volume of the gas phase, and M and r_{int} are the mass and partition function for the internal degrees of freedom, respectively, of the molecule. It follows from (C.2) and (C.4) that

$$
\lambda_G(m) = (m+1)/r.
$$

In practice the number of molecules m is very large compared with unity; therefore the right hand side of the above equation can be replaced by m/r. With this understanding we have

$$
\lambda_G(m) = m/r, \qquad \mu_G(m) = RT \ln(m/r). \tag{C.5}
$$

These relations for the absolute activity and chemical potential of a perfect gas are well-known (*cf.* HILL,[4] Eq. 4.22, etc.).

We find from (C.2) that

$$R_m = \lambda_G(m) R_{m+1},$$

and therefore

$$R_{N-n} = \left[\prod_{j=1}^{n} \lambda_G(N-j) \right] R_N.$$

In this connection, it is interesting to consider a special situation where the total number of molecules N is extremely large as compared with the largest possible number, M, of adsorbed molecules. Provided that the number j does not exceed M, $N-j$ can be regarded as very close to N and we can to a good approximation write

$$\lambda_G(N) = \lambda_G(N-1) = \lambda_G(N-2) = \cdots = \lambda_G(N-j).$$

Thus in the limit of very large N,

$$R_{N-n} = \left[\lambda_G(N) \right]^n R_N = \lambda^n R_N,$$

where we have written λ for $\lambda_G(N)$. Thus it follows from (7.4), (7.3) and (C.1) that

$$P_n = R_{N-n} Z_n \Big/ \sum_{j=0}^{M} R_{N-j} Z_j = \lambda^n Z_n \Big/ \sum_{j=0}^{M} \lambda^j Z_j \qquad (n \leq M).$$

That is,

$$P_n = \lambda^n Z_n / \Xi, \tag{C.6}$$

where Ξ is the *grand partition function* of the subsystem A, defined by

$$\Xi = \sum_{j=0}^{M} \lambda^j Z_j. \tag{C.7}$$

The distribution of n of the form (C.6) is known as the *grand canonical distribution* (*cf.* HILL,[4] 1.62). In the above case the number of gas molecules $N-n$ is so large that the absolute activity of the gas phase G or, what amounts to the same thing, the chemical potential of G is practically held fixed irrespective of the number of adsorbed molecules or, in other words, regardless of how many molecules go into the adsorbed state. Thus the gas phase G acts as a *reservoir* of molecules and the grand canonical distribution is established (HILL,[4] p. 132). There exist a well-known relation between the mean value of n given by (7.5) and the grand partition function Ξ; namely,

$$\lambda \frac{\partial}{\partial \lambda} \ln \Xi = \sum_{j=1}^{M} j \lambda^j Z_j \Big/ \Xi = \sum_{n=0}^{M} n P_n = \langle n \rangle, \tag{C.8}$$

which is often used to calculate the surface coverage θ defined by (7.7) (*cf.* HILL,[4] Eq. 7.16).

Now let us turn to Z_n, the partition function of the subsystem A (= the adsorbent plus n adsorbed molecules). In (C.1), $E_A(n; J')$ is the energy of the J'-th quantum state of A, the number n in the parentheses indicating that the subsystem A involves n adsorbed molecules. In current statistical-mechanical calculations of localized adsorptions (including those by HORIUTI), it is customary to rely on the following simpifying assumption regarding the energy $E_A(n; J')$: We write

$$E_A(n; J') = E_j + \sum_{s}^{occ} \varepsilon^{(s)}(k_s) + \sum_{(s,t)}^{occ} \varepsilon_{st}, \qquad (C.9)$$

where E_j represents the energy of the adsorbent and the second and third terms on the right hand side represent the energy of adsorbed molecules. More precise description of these quantities is given below.

Let E_j denote the energy levels of the adsorbent solid, which are assumed to be essentially unperturbed by the presence of n adsorbed molecules.[*] Next suppose that one of the gas molecules is adsorbed on site s. The energy levels of this molecule, in the absence of the interactions between it and other adsorbed molecules, are represented by $\varepsilon^{(s)}(k_s)$, where k_s is the quantum number specifying its quantum state. The interaction energy between the molecules adsorbed an sites s and t is assumed to depend only on the distance between the centers of sites s and t, and is denoted by ε_{st}. The interaction is *repulsive* or *attractive* depending on whether ε_{st} is positive or negative. The energy expression (C.9) is obtained by adding the energies E_j, $\varepsilon^{(s)}(k_s)$ and ε_{st} together, in which case the summation $\sum_{s}^{occ}$ is taken over all occupied sites and the summation $\sum_{(s,t)}^{occ}$ over all pairs of occupied sites. Hence the second and third terms on the right hand side of (C.9) depend on the way of choosing n occupied sites out of the M sites on the adsorbent surface. Note that there are $M!/(M-n)!\, n!$ ways of doing this or, in other words, $M!/(M-n)!\, n!$ ways of distributing n identical molecules among M sites, which fact should be taken into account in constructing the partition function Z_n of the subsystem A in the following.

It would be interesting to explore how far the approximation (C.9) remains

---

[*] Thus we suppose, for example, that the lattice structure and/or lattice vibrations of the adsorbent solid are essentially unaffected by the adsorbed molecules. This assumption is closely connected with the concept of *inert adsorbent* used in the thermodynamical theories of adsorption (*cf.* HILL B,[6] pp. 245, 248 and 252).

good one or in what cases it fails, but its detailed discussion is beyond the scope of the present notes. In substituting (C.9) into (C.1) we note that the summation $\sum_{j}$ over all the quantum states of A is equivalent to taking multiple summation over quantum numbers j and k_s's and also over all the $M!/(M-n)!\,n!$ configurations of n adsorbed molecules (see above). Hence after a bit of algebra we obtain

$$Z_n = Z_0 \sum_{[n]} \left(\overset{\text{occ}}{\underset{s}{\prod}} z_s \right) \exp\left(- \overset{\text{occ}}{\underset{(s,t)}{\sum}} \varepsilon_{st}/kT \right), \tag{C.10}$$

where $\sum_{[n]}$ indicates the summation over all the possible configurations of n adsorbed molecules, the product $\overset{\text{occ}}{\underset{s}{\prod}}$ is taken over all occupied sites, and Z_0 and z_s are the partition function of the adsorbent and that of the adsorbed molecule on site s, respectively, which are defined by

$$Z_0 = \sum_{j} \exp\left(-E_j/kT\right),$$

$$z_s = \sum_{k_s} \exp\left[-\varepsilon^{(s)}(k_s)/kT \right].$$

When the M sites are equivalent (that is, the M sites are of the same kind), we have $z_1 = z_2 = \cdots = z_M$; hence omitting the subscript s appended to z we can write

$$\overset{\text{occ}}{\underset{s}{\prod}} z_s = z^n.$$

In this particular case, (C.10) reads

$$Z_n = Z_0 z_n \sum_{[n]} \exp\left(- \overset{\text{occ}}{\underset{(s,t)}{\sum}} \varepsilon_{st}/kT \right). \tag{C.11}$$

If, furthermore, the interactions between adsorbed molecules are absent, the exponential function on the right hand side of (C.11) equals unity and Z_n becomes

$$Z_n = Z_0 \frac{M!}{(M-n)!\,n!} z^n. \tag{C.12}$$

This implies that the partition function of the adsorbed phase is

$$\frac{M!}{(M-n)!\,n!} z^n,$$

which is in agreement with HILL, Eq. 7.4. From (C.12) and (C.3) the absolute activity λ_A is calculated as

$$\lambda_A = \frac{Z_n}{Z_{n+1}} = \frac{n+1}{M-n}\frac{1}{z}, \tag{C.13}$$

and the condition for adsorption equilibrium (7.17) becomes

$$\frac{n^*+1}{M-n^*}\frac{1}{z} = \lambda_G. \tag{C.14}$$

Since, in practice, n^* is a very large number as compared with unity, (C.14) leads to

$$\frac{\theta}{1-\theta} = \lambda_G z = z \exp(\mu_G/RT), \tag{C.15}$$

where (7.7) has been used. The relation (C.15) is equivalent to HILL's[4] Eq. 7.8, from which the well-known LANGMUIR *adsorption isotherm* is immediately derived. Substitution of (C.12) into (C.7) yields

$$\Xi = \sum_{n=0}^{M} \frac{M!}{(M-n)!\,n!}(\lambda z)^n Z_0 = (1+\lambda z)^M Z_0.$$

Using (7.7) and (C.8) we thus obtain

$$\theta = \frac{\langle n \rangle}{M} = \frac{1}{M}\lambda\frac{\partial}{\partial\lambda}\ln\Xi = \frac{\lambda z}{1+\lambda z},$$

that is,

$$\frac{\theta}{1-\theta} = \lambda z,$$

which is the same as (C.15) (see also HILL,[4] Eq. 7.16).

Appendix D

Let us start with the expression (C.10) of Appendix C for the partition function Z_n, which reduces to (C.11) when the M sites are identical. For some purposes it is convenient to rewrite (C.10) or (C.11) in a slightly different form. We define a function $f_n(t)$ such that

$$f_n(t) = \begin{cases} 1 & \text{when } t = n \\ 0 & \text{otherwise}, \end{cases}$$

and also variables t_p $(p=1,2,\cdots,M)$ which take on two values 1 or 0 depending on whether site p is occupied by a molecule or not. Evidently the number of adsorbed molecules equals $t_1+t_2+\cdots+t_M$, so that (C.10) becomes

$$Z_n = Z_0 \sum_{t_1}\sum_{t_2}\cdots\sum_{t_M} f_n(t_1+t_2+\cdots+t_M)\left[\prod_{p=1}^{M}(z_p)^{t_p}\right]\exp\left(-\sum_{(p,q)} t_p t_q \varepsilon_{pq}/kT\right),$$

and (C.11) becomes

$$Z_n = Z_0 \sum_{t_1} \sum_{t_2} \cdots \sum_{t_M} f_n(t_1 + t_2 + \cdots + t_M) z^{t_1 + t_2 + \cdots + t_M} \exp(- \sum_{(p,q)} t_p t_q \varepsilon_{pq}/kT) . \tag{D. 1}$$

$$\tag{D. 2}$$

On the right hand side of (D.1) or (D.2), $f_n(t_1 + t_2 + \cdots + t_M)$ has been inserted in order to pick out only those terms which fulfil the condition that $t_1 + t_2 + \cdots + t_M = n$, and the sum $\sum_{(p,q)}$ is taken over all pairs of sites. If we assume that the interactions vanish except between adsorbed molecules on a nearest-neighbor pair of sites, then (D.2) takes the form,

$$Z_n = Z_0 \sum_{t_1} \sum_{t_2} \cdots \sum_{t_M} f_n(t_1 + t_2 + \cdots + t_M) z^{t_1 + t_2 + \cdots + t_M} \exp(- \sum_{(p,q)} t_p t_q w/kT) , \tag{D. 3}$$

with the understanding that the sum $\sum_{(p,q)}$ is taken over all nearest-neighbor pairs of sites and w is the nearest-neighbor interaction energy.
Substitution of (D.3) into (C.7) yields

$$\mathcal{E} = \sum_{n=0}^{M} \lambda^n Z_n = Z_0 \sum_{t_1} \sum_{t_2} \cdots \sum_{t_M} (z\lambda)^{t_1 + t_2 + \cdots + t_M} \exp(- \sum_{(p,q)} t_p t_q w/kT) . \tag{D. 4}$$

It is interesting to compare (D.3) and (D.4) with the expressions of the partition functions for the spin system derived in Sections 3 and 4. The variable t_p in (D.1)–(D.4) is an analog of the variable s_p used in the spin problem. Setting $y = \exp(mH/kT)$ and remembering that $-\frac{1}{2} s_1 - \frac{1}{2} s_2 - \cdots - \frac{1}{2} s_N + \frac{1}{2} N$ equals the number of $\downarrow$-spins, we obtain, from (3.17), (3.22), (3.25) and (4.8),

$$Q = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} y^{s_1 + s_1 + \cdots + s_N} \exp(\sum_{(p,q)} s_p s_q J/kT) \tag{D. 5}$$

and

$$Q_n = \sum_{s_1} \sum_{s_1} \cdots \sum_{s_N} f_n \left(-\frac{1}{2} s_1 - \frac{1}{2} s_2 - \cdots - \frac{1}{2} s_N + \frac{1}{2} N \right)$$
$$\times y^{s_1 + s_2 + \cdots + s_N} \exp(\sum_{(p,q)} s_p s_q J/kT) , \tag{D. 6}$$

with

$$y = \exp(mH/kT) .$$

We immediately observe the close similarity between the grand partition function (D.4) and the partition function (D.5) and that between the partition functions (D.3) and (D.6). See also HILL,[4] Section 14.4 and HILL A,[5] Section 41.

The exponential function appearing on the right hand side of (C.11) is

the BOLTZMANN factor of the interaction energy. When only the nearest-neighbor interactions are taken into account (see above), the interaction energy is proportional to b_{11}, the number of nearest-neighbor pairs of sites both occupied; that is, it equals

$$b_{11}w = \left(n - \frac{1}{2}b_{10}\right)w, \qquad (D.7)$$

where b_{10} is the number of nearest-neighbor pairs of sites with one site vacant and one site ocuppied (HILL,[4] p. 236). Of course, the numbers b_{11} and b_{10} depend on the configuration of n adsorbed molecules. Let $g(n; b_{10})$ be the number of the configurations with the same interaction energy $(n - \frac{1}{2}b_{10})w$; then (C.11) is cast into the form,

$$\begin{aligned}
Z_n &= Z_0 z^n \sum_{[n]} \exp\left[-\left(n - \frac{1}{2}b_{10}\right)w/kT\right] \\
&= Z_0(ze^{-w/kT})^n \sum_{[n]} \exp(b_{10}w/2kT) \\
&= Z_0(ze^{-w/kT})^n \sum_{b_{10}} g(n; b_{10})(e^{w/2kT})^{b_{10}}, \qquad (D.8)
\end{aligned}$$

which is in agreement with HILL's[4] Eq. 14.3

Appendix E

Starting with the energy expression (C.9), the construction of HORIUTI's statistical mechanical functions appearing in (7.21) is illustrated here. We have seen that the partition function $\mathfrak{Q}C$ of the system AG is given by (7.25). Also we go back to (C.10) and (C.1) to find that $\mathfrak{Q}C$ is expressed as

$$\mathfrak{Q}C = Q(n, m) = R_m Z_0 \sum_{[n]} \left(\overset{occ}{\underset{s}{\amalg}} z_s\right) \exp\left(-\overset{occ}{\underset{(s,t)}{\sum}} \varepsilon_{st}/kT\right). \qquad (E.1)$$

The expression (E.1) might look quite different from the expression (7.25). However, after substituting the equations which define R_m, Z_0 and z_s (see Appendix C) into (E.1) and after a bit of rearrangement the expression (E.1) is readily cast into a form which is essentially the same as (7.25).

As we have seen in Appendix C, the summation $\sum_{[n]}$ in (E.1) takes care of the fact that there are $M!/(M-n)!\,n!$ different configurations of n adsorbed molecules. Suppose we are concerned with one of the M sites, which we call the site σ. It is vacant in $(M-1)!/(M-n-1)!\,n!$ configurations among the above $M!/(M-n)!\,n!$ configurations; it is occupied by an adsorbed molecule in the remaining $(M-1)!/(M-n)!\,(n-1)!$ configurations.[*] Thus we write

---

*) We have seen a similar thing in the problem of spin distrbution in p. 142. The simple illustrative example given in Table E.1 might be helpful.

$$\mathfrak{Q}C_{\sigma(0)} = R_m Z_0 \sum_{[n]}^{\sigma(0)} \left(\overset{\text{occ}}{\underset{s}{\coprod}} z_s \right) \exp\left(- \sum_{(s,t)}^{\text{occ}} \varepsilon_{st}/kT \right), \qquad (\text{E. 2})$$

and

$$\mathfrak{Q}C_{\sigma(\delta)} = R_m Z_0 \sum_{[n]}^{\sigma(\delta)} \left(\overset{\text{occ}}{\underset{s}{\coprod}} z_s \right) \exp\left(- \sum_{(s,t)}^{\text{occ}} \varepsilon_{st}/kT \right), \qquad (\text{E. 3})$$

where the summation $\sum_{[n]}^{\sigma(0)}$ is taken over the above $(M-1)!/(M-n-1)!\, n!$ configurations and $\sum_{[n]}^{\sigma(\delta)}$ is over the above $(M-1)!/(M-n)!\,(n-1)!$ configurations.

TABLE E. 1. The case, $M=3$ and $n=2$. In the second column, $\bigcirc$ signifies a vacant site and $\oplus$ signifies an occupied site. Note that $M!/(M-n)!\,n! = 3$, $(M-1)!/(M-n-1)!\,n! = 1$, $(M-1)!/(M-n)!\,(n-1)! = 2$.

	sites	remark
configuration 1	$\overset{1}{\bigcirc}$——$\overset{2}{\oplus}$——$\overset{3}{\oplus}$	site 1 (= site σ) is vacant
configuration 2	$\oplus$——$\oplus$——$\bigcirc$	site 1 (= site σ) is occupied
configuration 3	$\oplus$——$\bigcirc$——$\oplus$	

Thus we have the operator relation,

$$\sum_{[n]} = \sum_{[n]}^{\sigma(0)} + \sum_{[n]}^{\sigma(\delta)},$$

and the relation,

$$\mathfrak{Q}C = \mathfrak{Q}C_{\sigma(0)} + \mathfrak{Q}C_{\sigma(\delta)},$$

which is the same as (7.26).

The expression (E.1) has been derived from (C.10) and (C.1), but we could have used (D.1) and (C.1) instead. Then we would have obtained

$$\mathfrak{Q}C = R_m Z_0 \sum_{t_1} \sum_{t_2} \cdots \sum_{t_M} f_n(t_1 + t_2 + \cdots + t_M) \left[\prod_{p=1}^{M} (z_p)^{t_p} \right]$$
$$\times \exp\left(- \sum_{(p,q)} t_p t_q \varepsilon_{pq}/kT \right), \qquad (\text{E. 4})$$

$$\mathfrak{Q}C_{\sigma(0)} = R_m Z_0 \sum_{t_1} \sum_{t_2} \cdots \sum_{t_M} (1-t_1) f_n(t_1 + t_2 + \cdots + t_M) \left[\prod_{p=1}^{M} (z_p)^{t_p} \right]$$
$$\times \exp\left(- \sum_{(p,q)} t_p t_q \varepsilon_{pq}/kT \right), \qquad (\text{E. 5})$$

$$\mathfrak{Q}C_{\sigma(\delta)} = R_m Z_0 \sum_{t_1} \sum_{t_2} \cdots \sum_{t_M} t_1 f_n(t_1 + t_2 + \cdots + t_M) \left[\prod_{p=1}^{M} (z_p)^{t_p} \right]$$

$$\times \exp \left(- \sum_{(p,q)} t_p t_q \varepsilon_{pq} / kT \right) . \tag{E. 6}$$

It is to be understood that in (E.5) and (E.6) the M sites are so numbered that the site σ is here renamed site 1. Thus t_1 takes the value 0 or 1 depending on whether the site σ is vacant or occupied. Of course (E.4), (E.5) and (E.6) are completely equivalent to (E.1), (E.2) and (E.3). Now we specialize to a simpler case; let us suppose that the M sites are equivalent, in which case (C.11) and (D.2) hold. Then (E.1) or (E.4) becomes

$$\Omega C = R_m Z_0 z^n I^{(n)} , \tag{E. 7}$$

where $I^{(n)}$ is what might be called the *configurational partition function* or the partition function for the interaction energy and is given by

$$I^{(n)} = \sum_{[n]} \exp \left(- \sum_{(s,t)}^{\text{occ}} \varepsilon_{st} / kT \right)$$

$$= \sum_{t_1} \sum_{t_2} \cdots \sum_{t_M} f_n (t_1 + t_2 + \cdots + t_M) \exp \left(- \sum_{(p,q)} t_p t_q \varepsilon_{pq} / kT \right) . \tag{E. 8}$$

Also (E.2) and (E.3), or (E.5) and (E.6) become

$$\Omega C_{\sigma(0)} = R_m Z_0 z^n I^{(n)}_{\sigma(0)} , \tag{E. 9}$$

$$\Omega C_{\sigma(\delta)} = R_m Z_0 z^n I^{(n)}_{\sigma(\delta)} . \tag{E. 10}$$

The expression for the partition function $I^{(n)}_{\sigma(0)}$ is obtained from (E.8) by replacing $\sum_{[n]}$ by $\sum_{[n]}^{\sigma(0)}$, and $f_n (t_1 + t_2 + \cdots + t_M)$ by $(1 - t_1) f_n (t_1 + t_2 + \cdots + t_M)$. That for $I^{(n)}_{\sigma(\delta)}$ is written in a very similar way. In (E.7)–(E.10), the superscript (n) on I implies that the configurational partition functions $I^{(n)}$, $I^{(n)}_{\sigma(0)}$ and $I^{(n)}_{\sigma(\delta)}$ are to be calculated for the adsorbed phase consisting of n molecules. Therefore, extending the above calculations, we find

$$\Omega C^\delta = R_m Z_0 z^{n+1} I^{(n+1)} , \tag{E. 11}$$

$$\Omega C^\delta_{\sigma(\delta)} = R_m Z_0 z^{n+1} I^{(n+1)}_{\sigma(\delta)} . \tag{E. 12}$$

Finally we obtain, from the above results,

$$p^\delta = \Omega C^\delta / \Omega C = z I^{(n+1)} / I^{(n)} , \tag{E. 13}$$

$$q^\delta_\sigma = \Omega C^\delta_{\sigma(\delta)} / \Omega C_{\sigma(0)} = z I^{(n+1)}_{\sigma(\delta)} / I^{(n)}_{\sigma(0)} , \tag{E. 14}$$

$$\Theta_{\sigma(\delta)} = \Omega C^\delta_{\sigma(\delta)} / \Omega C^\delta = I^{(n+1)}_{\sigma(\delta)} / I^{(n+1)} . \tag{E. 15}$$

If we assume further that the interactions between adsorbed molecules are absent, the exponential functions in (E.8) equal unity. Thus,[*]

---

[*] *Cf.* the paragraph preceding (E. 2).

$$I^{(n)} = \frac{M!}{(M-n)!\,n!}\,, \quad I_{\sigma(0)}^{(n)} = \frac{(M-1)!}{(M-n-1)!\,n!}\,, \quad I_{\sigma(\delta)}^{(n)} = \frac{(M-1)!}{(M-n)!\,(n-1)!}\,.$$

Similarly,

$$I^{(n+1)} = \frac{M!}{(M-n-1)!\,(n+1)!}\,, \quad I_{\sigma(0)}^{(n+1)} = \frac{(M-1)!}{(M-n-2)!\,(n+1)!}\,,$$

$$I_{\sigma(\delta)}^{(n+1)} = \frac{(M-1)!}{(M-n-1)!\,n!}\,.$$

In this particular case, (E.13), (E.14) and (E.15) read

$$p^{\delta} = \frac{M-n}{n+1}\,z\,, \quad q_{\sigma}^{\delta} = z\,, \quad \Theta_{\sigma(\delta)} = \frac{n+1}{M}\,. \tag{E.16}$$

For large n it is justifiable to replace $n+1$ in (E.16) by n. Also in the state of adsorption equilibrium, $n = n^* = \theta M$ (see Section 7). Therefore (E.16) is rewritten as

$$p^{\delta} = \frac{1-\theta}{\theta}\,z\,, \quad q_{\sigma}^{\delta} = z\,, \quad \Theta_{\delta(\sigma)} = \theta\,. \tag{E.17}$$

In the adsorption equilibrium, (7.20) holds; thus the first of (E.17) becomes

$$\frac{\theta}{1-\theta} = \frac{z}{p^{\delta'}} = \lambda_{\mathrm{G}} z\,,$$

which coincides with (C.15).

In passing, we note that the partition functions of the spin system listed in Table 1 are cast into forms quite similar to (E.7) and (E.9)–(E.12). Since the relation $-\frac{1}{2}s_1 - \frac{1}{2}s_2 - \cdots - \frac{1}{2}s_N + \frac{1}{2}N = n$ implies that

$$s_1 + s_2 + \cdots + s_N = N - 2n\,,$$

we obtain from (D.6)

$$\mathfrak{Q}C = Q_n = y^{N-2n} I^{(n)}\,, \tag{E.18}$$

with

$$I^{(n)} = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} f_n \left(-\frac{1}{2}s_1 - \frac{1}{2}s_2 - \cdots - \frac{1}{2}s_N + \frac{1}{2}N \right)$$
$$\times \exp\left(\sum_{(p,q)} s_p s_q J/kT \right). \tag{E.19}$$

In much the same way that we have obtained (E.13)–(E.15), we find

$$p^{+} = \mathfrak{Q}C^{+}/\mathfrak{Q}C = y^{-2} I^{(n+1)}/I^{(n)}\,, \tag{E.20}$$

Method of Statistical-Mechanical Calculations

$$q_\sigma^+ = \mathfrak{Q}C_{\sigma(\downarrow)}^+ / \mathfrak{Q}C_{\sigma(\uparrow)} = y^{-2}I_{\sigma(\downarrow)}^{(n+1)} / I_{\sigma(\uparrow)}^{(n)} , \tag{E.21}$$

$$\Theta_{\sigma(\downarrow)} = \mathfrak{Q}C_{\sigma(\downarrow)}^+ / \mathfrak{Q}C^+ = I_{\sigma(\downarrow)}^{(n+1)} / I^{(n+1)} . \tag{E.22}$$

The expressions for $I_{\sigma(\uparrow)}^{(n)}$ and $I^{(n+1)}$ are obtained from (E.19) by inserting the factor $\frac{1}{2}(1+s_1)$ in front of f_n and by replacing f_n by f_{n+1}, respectively. That for $I_{\sigma(\downarrow)}^{(n+1)}$ is obtained from (E.19) by inserting the factor $\frac{1}{2}(1-s_1)$ in front of f_n and replacing f_n by f_{n+1} at the same time. In the absence of the spin-spin interactions, (E.20), (E.21) and (E.22) become

$$p^+ = \frac{N-n}{n+1}y^{-2} , \quad q_\sigma^+ = y^{-2} , \quad \Theta_{\sigma(\downarrow)} = \frac{n+1}{N} , \tag{E.23}$$

which are quite similar to (E.16) and coincide with (6.15), (6.19) and (6.20).

References

1) DENBIGH: K. DENBIGH, *The Principles of Chemical Equilibrium*, University Press, Cambridge, 1961.

2) FOWLER-GUGGENHEIM: R. H. FOWLER and E. H. GUGGENHEIM, *Statistical Thermodynamics*, University Press, Cambridge, 1939.

3) GLASSTONE *et al.*: S. GLASSTONE, K. J. LAIDLER and H. EYRING, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.

4) HILL: T. L. HILL, *Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, 1960.

5) HILL A: T. L. HILL, *Statistical Mechanics*, McGraw-Hill, New York, 1956.

6) HILL B: T. L. HILL, Advances in Catalysis, 4, 211 (1952).

7) HORIUTI: J. HORIUTI, This Journal 1, 8 (1948).

8) HORIUTI-NAKAMURA: J. HORIUTI and T. NAKAMURA, Advances in Catalysis, 17, 1 (1967).

9) KIRKWOOD: J. G. KIRKWOOD, J. Chem. Phys. 3, 300 (1935).

10) MAYER-MAYER: J. E. MAYER and M. GOEPPERT-MAYER, *Statistical Mechanics*, John Wiley and Sons, Inc., New York, 1940.

10a) RUSHBROOKE: G. S. RUSHBROOKE, *Introduction to Statistical Mechanics*, University Press, Oxford, 1949.

11) WANNIER: G. WANNIER, *Statistical Physics*, John Wiley and Sons, New York, 1966.