In the first two analyses the zinc chloride contained a small quantity of the black insoluble material discussed on p. 1243. This remained chiefly suspended in the electrolyte and was collected on a small weighed platinum-sponge crucible and weighed. The weight was only 0.1 mg. in the first, and 0.7 mg. in the second experiment. In all the succeeding analyses the zinc bromide was initially freed from the residue by distillation. In analysis 8, the solution of the chloride after it had been electrolyzed for an instant, was faintly tinged with yellow, indicating a trace of bromide. The difficulty in detecting this effect leads to the suspicion that Analyses 5 and 6 were similarly affected. In Analysis 10, the quartz boat which remained practically unchanged in appearance and weight through the earlier experiments, was perceptibly attacked, by probably owing to the presence of basic salt. Therefore the average obtained omitting Analyses 5, 6, 8 and 10 is probably more reliable than the average of all the results. The difference is small, however, and judging from the evident difficulty of securing concordant results is within the limit of experimental error.

The agreement of the first average with Richards and Roger's value, 65.376, and with Baxter and Grose's 65.388, indicates very clearly that the otomic weight of zinc cannot be far from 65.38.

The results of this investigation may be summarized as follows.

1. A satisfactary method for preparing pure anhydrous zinc chloride has been devised. This consists in first dehydrating zinc bromide and then converting the bromide to chloride in a current of dry chlorine.

2. The percentage of zinc in zinc chloride has been found to be 47.970, and the atomic weight of zinc 65.38.

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STATISTICAL MECHANICS AND CHEMISTRY.

BY E. P. ADAMS.

In the last few years many attempts have been made to apply the quantum theory to problems of chemical dynamics. Some of these applications have made use of a quantum theory in a rather more definite form than has been found necessary in the physical applications where the theory has had much success. If the laws of chemical dynamics are found to be consistent with the principles of statistical mechanics it would seem to be not only unnecessary, but unjustifiable, to introduce the quantum theory in order to derive these laws. That the quantum theory is of importance in general chemical theory is probable; neither statistical mechanics nor the first two laws of thermodynamics give any information as to the constants which enter into the various thermodynamic functions. These constants depend upon the behavior of systems at or near the absolute zero of temperature, and it is in this region that the quantum theory has

had considerable success.   But this is quite a different matter from assuming that the mechanism of chemical reactions and transformations re quires the use of the discontinuities inherent in any form of a quantum theory.

The attempt of Marcelin[1] to base a theory of chemical dynamics upon the principles of statistical mechanics is therefore of great importance. Tolman[2] has recently criticized the work of Marcelin on the ground that the latter has confused Gibbs' canonical distribution of an ensemble of systems with the Maxwell-Blotzmann distribution.   It is the main object of this note to show that this criticism is unfounded.

Consider a system of a very large number, N, of similar molecules. Let each molecule have n degrees of freedom, the coördinates and momenta being q_1, q_2, ..., q_n and p_1, p_2, ..., p_n respectively.   The Maxwell-Boltzmann law states that the number of molecules whose representative points in the $2n$-dimensional space lie within the element of extension-in-phase $dq_1 dq_2 .... dp_n$ is

$$dN = C\, e^{\cdot \epsilon/kT}\, dq_1 dq_2 .... dp_n. \tag{1}$$

ϵ is the energy of a single molecule expressed as a function of q_1, q_2, ...p_n, and also of certain external parameters, a_1, a_2, ... k is the gas constant for a single molecule, and T the absolute temperature. C is a constant as far as depending upon the individual molecules is concerned, but does depend upon T and the parameters a_1, a_2....   We can accordingly write $C = e^{\psi/kT}$ where ψ may depend upon T and a_1, a_2.....   Then (1) becomes

$$dN = e^{(\psi-\epsilon)/kT}\, dq_1 .... dp_n. \tag{2}$$

In this form the Maxwell-Boltzmann distribution law is similar in form to the Gibbs law of canonical distribution.   Instead of considering one system made up of individual molecules, Gibbs considers an ensemble of N' systems each of which is a system of N' molecules, represented by a single point in $2Nn$-dimensional space.   The canonical distribution is a distribution of these points such that the number in an element of extension-in-phase $dq_1 dq_2 .... dp_2\; N$ is

$$dN' = N'e^{(\psi'-\epsilon)/\Theta}\, dq_1 dq_2 ..... dp_{2nN'} .$$

ϵ' is the whole energy of any system; ψ' has the same value for all the systems, and when applied to a gas Θ may be taken equal to kT.   Gibbs shows that ψ' is analogous to the free energy of any one of the systems of the ensemble.   It will now be shown that the ψ in Equation 2 may be interpreted as proportional to the free energy of the single system considered, without making any use of the Gibbs canonical distribution.

Write $\Theta = kT$ in (2) and integrate over all phases of the q's and p's. The whole number of molecules in the system is then

$$N = \int .... \int e^{(\psi-\epsilon)/\Theta}\, dq_1 .... dp_n. \tag{3}$$

[1] Marcelin, *Ann. Phys.*, **3**, 120 (1915).

[2] Tolman, THIS JOURNAL, **42**, 2506 (1920).

The average value of any function of the coördinates and momenta is

$$\overline{F} = 1/N \int \ldots\ldots \int F\, e^{\,(\psi-\epsilon)/\Theta}\, dq_1\ldots\ldots dp_n. \tag{4}$$

The whole energy of the gas is

$$E = N\bar{\epsilon} = \int \ldots\ldots \int \epsilon\, e^{\,(\psi-\epsilon)/\Theta}\, dq_1\ldots dp_n. \tag{5}$$

The force exerted by the gas as a whole along any one of the external parameters, a_s, is

$$A_s = \int \ldots\ldots \int (-\partial\epsilon/\partial a_s)\, e^{\,(\psi-\epsilon)/\Theta}\, dq_1\ldots\ldots dp_n. \tag{6}$$

Differentiate (3) by a_s.

$$0 = \int \ldots \int {}^1/_\Theta\, \partial\psi/\partial a_s\, e^{(\psi-\epsilon)/\Theta}\, dq_1\ldots dp_n - \int \ldots \int {}^1/_\Theta\, \partial\epsilon/\partial a_s \epsilon^{\,(\psi-\epsilon)/\Theta}\, dq_1\ldots dp_n$$

By (3) and (6) this becomes

$$A_s = \partial/\partial a_s\,(N\psi). \tag{7}$$

Now take the complete differential of (3).

$$0 = d\,(^\psi/_\Theta)\, N + d\Theta/\Theta^2 \int \ldots\ldots \int \epsilon\, e^{\,(\psi-\epsilon)/\Theta}\, dq_1\ldots dp_n -$$
$${}^1/_\Theta\Sigma \int \ldots\ldots \int \partial\epsilon/\partial a_s\, e^{\,(\psi-\epsilon)/\Theta}\, dq_1\ldots dp_n,$$

where the summation in the last term is over all the external parameters a_s. By (5) and (6) this becomes

$$N d\,(^\psi/_\Theta) + E\, d^\Theta/_{\Theta^2} + {}^1/_\Theta\Sigma\, A_s da_s = 0.$$

The work done by the gas against the external parameters is

$$dW = \Sigma\, A_s da_s;$$

and writing $\Theta = kT$, we get

$$N d\psi + (E - N\psi)\, dT/T + dW = 0. \tag{8}$$

Equation 8 is a statistical equation obtained from the Maxwell-Boltzmann distribution law.

The thermodynamic definition of free energy is $F = E - TS$, where S is the entropy. Therefore

$$dF - dE + T\, dS + S\, dT = 0.$$

The first and second laws of thermodynamics give

$$dE = dQ - dW = T\, dS - dW.$$

Therefore

$$dF + S\, dT + dW = 0. \tag{9}$$

This is a thermodynamic relation. Comparing with (8) we see that with

$$F = N\psi \tag{10}$$

the statistical and thermodynamic relations are consistent with each other.

Now consider m gram-molecules of a gas consisting of N' molecules. Then $N' = mN$, where as usual, N is the number of molecules in one gram, molecule. In place of the gas constant, k, for a single molecule use R-

the gas constant for one gram-molecule, $R = Nk$. The Maxwell-Boltzmann distribution law may now be written

$$dN' = e^{F/mRT - N\epsilon/RT}T \ dq_1\ldots\ldots dp_n \ .$$

If we write

$$Z = \int \ldots\ldots \int \ e^{-N\epsilon/RT} \ dq_1\ldots\ldots dq_n.$$

where the integration is over all phases, we have

$$N' = e^{F/mRT} \ Z;$$

or

$$F = -mRT \log Z + mRT \log N'.$$

This gives the free energy of m gram-molecules of the gas. The affinity is

$$A = -\partial F/\partial m = RT \log Z - RT \log N' ;$$

from which

$$N' = e^{-A/RT} Z.$$

The Maxwell-Boltzmann distribution law may now be written

$$dN' = e^{-A - N\epsilon/RT} \ dq_1\ldots\ldots\ldots dp_n, \tag{11}$$

which is the form used by Marcelin, and may thus be derived without making use of the canonical distribution of Gibbs.

Another criticism that Tolman makes of Marcelin's theory is that the latter has not considered the rôle of radiant energy in chemical transformations. There is, however, nothing in Marcelin's theory opposed to the view that radiant energy may be of primary importance in chemical transformations. If, as is probable, radiation is a determining factor in problems of chemical dynamics, emission and absorption of radiation by the molecules, in Marcelin's theory, are continuous. In this connection it should be noted that Bohr has shown that in the region of long wave lengths the frequencies of emission of radiation may be determined by the principles of ordinary dynamics and electrodynamics without the use of any quantum hypothesis. If the general validity of Marcelin's argument be admitted, and, as in other applications of the principles of statistical mechanics, there are many difficulties to be overcome before this can be done, it would appear that the frequencies effective in ordinary chemical transformations lie within the region of the long wave lengths.

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