Fundamentals of Statistical Thermodynamics

By Noboru NAGASAKO

(Received June 15, 1961)

Physico-chemical phenomena in stationary states obey not only thermodynamics, but also the theoretical probability distributions of mathematical statistics. These two branches of science can be connected more closely by a new definition of entropy.

1. Probability of Microscopic States. — We confine our attention to a homogeneous system in a stationary state which has been placed for a long period of time in a thermostat of temperature T. Let $\varepsilon_i (i=0, 1, \cdots\cdots, r)$ denote the energy level of a single particle, and n_i the number of particles in state ε_i. If the particles are independent, the probability of the microscopic states assigned by $n_0, n_1, \cdots\cdots, n_r$ will be given by

$$p(n_0, n_1, \cdots\cdots, n_r) = W\cdot p_0^{n_0} p_1^{n_1} \cdots\cdots p_r^{n_r}/\Xi \quad (1.1)$$

in which p_i denotes the relative probability of finding a particle in state ε_i, W a statistical weight or the number of complexions, and Ξ a normalizing factor.

For example, if we set $p_0+p_1+\cdots\cdots+p_r=1$, we have

$$1=(\sum_i p_i)^N=\sum \frac{N!}{n_0!\ n_1! \cdots n_r!} p_0^{n_0} p_1^{n_1} \cdots p_r^{n_r}$$

We have, therefore, as the multinomial distribution for N independent events, $(0<p_i<1)$,

$$p(n_0, n_1, \cdots\cdots, n_r) = \frac{N!}{n_0!\ n_1! \cdots\cdots n_r!} p_0^{n_0} p_1^{n_1} \cdots\cdots p_r^{n_r} \quad (1.2)$$

in which $N=\sum_i n_i=\sum_i \bar{n}_i$ and $\Xi=1$.

If every state ε_i is g_i-fold degenerate, and if we set $\sum_i g_i p_i=1$, in place of $\sum_i p_i=1$, we have

$$p(n_0, n_1, \cdots\cdots, n_r) = N! \frac{g_0^{n_0} g_1^{n_1} \cdots\cdots g_r^{n_r}}{n_0!\ n_1! \cdots\cdots n_r!} p_0^{n_0} p_1^{n_1} \cdots\cdots p_r^{n_r} \quad (1.3)$$

On the other hand, we have by binomial expansions

$$1=(1+p)^g/(1+p)^g=\sum \binom{g}{n} p^n/(1+p)^g$$

and $1=(1-p)^{-g}/(1-p)^{-g}$

$$=\sum \binom{g+n-1}{n} p^n/(1-p)^{-g}$$

We have, therefore, as the product of binomial distributions

$$p(n_0, n_1, \cdots\cdots, n_r) = \prod_i \binom{g_i}{n_i} p_i^{n_i}/(1+p_i)^{g_i} \quad (0<p_i) \quad (1.4)$$

and

$$p(n_0, n_1, \cdots\cdots, n_r) = \prod_i \binom{g_i+n_i-1}{n_i} p_i^{n_i}/(1-p_i)^{-g_i} \quad (0<p_i<1) \quad (1.5)$$

For (1.4) and (1.5) we have $\bar{N}=\sum_i \bar{n}_i$

and
$$\Xi=\prod_i (1\pm p_i)^{\pm g_i} \quad (1.6)$$

When $p_i \ll 1$, both (1.4) and (1.5) lead to the multiple Poisson distribution given by

$$p(n_0, n_1 \cdots\cdots n_r) = \exp[-\bar{N}] \times \frac{g_0^{n_0} g_1^{n_1} \cdots\cdots g_r^{n_r}}{n_0!\ n_1! \cdots\cdots n_r!} p_0^{n_0} p_1^{n_1} \cdots\cdots p_r^{n_r} \quad (1.7)$$

It is evident that these theoretical probability distributions may be reduced to (1.1). In place of the ergodic hypothesis by Boltzmann, the equal a priori probability of finding a particle in each energy level of a single particle has been postulated by $p_i^{n_i}$ of (1.1).

When a probability distribution is given, we can obtain the mean value and the other moments by a moment-generating function[1] defined by $\Phi=\sum p(x)\exp[xt]$, where $p(x)$ denotes the probability of a random variable x. Hence, we have

---

[1] P. G. Hoel, "Introduction to Mathematical Statistics", John Wiley and Sons, Inc., New York (1951).

$$\Phi=\sum_x p(x)(1+xt+\cdots\cdots+x^m t^m/m!+\cdots\cdots)$$

$$=1+\bar{x}t+\cdots\cdots+\overline{x^m}t^m/m!+\cdots\cdots$$

Differentiating Φ with respect to t, and putting $t=0$,

$$\overline{x^m}=\left.\frac{\partial^m\Phi}{\partial t^m}\right|_{t=0} \tag{1.8}$$

The moment-generating function for the multinomial distribution will be given by

$$\Phi=(p_0+p_1+\cdots\cdots+e^t p_i+\cdots\cdots+p_r)^N \tag{1.9}$$

Hence, $$\bar{n}_i=\left.\frac{\partial\Phi}{\partial t}\right|_{t=0}=Np_i \tag{1.10}$$

The moment-generating function for the binomial distributions will be given by

$$\Phi=(1\pm e^t p_i)^{\pm g_i}(1\pm p_i)^{\mp g_i} \tag{1.11}$$

Hence, $$\bar{n}_i=\left.\frac{\partial\Phi}{\partial t}\right|_{t=0}=g_i p_i/(1\pm p_i) \tag{1.12}$$

2. Probability and Entropy. — The probability (1.1) is given in a form $W\times P$, where

$$P=p_0{}^{n_0}p_1{}^{n_1}\cdots\cdots p_r{}^{n_r}/\Xi$$

denotes the probability of a set of microscopic states. Taking the logarithm of P, we have

$$\ln P=\sum_i n_i\ln p_i-\ln\Xi$$

The mean value of $\ln P$ is given by

$$\overline{\ln P}=\sum_i \bar{n}_i\ln p_i-\ln\Xi$$

We define the entropy not by $S=\boldsymbol{k}\ln W$, but by

$$S=-\boldsymbol{k}\,\overline{\ln P}$$

i. e., $$S=-\boldsymbol{k}\sum_i\bar{n}_i\ln p_i+\boldsymbol{k}\ln\Xi \tag{2.1}$$

in which $\boldsymbol{k}$ denotes Boltzmann's constant.

We have, therefore, by (1.2)

$$S=-\boldsymbol{k}\sum_i\bar{n}_i\ln p_i \tag{2.2}$$

and then we have by (1.10)

$$S=-\boldsymbol{k}N\sum_i p_i\ln p_i$$

or $$S=-\boldsymbol{k}\sum_i\bar{n}_i\ln\bar{n}_i+\boldsymbol{k}\sum_i\bar{n}_i\ln N \tag{2.3}$$

We have by (1.6) and (2.1)

$$S=-\boldsymbol{k}\sum_i\bar{n}_i\ln p_i\pm\boldsymbol{k}\sum_i g_i\ln(1\pm p_i) \tag{2.4}$$

and then we have by (1.12)

$$S=-\boldsymbol{k}\sum_i\bar{n}_i\ln\bar{n}_i\pm\boldsymbol{k}\sum_i g_i\ln g_i$$

$$\mp\boldsymbol{k}\sum_i(g_i\mp\bar{n}_i)\ln(g_i\mp\bar{n}_i) \tag{2.5}$$

Thus we obtain the entropies, nearly identical with the familiar expressions, without the aid of Stirling's approximation formula.

By differentiation of (2.2) we have

$$dS=-\boldsymbol{k}\sum_i\ln p_i d\bar{n}_i$$

Since every g_i is maintained constant at constant volume, we have by differentiation of (2.4) at constant volume V

$$(dS)_V=-\boldsymbol{k}\sum_i\ln p_i(d\bar{n}_i)_V$$

We may generalize the above results by differentiation of (2.1), which gives

$$dS=-\boldsymbol{k}\sum_i\ln p_i d\bar{n}_i-\boldsymbol{k}\sum_i\bar{n}_i d\ln p_i+\boldsymbol{k}d\ln\Xi$$

We have, therefore,

$$dS=-\boldsymbol{k}\sum_i\ln p_i d\bar{n}_i \tag{2.6}$$

if we may write

$$\sum_i\bar{n}_i d\ln p_i=0\quad\text{and}\quad d\ln\Xi=0 \tag{2.7}$$

which is fulfilled to obtain (2.6) form (2.2). We have also

$$(dS)_V=-\boldsymbol{k}\sum_i\ln p_i(d\bar{n}_i)_V \tag{2.8}$$

if we may write

$$\sum_i\bar{n}_i(d\ln p_i)_V=(d\ln\Xi)_V$$

i. e., $$\bar{n}_i=(\partial\ln\Xi/\partial\ln p_i)_V \tag{2.9}$$

which is fulfilled to obtain (2.8) from (2.4).

Now let us assume that a system obeys the thermodynamic equation

$$dU=TdS-pdV+\mu dN_t \tag{2.10}$$

in which U denotes the energy, p the pressure, μ the chemical potential, and N_t the total number of particles of the system. We have, therefore, at constant volume

$$(dU)_V=T(dS)_V+\mu(dN_t)_V \tag{2.11}$$

When the particles are independent, we may write

$$E=\varepsilon_0 n_0+\varepsilon_1 n_1+\cdots\cdots+\varepsilon_r n_r \tag{2.12}$$

and $$\bar{E}=\varepsilon_0\bar{n}_0+\varepsilon_1\bar{n}_1+\cdots\cdots+\varepsilon_r\bar{n}_r \tag{2.13}$$

in which E denotes the total energy of the system and $\bar{E}$ its mean value. Writing $U=\bar{E}$, we have

$$dU=\sum_i\varepsilon_i d\bar{n}_i+\sum_i\bar{n}_i d\varepsilon_i$$

Since we may write, in general, $d\varepsilon_i=0$ for $dV=0$, it follows that

$$(dU)_V=\sum_i\varepsilon_i(d\bar{n}_i)_V \tag{2.14}$$

Moreover, we may write

$$dN_t=\sum_i d\bar{n}_i \tag{2.15}$$

Substituting (2.8), (2.14) and (2.15) into (2.11), we have

$$\sum_i(\varepsilon_i+\boldsymbol{k}T\ln p_i-\mu)(d\bar{n}_i)_V=0$$

Since we may write, in general, $(\mathrm{d}\bar{n}_i) \neq 0$, it follows that

$$\varepsilon_i + \boldsymbol{k}T \ln p_i - \mu = 0$$

or

$$p_i = \exp[(\mu - \varepsilon_i)/\boldsymbol{k}T] \tag{2.16}$$

which enormously simplifies the discussions.

Substituting (2.16) into (2.1), we obtain as the general equation of statistical-thermodynamic entropy

$$S = \bar{E}/T - \mu \sum_i \bar{n}_i/T + \boldsymbol{k} \ln \Xi \tag{2.17}$$

Since the Gibbs free energy of a homogeneous system will be given by $G = \mu \sum_i \bar{n}_i$, it follows that

$$pV = \boldsymbol{k}T \ln \Xi \tag{2.18}$$

3. Fermi-Dirac and Bose-Einstein Statistics.—Dividing the $2f$-dimensional μ-space into many cells with the volume $\boldsymbol{h}^f$, where $\boldsymbol{h}$ denotes Planck's constant and f the degrees of freedom for a single particle, we shall find g_i cells for the same energy ε_i, when a state ε_i is g_i-fold degenerate. We now try to discover the law of probability by which these cells will be occupied by the particles.

If there are n_i particles in a g_i-fold degenerate energy level ε_i, and if the particles obey the Fermi-Dirac statistics, it is known that the number of complexions will be given by[2)]

$$W(\text{Fermi-Dirac}) = \prod_i \binom{g_i}{n_i} \tag{3.1}$$

and for the Bose-Einstein statistics

$$W(\text{Bose-Einstein}) = \prod_i \binom{g_i + n_i - 1}{n_i} \tag{3.2}$$

We may consider by (1.1) and (3.1) that the probability distribution for the Fermi-Dirac statistics will be given by (1.4), the product of positive binomial distributions. Similarly, by (3.2) we obtain (1.5), the product of negative binomial distributions, for the Bose-Einstein statistics. Moreover, it is assumed by (1.4) and by (1.5) that the particles occupy each energy level independently.

The translational energy of an independent material particle of mass m in a state described by the three quantum numbers, k_x, k_y, k_z, is given by $\varepsilon_i = \boldsymbol{h}^2(k^2_x + k^2_y + k^2_z)/8mV^{2/3}$, which gives $\mathrm{d}\varepsilon_i = 0$ for $\mathrm{d}V = 0$. The energy of a photon in given by $\varepsilon_i = \boldsymbol{h}\nu$, i. e., $\mathrm{d}\varepsilon_i = 0$. We may use (2.14), therefore, to obtain (2.16).

We may write for material particles $g_i = 4\pi V q^2 \mathrm{d}q/\boldsymbol{h}^3$, in which q denotes the momentum of a single particle, and for photons, $g_i = (8\pi V/c^3)\nu^2 \mathrm{d}\nu$. At constant volume, therefore, every g_i remains constant. Taking the logarithm of (1.6) for the probability distributions (1.4) and (1.5), we have

$$\ln \Xi = \pm \sum_i g_i \ln(1 \pm p_i)$$

Hence, $$(\mathrm{d} \ln \Xi)_V = \sum_i g_i \mathrm{d}p_i/(1 \pm p_i)$$

Since we have by (1.12)

$$\bar{n}_i = g_i p_i/(1 \pm p_i)$$

it follows that

$$\bar{n}_i = (\partial \ln \Xi/\partial \ln p_i)_V$$

which is the condition (2.9) to obtain (2.8).

Having examined the derivation of (2.16), and substituting (2.16) into (1.6), we have

$$\Xi = \prod_i (1 \pm \exp[(\mu - \varepsilon_i)/\boldsymbol{k}T])^{\pm g_i} \tag{3.3}$$

Substituting (3.3) into (2.17), we obtain as the statistical-thermodynamic entropy of the Fermi-Dirac and the Bose-Einstein system

$$S = \bar{E}/T - \mu\bar{N}/T \pm \boldsymbol{k} \sum_i g_i \ln(1 \pm \exp[(\mu - \varepsilon_i)/\boldsymbol{k}T]) \tag{3.4}$$

Substituting (3.3) into (2.18), we obtain

$$pV = \pm \boldsymbol{k}T \sum_i g_i \ln(1 \pm \exp[(\mu - \varepsilon_i)/\boldsymbol{k}T]) \tag{3.5}$$

Substituting (2.16) into (1.12), we obtain as the distribution law

$$\bar{n}_i = g_i \exp[(\mu - \varepsilon_i)/\boldsymbol{k}T] / (1 \pm \exp[(\mu - \varepsilon_i)/\boldsymbol{k}T]) \tag{3.6}$$

Although a different method has been used to obtain (3.4), (3.5) and (3.6), these equations are identical with those proposed by Fowler and Guggenheim[3)].

When $p_i \ll 1$, we have by (1.6)

$$\Xi = \exp[\sum_i g_i p_i]$$

and by (1.12)

$$\bar{n}_i = g_i p_i \tag{3.7}$$

Hence, $$\Xi = \exp[\sum \bar{n}_i]_i = \exp[\bar{N}] \tag{3.8}$$

The probability distribution for this case is given, therefore, by the multiple Poisson distribution (1.7), in which

$$W = \prod_i g_i^{n_i}/n_i\,! \tag{3.9}$$

Substituting (3.8) into (2.17), we have

$$S = \bar{E}/T - \mu\bar{N}/T + \boldsymbol{k}\bar{N} \tag{3.10}$$

Substituting (3.8) into (2.18), we obtain the equation of the state of an ideal gas given by $pV = \boldsymbol{k}T\bar{N}$.

Substituting (2.16) into (3.7), we obtain the Boltzmann distribution law for an ideal gas given by

---

[2)] J. E. Mayer and M. G. Mayer, "Statistical Mechanics", John Wiley & Sons, Inc., New York (1940), p. 111.

[3)] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge University Press (1939). pp. 50-67, 234.

$$\bar{n}_i=g_i \exp[(\mu-\varepsilon_i)/\boldsymbol{k}T] \tag{3.11}$$

Hence,
$$\bar{N}=\sum_i \bar{n}_i=(p.f.)\exp[\mu/\boldsymbol{k}T] \tag{3.12}$$

where $(p.f.)$ denotes the partition function. We can eliminate, therefore, μ from (3.10) by (3.12) to obtain

$$S=\bar{E}/T+\boldsymbol{k}\bar{N}\ln[(p.f.)/\bar{N}]+\boldsymbol{k}\bar{N} \tag{3.13}$$

which is identical with the Sackur-Tetrode equation for the entropy of an ideal gas.

4. Multinomial Distributions.—In statistical mechanics the number of complexions was given first by

$$W=N!/n_0!\ n_1!\cdots\cdots n_r! \tag{4.1}$$

which may be interpreted as the number of ways that $n_0, n_1, \cdots\cdots, n_r$ identical particles with energies $\varepsilon_0, \varepsilon_1, \cdots\cdots, \varepsilon_r$ will be placed in N numbered, i. e., physically distinguishable, cells, one particle to each cell. The particles may or may not be localized, although the application of (4.1) has been restricted to the localized particles by Fowler and Guggenheim[4].

When W is given by (4.1), we obtain the multinomial distribution (1.2), with $\Xi=1$. It may be noticed that we have $\Xi=(\sum_i p_i)^N$ for (4.1), if we set $\sum_i p_i \neq 1$. However, we can reduce this probability distribution to (1.2), if W is given by (4.1). When every state ε_i is g_i-fold degenerate, we have the probability distribution (1.3)

and
$$W=N!\prod_i g_i^{n_i}/n_i! \tag{4.2}$$

Substituting $\Xi=1$ into (3.18), we obtain $pV=0$. We may apply the probability distributions (1.2) and (1.3), therefore, to the vibrational and rotational motions of gas molecules, since these motions have nothing to do with pV. In these cases we may omit the term $p\mathrm{d}V$ in (2.10) and may write $\mathrm{d}\varepsilon_i=0$, i. e.,

$$\mathrm{d}U=\sum_i \varepsilon_i \mathrm{d}\bar{n}_i \tag{4.3}$$

We have, therefore, by (2.10), (4.3), (2.6) and (2.15)

$$\sum_i(\varepsilon_i+\boldsymbol{k}T\ln p_i-\mu_0)\mathrm{d}\bar{n}_i=0$$

or
$$p_i=\exp[(\mu_0-\varepsilon_i)/\boldsymbol{k}T] \tag{4.4}$$

Substituting $\Xi=1$ and (4.4) into (2.1), we have

$$S=\bar{E}/T-\mu_0 N/T \tag{4.5}$$

which is also obtained by substituting $\Xi=1$ into (2.17). Denoting by A the Helmholtz free energy, we have, therefore, $\mu_0=A/N$ which holds for the systems with $pV=0$ and which has been distinguished from $\mu=G/N$.

Substituting (4.4) into $\sum_i p_i=1$ of (1.2) and into $\sum_i g_i p_i=1$ of (1.3), we have

$$1=(p.f.)\exp[\mu_0/\boldsymbol{k}T] \tag{4.6}$$

We can eliminate, therefore, μ_0 from (4.5) by (4.6) to obtain

$$S=\bar{E}/T+\boldsymbol{k}\ln[(p.f.)^N] \tag{4.7}$$

For the non-localized gas molecules, the entropy due to vibrations of atoms and that due to rotations can be calculated by (4.7); these results have been verified by experiments.

Substituting (4.4) into (1.10), we have again the Boltzmann distribution law given by

$$\bar{n}_i=N\exp[(\mu_0-\varepsilon_i)/\boldsymbol{k}T] \tag{4.8}$$

For the probability distribution (1.3), we have

$$\bar{n}_i=Ng_i\exp[(\mu_0-\varepsilon_i)/\boldsymbol{k}T] \tag{4.9}$$

We could also apply the probability distribution (1.2) and (1.3) to the localized oscillators in a crystal at low pressures.

If the number of complexions is given by (3.9), we can construct another probability distribution, i. e., the multinomial distribution for the translational motions of an ideal gas. If we set $N=\sum_i g_i p_i$, we have

$$1=(\sum_i g_i p_i/N)^N=(N!/N^N)\sum\prod_i g_i^{n_i}p_i^{n_i}/n_i! \tag{4.10}$$

Hence,

$$p(n_0, n_1, \cdots\cdots, n_r)=(N!/N^N)\prod_i g_i^{n_i}p_i^{n_i}/n_i! \tag{4.11}$$

and $\bar{n}_i=g_i p_i$ which is identical with (3.7).

Substituting $\Xi=N^N/N!$ and (3.7) into (2.1), we have

$$S=-\boldsymbol{k}\sum_i g_i p_i\ln p_i+\boldsymbol{k}\ln(N^N/N!) \tag{4.12}$$

Differentiating (4.12) at constant V and N, we have

$$(\mathrm{d}S)_{N,V}=-\boldsymbol{k}\sum_i \ln p_i(\mathrm{d}\bar{n}_i)_{N,V} \tag{4.13}$$

Substituting (2.14) and (4.13) into the thermodynamic equation $(\mathrm{d}U)_{N,V}=T(\mathrm{d}S)_{N,V}$, we have

$$\sum_i(\varepsilon_i+\boldsymbol{k}T\ln p_i)(\mathrm{d}\bar{n}_i)_{N,V}=0$$

Since $\sum_i(\mathrm{d}\bar{n}_i)_{N,V}=0$, we may write

$$\varepsilon_i+\boldsymbol{k}T\ln p_i=\mu' \ \text{(constant)}$$

or
$$p_i=\exp[(\mu'-\varepsilon_i)/\boldsymbol{k}T] \tag{4.14}$$

Substituting (4.14) into (4.12), we have

$$S=\bar{E}/T-\mu' N/T+\boldsymbol{k}\ln(N^N/N!) \tag{4.15}$$

Since $N=\sum_i g_i p_i$, it follows that

$$N=(p.f.)\exp[\mu'/\boldsymbol{k}T] \tag{4.16}$$

Now we can eliminate μ' from (4.15) by (4.16) to obtain

---

[4] R. H. Fowler and E. A. Guggenheim, loc. cit., pp. 20-29.

$$S=\overline{E}/T+\boldsymbol{k}\ln[(p.f.)^N/N!] \qquad (4.17)$$

which is identical with (3.13), when $\overline{N}=N\gg 1$.

Comparing (4.7) with (4.17), we find the well known difference, $N!$, in the divisor, which is often introduced ambiguously to obtain (4.17) from (4.7). It is evident that the number of complexions ((4.1) or (4.2)) and the entropy (4.7) can be applied solely to the system with $pV=0$. It is not legitimate, therefore, to try to obtain (4.17) for $pV=\boldsymbol{k}TN$ from (4.7) for $pV=0$, although the difference between these equations is apparently simple.

5. Grand-canonical and Canonical Distributions. — Substituting (2.16) into (1.1) and considering (2.12) and (2.18), we have

$$p(n_0, n_1, \cdots\cdots, n_r) = W\exp[(\mu N-E-pV)/\boldsymbol{k}T] \qquad (5.1)$$

Denoting by Ω the total number of complexions for the given N, E, and by $\sum_c$ the conditioned sum of W of which $n_0, n_1, \cdots\cdots, n_r$ satisfy the given N, E, we may write

$$\Omega(N,E)=\sum_c W(n_0, n_1, \cdots\cdots, n_r) \qquad (5.2)$$

The probability that the system contains N particles and is in state E is given, therefore, by

$$p(N,E)=\Omega(N,E)\exp[(\mu N-E-pV)/\boldsymbol{k}T] \qquad (5.3)$$

which corresponds to the Gibbs grand ensemble canonically distributed[5], i. e., the grand-canonical distribution. The probability distributions ((1.4), (1.5) for the Fermi-Dirac and Bose-Einstein statistics and (1.7) for an ideal gas) lead, therefore, to the grand-canonical distributions.

Substituting $\Xi=1$ and (4.4) into (1.1), we have

$$p(n_0, n_1, \cdots\cdots, n_r)=W\exp[(\mu_0 N-E)/\boldsymbol{k}T] \quad (5.4)$$

The probability that the system is in state E is given, therefore, by

$$p(E)=\Omega(N,E)\exp[(A-E)/\boldsymbol{k}T] \qquad (5.5)$$

which corresponds to the Gibbs canonical distribution. The multinomial distributions ((1.2) and (1.3)) lead, therefore, to the canonical distributions.

Substituting (4.14) into (1.1), we have

$$p(n_0, n_1, \cdots\cdots, n_r) = W\exp[(\mu' N-E-\boldsymbol{k}T\ln\Xi)/\boldsymbol{k}T] \qquad (5.6)$$

Since we may write by (4.15) $A=\mu' N-\boldsymbol{k}T\ln\Xi$, we have again (5.5) for $p(E)$. The probability distribution (4.11) for an ideal gas leads, therefore, to the canonical distribution. It may be mentioned that it is difficult to treat the Fermi-Dirac and the Bose-Einstein statistics canonically, since, for these statistics, there is no simple probability distribution in which the total number of particles is maintained constant, while the total energy is variable.

For the linear harmonic oscillators with frequency ν, i. e., $\varepsilon_i=\boldsymbol{h}\nu/2+i\boldsymbol{h}\nu(i=0,1,\cdots\cdots,\infty)$, we have by (4.4)

$$\begin{aligned}1&=(\sum_i p_i)^N\\ &=(1-\exp[-\boldsymbol{h}\nu/\boldsymbol{k}T])^{-N}\cdot\\ &\quad\exp[\mu_0 N/\boldsymbol{k}T-N\boldsymbol{h}\nu/2\boldsymbol{k}T]\\ &=\sum_{J=0}^{\infty}\binom{N+J-1}{J}\exp[(A-E)/\boldsymbol{k}T]\end{aligned}$$

in which $E=N\boldsymbol{h}\nu/2+J\boldsymbol{h}\nu(J=0,1,\cdots\cdots,\infty)$. We have, therefore the canonical distribution in a compact form

$$p(E)=\binom{N+J-1}{J}\exp[(A-E)/\boldsymbol{k}T] \qquad (5.7)$$

for which we may write by (5.2) and (5.5)

$$\Omega(N,E)=\binom{N+J-1}{J}=\sum_c N!/n_0!\ n_1!\cdots\cdots n_r!$$

Thus we obtain, in general, either the canonical or the grand-canonical distribution by the probability distribution (1.1).

6. Fluctuations. — By means of a moment-generating function we can calculate fluctuations. We have by (1.8) as the variance

$$\sigma^2=(\overline{x^2})-(\overline{x})^2=\left.\frac{\partial^2\Phi}{\partial t^2}\right|_{t=0}-\left.\left(\frac{\partial\Phi}{\partial t}\right)^2\right|_{t=0}$$

Calculations will be performed more simply by the following relations:

$$\frac{\partial\ln\Phi}{\partial t}=\frac{1}{\Phi}\frac{\partial\Phi}{\partial t}$$

and

$$\frac{\partial^2\ln\Phi}{\partial t^2}=\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial t^2}-\frac{1}{\Phi^2}\left(\frac{\partial\Phi}{\partial t}\right)^2$$

Since $\Phi(t=0)=1$, it follows that

$$\overline{x}=\left.\frac{\partial\ln\Phi}{\partial t}\right|_{t=0}$$

and

$$\sigma^2=\left.\frac{\partial^2\ln\Phi}{\partial t^2}\right|_{t=0} \qquad (6.1)$$

For the binomial distributions (1.4) and (1.5), we have by (6.1) and the moment-generating function (1.11)

$$\sigma^2=(\overline{n_i^2})-(\overline{n}_i)^2=g_i p_i/(1\pm p_i)^2 \qquad (6.2)$$

Since the particles occupy each energy level independently, we have for $N=\sum_i n_i$

---

[5] J. W. Gibbs, "Elementary Rrinciples in Statistical Mechanics", Yale University Press (1902).

$$\sigma^2{}_N=\overline{(N^2)}-(\overline{N})^2=\sum_i g_i p_i/(1\pm p_i)^2 \tag{6.3}$$

and for $E=\sum_i \varepsilon_i n_i$

$$\sigma^2{}_E=\overline{(E^2)}-(\overline{E})^2=\sum_i \varepsilon^2{}_i g_i p_i/(1\pm p_i)^2 \tag{6.4}$$

For the multiple Poisson distribution (1.7), in which $p_i\ll 1$, we have

$$\sigma^2{}_N=\sum_i g_i p_i=\overline{N}$$

and

$$\sigma^2{}_E=\sum_i \varepsilon^2{}_i g_i p_i=\sum_i \varepsilon^2{}_i \bar{n}_i \tag{6.5}$$

Applying (1.7) to an ideal gas, and setting $g_i=4\pi V\, q^2\mathrm{d}q/\boldsymbol{h}^3$, we have by (2.13) and (3.11)

$$\begin{aligned}\overline{E}&=\exp[\mu/\boldsymbol{kT}]\cdot(2\pi V/m\boldsymbol{h}^3)\\&\quad\times\int_0^\infty q^2\exp[-q^2/2m\boldsymbol{kT}]\cdot\mathrm{d}q\\&=\exp[\mu/\boldsymbol{kT}]\cdot(3/2)\boldsymbol{kT}\cdot V(2\pi m\boldsymbol{kT})^{3/2}/\boldsymbol{h}^3\end{aligned}$$

Since $(p.f.)=V(2\pi m\boldsymbol{kT})^{3/2}/\boldsymbol{h}^3$, we have by (3.12)

$$\overline{E}=\overline{N}(3/2)\boldsymbol{kT} \tag{6.6}$$

We have by (3.11) and (6.5)

$$\sigma^2{}_E=\overline{N}(15/4)(\boldsymbol{kT})^2$$

i. e.,

$$\sigma_E=\sqrt{\overline{N}}(\sqrt{15}/2)\boldsymbol{kT} \tag{6.7}$$

On the other hand, we have, in general, with respect to the variance

$$\sigma^2=\int_{-\infty}^{\infty}(x-\bar{x})^2p(x)\mathrm{d}x=\int_{|x-\bar{x}|\geqq\xi\sigma}+\int_{|x-\bar{x}|<\xi\sigma}$$

Since

$$\int_{|x-\bar{x}|\geqq\xi\sigma}\geqq\xi^2\sigma^2p(|x-\bar{x}|\geqq\xi\sigma)$$

we obtain Tchebychev's theorem given by

$$p(|x-\bar{x}|\geqq\xi\sigma)\leqq1/\xi^2$$

where $p(|x-\bar{x}|\geqq\xi\sigma)$ denotes the probability that the deviation from the mean value $x-\bar{x}$ is greater than $\xi\sigma$.

We have, therefore, as the estimations for the grand ensemble

$$p(|N-\overline{N}|\geqq100\sigma_N)\leqq0.0001$$

and

$$p(|E-\overline{E}|\geqq100\sigma_E)\leqq0.0001 \tag{6.8}$$

For an ideal gas obeying (1.7), we may write $\overline{N}=2.7\times10^{19}$/cc. at N. T. P and by (6.5) $\sigma_N=\sqrt{\overline{N}}=5.2\times10^9$. $\overline{E}$ is given by (6.6) proportional to $\overline{N}$. σ_E is given by (6.7) proportional to $\sqrt{\overline{N}}$. It is evident, therefore, that we may neglect the probability of finding a system with N, E deviated from the physically observable mean values $\overline{N}, \overline{E}$. In other words, there is no significant difference between the grand ensemble from (1.7) for an ideal gas and the micro-canonical ensemble in which the total number of particles is fixed and the total energy falls within the narrow limits between E and $E+\varDelta E$.

This is also the case with the Fermi-Dirac statistics. Comparing (6.3) and (6.4) with (6.5), it is seen that the probability distribution (1.4) for the Fermi-Dirac statistics is more sharply concentrated near the mean values than the distribution (1.7).

The probability distribution (1.5) for the Bose-Einstein statistics is more broadly distributed than the distribution (1.7). Applying the distribution (1.5) to the temperature radiation, and setting $g_i=(8\pi V/c^3)\,\nu^2\mathrm{d}\nu$, $\mu=0$ and $x=\boldsymbol{h}\nu/\boldsymbol{kT}$, we have by (3.6)

$$\begin{aligned}\overline{N}&=(8\pi V/c^3)\int_0^\infty\nu^2\mathrm{e}^{-x}(1-\mathrm{e}^{-x})^{-1}\mathrm{d}\nu\\&=16\pi^4(\boldsymbol{kT})^3V/(25.8)c^3\boldsymbol{h}^3\end{aligned} \tag{6.9}$$

Hence, we obtain $\overline{N}=2.03\times10^{13}$/cc. at $T=1000°\mathrm{K}$. We have also by (6.3)

$$\sigma^2{}_N=8\pi^3(\boldsymbol{kT})^3V/3c^3\boldsymbol{h}^3=1.37\overline{N}$$

i. e.,

$$\sigma_N=1.17\sqrt{\overline{N}}$$

by (2.13) and (6.9)

$$\overline{E}=8\pi^5(\boldsymbol{kT})^4V/15c^3\boldsymbol{h}^3=2.70\overline{N}\boldsymbol{kT}$$

and by (6.4)

$$\sigma^2{}_E=32\pi^5(\boldsymbol{kT})^5V/15c^3\boldsymbol{h}^3=10.8\overline{N}(\boldsymbol{kT})^2$$

i. e.,

$$\sigma_E=3.29\sqrt{\overline{N}}\boldsymbol{kT}$$

Combining the above results with the estimations (6.8), we may consider that there is, in general, no significant difference between the grand ensemble from (1.5) for the temperature radiation and the micro-canonical.

Analytically the canonical and the grand-canonical distributions are much more manageable than the micro-canonical. It is especially simple and exact when we employ the theoretical probability distribution of mathematical statistics reducible to Eq. 1.1 to describe the probability of microscopic states and we define the entropy by Eq. 2.1.

It is possible to extend the present method to more complicated physico-chemical phenomena, such as chemical equilibria, adsorption and cooperative phenomena.

Tokyo Institute of Technology
Meguro-ku, Tokyo