the ONSAGER CONFERENCE

By Martin J. Klein

L. Onsager, P. H. E. Meijer, N. G. van Kampen, and J. Gibbs on the campus of Brown University, where the International Conference on Irreversible Thermodynamics and Statistical Mechanics of Phase Transitions was held June 11–16, 1962. *(Photo by E. Meeron)*

IN 1931, while he was a research instructor in chemistry at Brown University, Lars Onsager published two papers on the theory of reciprocal relations for irreversible processes, and thereby laid the foundations for the now flourishing subject of irreversible thermodynamics. As a most fitting recognition of the thirtieth anniversary of this achievement, Brown University played host, this past June, to an International Conference on Irreversible Thermodynamics and the Statistical Mechanics of Phase Transitions (sponsored by the International Union of Pure and Applied Physics, the National Science Foundation, and the Air Force Office of Scientific Research). The conference began with a suitably impressive ceremonial session at which President Barnaby Keney of Brown conferred the University's honorary degree of Doctor of Science upon Onsager, who is now J. Willard Gibbs Professor at Yale.

Onsager's name is, of course, as inseparably linked to the theory of phase transitions as it is to irreversible thermodynamics, and the conference at Brown could just as well have marked the twentieth anniversary of Onsager's exact solution of the two-dimensional Ising problem. The paper in which Onsager published this solution in 1944 contains the first rigorous theory ever developed for a phase transition. In the speech he made in 1958, when the Lorentz medal was awarded to Onsager, F. Zernike rightly referred to this paper as "a truly incomparable memoir", whose mathematical heights "most theoretical physicists would have to be content to observe with respectful deference—from afar".

About a hundred physicists, chemists, and mathematicians gathered in Providence for this conference honoring Onsager to discuss the two themes of irreversible processes and phase transitions over the course of a week. It was indeed an international gathering, with representatives from most countries of western Europe and from Japan making up close to a quarter of the membership. The program, which was arranged by John Ross of Brown, George Uhlenbeck of the Rockefeller Institute, and Elliott Montroll of the IBM Research Center, covered many of the problems under most active study in the two areas of interest. Although there were only about thirty papers presented, they extended over a surprising range of problems and techniques, and gave a lively impression fo the activity in present-day statistical mechanics. Since the full proceedings of the conference will be published in the *Journal of Mathematical Physics*, I shall try to give a complementary account here, with emphasis on the background and setting of some of the papers, and with no attempt at complete coverage.*

THE intense current interest in the statistical mechanics of irreversibility marks the revival of a tradition which goes straight back to Maxwell and Boltzmann. Boltzmann, especially, wrestled long and hard with the problem of irreversibility, and had to defend his statistical interpretation of the second law of thermodynamics against strong opposition. It was also Boltzmann who first formulated the integrodifferential equation, the Boltzmann equation, which describes the irreversible behavior of a dilute gas. Both Maxwell and Boltzmann calculated transport coefficients, such as the viscosity coefficient, for dilute gases. All of these matters are once again the center of lively discussion. The years since the end of the Second World War have brought many studies of the nature of irreversibility, and of the status of the ergodic theorem and the Boltzmann H-theorem. There have also been many efforts to rederive the Boltzmann equation, and to do it in a more fundamental way which allows one both to assess the status of Boltzmann's assumption about the number of collisions of a given type (the "Stosszahlansatz"), and to generalize the Boltzmann equation so that one can discuss irreversible processes for systems more general and more complex than a dilute gas.

This program of establishing a general statistical mechanics of irreversible processes has been worked on by many physicists, in many countries, using many different approaches to the problems. The status of the field as it was in 1956 can be gauged by inspecting the proceedings of the international conference, held in

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* I should like to thank Professor John Ross for his help in assembling materials for this report, and also, on behalf of the conferees, for his efforts in making the conference the pleasant and fruitful event which it was.

Brussels that year, to discuss these subjects. If one tries to characterize the progress made since then, as it emerged from the papers presented at the Onsager conference at Brown, one dominant impression is of the great developments in the mathematical weapons used on the problem. In the work of Van Hove, of Prigogine and his co-workers, of Montroll and Ward, of Luttinger, and others, the powerful methods of quantum field theory have been brought to bear on statistical problems. Recent papers in statistical mechanics are at least as liberally illustrated with "diagrams", for schematic representation of the various kinds of terms in the series expansions used, as are papers in the field theory proper.

These methods have brought results. Both Van Hove and Prigogine and his group in Brussels have been able to derive systematic generalizations of the Pauli or master equation. (This latter is the simplest form of stochastic equation describing irreversibility, first derived by Pauli in 1927 in his study of the quantum-mechanical H-theorem.) The latest phase of the Brussels studies was reported on at Brown by Professor Prigogine and P. Résibois. E. Verboven discussed current work, done in collaboration with Van Hove and A. Janner, which is an attempt to see further into the rather complex equations of the general theory by carrying out detailed calculations for particular cases. A quite independent approach, also leading to generalized master equations, has been followed by R. Zwanzig of the Bureau of Standards, and there was some lively discussion of the relationships among the various methods.

One important step forward, now incorporated into almost all of these general theories of transport phenomena, was made several years ago by R. Kubo of Tokyo. Kubo developed a general method, or algorithm, for relating transport coefficients to time correlation functions. In a sense this provides a procedure for getting transport coefficients somewhat analogous to the use of the partition function in obtaining equilibrium thermodynamic properties. Professor Kubo reported at Brown on his current ideas on treating the Liouville equation stochastically.

A rather different approach to the description of irreversibility in dense gases was begun in 1946 by the work of N. N. Bogoliubov, in Moscow, and developed more recently by M. S. Green and by Professor Uhlenbeck and his students. Bogoliubov's approach leads to a systematic development of the equations describing the time evolution of the two-particle, three-particle, etc., distribution functions, and treats the time development as occurring in rather well-defined stages. At each stage the system has "forgotten" more and more of the information contained in the initial N-particle distribution function. Thus Bogoliubov assumes that after a time of the order of the duration of a collision between molecules, all the higher-order distribution functions depend on time only as functionals of the single-particle distribution function. At the next, or "hydrodynamic" stage, only the first few moments of the single-particle distribution, i.e., the local values of density, temperature, and flow velocities, are needed to describe the evolution of the system.

Bogoliubov's assumptions are rather hard to assess and several of the papers at Brown were devoted to exploring his ideas from various points of view. Melville Green reported on an attempt to investigate just how the higher-order distribution functions evolve into functionals of the single-particle function, and what this functional dependence is like. E. G. D. Cohen of Amsterdam showed how Bogoliubov's equations could be obtained from another starting point, and developed a detailed correspondence between the expansions of the nonequilibrium distribution functions and the well-known cluster expansions for the partition function of dense gases in the equilibrium theory.

To conclude my report on this first aspect of the conference, I should like to point out that there is still a gap between the theoretical developments and the experimental phenomena which they should presumably explain. The general theories, despite their apparent power and scope, or perhaps because of it, do not yet lead to very many predictions of behavior to be studied by the experimentalist. Emphasis was laid on this point by S. A. Rice, who reported on both experimental measurements of transport coefficients in simple dense fluids, and an attempt to understand them by the methods developed in the important series of papers by the late John Kirkwood and his many students.

PHYSICISTS have been trying to understand the occurrence of phase transitions by the use of statistical mechanics since the famous dissertation of van der Waals in 1873. The years just before and during the Second World War brought two most important steps forward in this effort. In 1937 J. E. Mayer and his co-workers developed a systematic procedure, the method of cluster expansion, for expressing the virial coefficients of the equation of state in terms of certain integrals involving the intermolecular potential energy. This method was quickly developed and put into more rigorous form by Born and Fuchs and by Kahn and Uhlenbeck, and, for a time, it looked as though one would soon be in a position really to understand the condensation of gases and the critical point. It has not worked quite that way; despite many valiant efforts and much mathematics, and despite important work by Van Hove and by Yang and Lee, we are not yet in possession of a real theory of condensation. All of us at the conference were properly reminded by Mark Kac in his banquet remarks that the theorists are still subject to the accusation in the clerihew:

"Sir James Dewar
Is cleverer than you are.
None of you asses
Can condense gases."

A second line in the growth of the theory of phase transitions began with the model put forward by Ising in 1925 in an attempted explanation of ferromagnetism.

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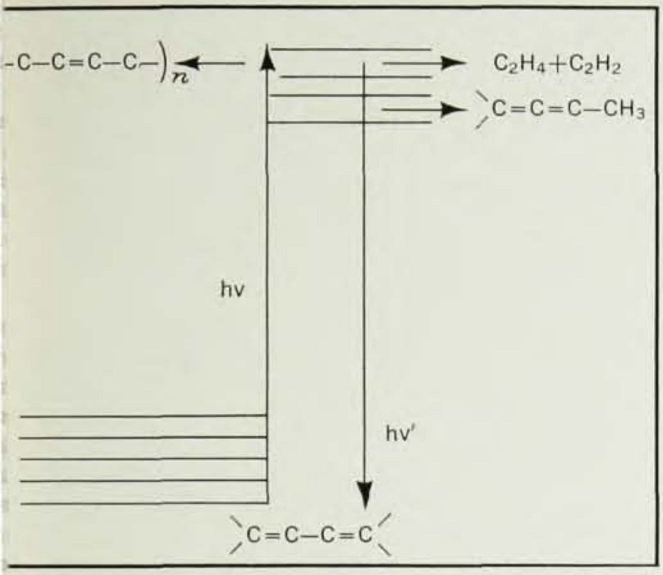
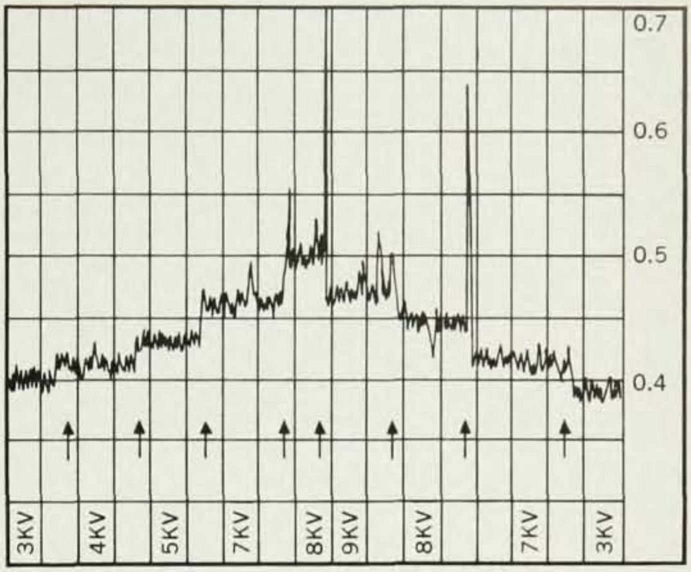


he Excited State. This sketch describes possible behavior molecules of butadiene upon absorbing light energy. 'ithin 1,000 nanoseconds, they may undergo either poly-erization, isomerization, or decomposition.



The Stark Effect. This spectrogram shows changes in optical density of methyl red at the absorption edge of the band. Similar measurements on the opposite edge of the band indicated a shift to the red rather than a band broadening.

'rganic materials are a potential source of new gh-speed components for data processing systems. he discovery of these components will depend on a :tailed understanding of the physical properties of oth known chemical systems and new systems. To :lp develop this understanding, IBM is investigating ıe mechanism of energy transfer which occurs 'hen light is absorbed by organic molecules.

n organic molecule can react to a quantum of ıergy in a number of ways, as shown above. In one :oject, aliphatic dienes and trienes are exposed to traviolet light. Then the effects produced by the ave length, pressure, and temperature are deter-ıined. This study will also help to define the con-ıtions required for photochemical synthesis of ınusual compounds.

ı another project, scientists are studying the physi-ıl properties of materials in the excited state. The ıift of an isolated absorption band due to an oplied electric field has been observed for an or-ınic dye molecule dispersed in a solid matrix. This as the first time that this shift, known as the Stark ffect, had been observed in an organic solid. The 'ganic dye (methyl red) was imbedded in a non-olar transparent plastic film. A high-voltage D.C. :ld was applied, and the resulting changes in op-:al density were measured with a spectrophotom-er. The spectrogram is shown above. Anticipation of these results led the scientists to conclude that the dipole moment of methyl red does not change significantly between the ground and excited states. They further concluded that a quantum mechanical explanation was required to describe this phenomenon. The development of this technique provides science with an additional independent physical parameter which can be used in the study of excited states of organic molecules.

IBM scientists are also investigating the chemical changes which take place when adsorbed gas molecules are elevated into excited states. They have examined mechanisms by which a polymer film is formed on a surface exposed to ultraviolet light in the presence of butadiene. Their results indicate a mechanism of selective surface photolysis in which reaction of the adsorbed gas occurs. From research like this will come new insights into the formation of new types of thin films which may prove to be of great importance in cryogenic and microelectronic devices.

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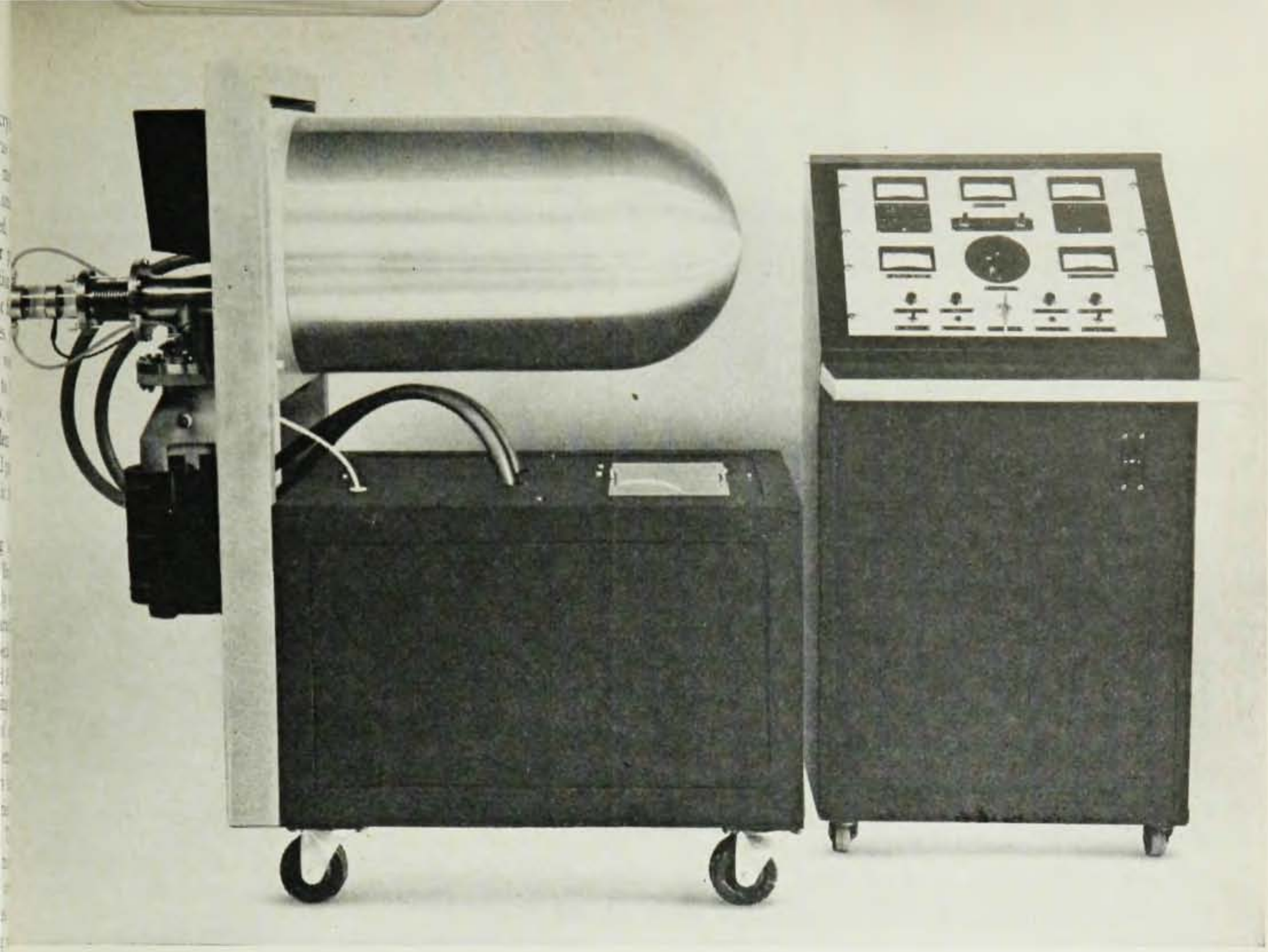
This Ising model, a system of scalar spins on a crystal lattice with nearest-neighbor interactions only, was developed during the 1930's by various approximate methods for the understanding of order-disorder phenomena in binary alloys. Few exact results were obtained, but finally in 1944, as already mentioned, Onsager published his exact solution for the partition function of the two-dimensional Ising model in zero magnetic field. Once again this major achievement raised hopes, this time hopes that the three-dimensional problem would prove tractable, but despite simplifications due to Onsager and Bruria Kaufman, despite a wholly new, combinatorial solution of the two-dimensional problem by Mark Kac and John Ward, the three-dimensional problem and the Ising model in an external magnetic field are still unclimbable peaks.

Nevertheless, progress *is* being made along both lines, and this progress was reported at the Brown meeting. There was only one paper dealing directly with the theory of condensation, but that was a characteristically masterful lecture by Professor Uhlenbeck on the work he has been doing with Mark Kac and P. C. Hemmer at the Rockefeller Institute. Considering the great difficulties which have blocked a theory of condensation based on the cluster integral—virial expansion approach, Uhlenbeck and his collaborators have gone back to van der Waals' ideas, and have tried to reformulate them along rigorous modern lines. Their starting point has been a one-dimensional gas model, introduced in 1959 by Kac, which has the great virtue that everything about it can really be calculated exactly. The model consists of N particles moving on a line of length L. The particles interact in pairs through a potential which consists of a hard core of radius δ and an exponential attraction of the form $(-\alpha e^{-\gamma x})$. This model does indeed show a phase transition in the limit where α and γ approach zero, but α/γ remains fixed. This van der Waals limit, as the authors call it, must be taken *after* the thermodynamic limit, in which N and L become infinite, but the ratio of N to L is fixed. If that is done, the van der Waals equation of state is obtained as an *exact* result, and one also *automatically* obtains the Maxwell construction which eliminates the unstable portion of the isotherm.

Uhlenbeck, Kac, and Hemmer have worked out a good many other features of the Kac model including the pair-distribution function, and its behavior at, and near, the critical point. This last is especially interesting as it shows that the theory of Ornstein and Zernike gives correct results for the pair-distribution function *except* in the immediate neighborhood of the critical point, despite the fact that Ornstein and Zernike developed their theory precisely for the study of the critical points.

Although the exact analysis of Uhlenbeck, Kac, and Hemmer is worked out only for this rather special one-dimensional model, it has led to a number of most suggestive ideas as to what one can expect from a theory of a real three-dimensional gas, and as to how such a rigorous condensation theory *might* be developed.



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Uhlenbeck was, of course, very careful to separate the rigorously proved theorems from the list of "hopes and dreams".

The last two sessions of the Onsager Conference dealt with current work on the Ising model and on a number of combinatorial and graph-theoretical problems closely related to the Ising problem. Michael Fisher of King's College, London, who has been among the most active in this field in the past few years, reviewed the general problem of lattice statistics and discussed the exact isotherm of a plane lattice gas. (The lattice gas is still another interpretation of the Ising problem due to Yang and Lee.) P. W. Kastelijn of the Shell Laboratory in Amsterdam reported on his elegant solution of the problem of the number of ways one can arrange dimers on certain plane lattices. Kastelijn's methods are related to the Kac-Ward combinatorial solution of the square Ising lattice, and his result is also reminiscent of the Onsager partition function. Although Kastelijn has already carried out a number of generalizations of his work, and has hopes for still further success here, he does not foresee any advance on the three-dimensional Ising problem by his methods.

In the concluding discussion on the Ising model, there were several brief reports on work in progress. Among the most interesting was S. Sherman's account of his work on the combinatorial analysis involved in the Kac-Ward solution. He did strike a hopeful note with respect to the three-dimensional Ising model. In this same session, Professor Onsager gave a brief description of the method by which he calculated the long-range order (or spontaneous magnetization) of the two-dimensional Ising model. (This is a result which he anounced at the Cornell Conference on Phase Transformations in 1948, but did not publish. It was subsequently rederived in another way by Yang.) The intricate and elaborate mathematical methods described in this talk made a nice contrast with the other paper which Professor Onsager read at the Brown meeting, a paper on the dielectric properties of ice, dealing with a theory very closely tied to the experimental situation!

STATISTICAL mechanics is one branch of theoretical physics where the links with the past, the continuity of the tradition, seem to be especially evident. The reader will have noted, for example, that the names of van der Waals and Boltzmann have appeared here for their direct connection with the current work under discussion at Brown, and not just to fill in the historical background. Because of this continuity of the tradition, it was particularly impressive, and rather moving, to have been addressed, at the conference banquet, by E. B. Wilson, who was one of the last students of J. Willard Gibbs, and the author of the famous Gibbs-Wilson text on vector analysis. The picture of Gibbs which he evoked in his reminiscences provided a most appropriate touch to this conference which honored the J. Willard Gibbs Professor at Yale, Lars Onsager.