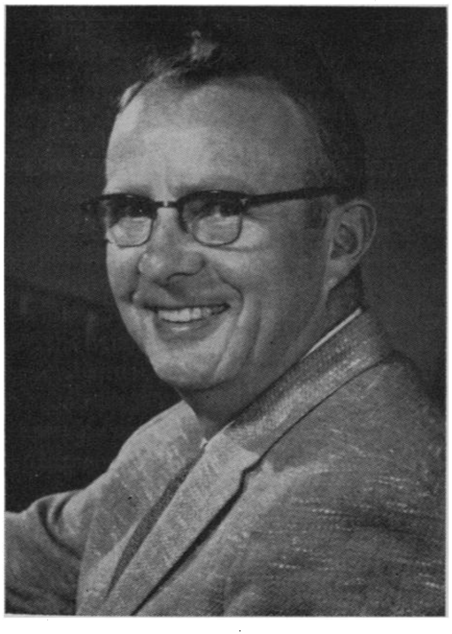
Nobel Laureates in Physics and Chemistry

1. Physics

The citation for the 1968 Nobel prize in physics, as stated in the telegram received by Luis Alvarez from the Swedish Royal Academy of Sciences on 30 October 1968, reads: ". . . for your decisive contributions to elementary particle physics, in particular the discovery of a large number of resonance states made possible through your development of the technique of using hydrogen bubble chambers and data analysis." Some call these states "resonances," as in the citation; some prefer to call them "particles"; but whatever they are called, they have aided a revolution in thought that is still going on. The familiar "elementary particles" that are commonly listed as the constituents of ordinary matter—the electron, proton, and neutron—are seen to be, not isolated entities, but members of large families of related entities, governed by laws that are not as yet completely formulated, although much insight has already been obtained. The raw material for these laws lies in the experimentally determined properties and relations of members of the particle families.

The electron and proton are stable, and can be observed at leisure. The neutron is almost stable as a free particle, and can become stable when bound in a nucleus. That is why these particles are "familiar." Other members of the particle families are unstable; they spontaneously disintegrate into other particles in a short interval after their creation and can only be observed in flight, or inferred from observations of the processes of creation and decay. This is where the bubble chamber becomes important. It allows one to see the tracks of charged particles as lines of tiny bubbles, formed in the liquid filling the chamber as the result of heat energy released along the tracks by the passage of the particles. The directions and lengths of tracks can be accurately measured, as well as their curvatures in a magnetic field, which depend on the momenta of the particles. From these data, with the help of the laws of conservation of energy and momentum, the processes leading to the formation, decay, or scattering of the particles that made the tracks can be reconstructed.

There are three major stages in bubble-chamber physics: the chamber itself with all its associated equipment, including the cameras that photograph the tracks; the track-measuring equipment; and the procedures for reducing the voluminous data obtained to meaningful form. Alvarez and his group have been pioneers in all of these stages. Alvarez first heard of the bubble-chamber idea from its originator, Donald Glaser, at a Washington meeting of the American Physical Society in 1953. With great foresight, he visualized the whole concept of large-scale bubble-chamber physics, based on the use of hydrogen as the chamber liquid because of its nuclear simplicity, which facilitates interpretation of the results. He realized that large numbers of events (such as particle decays in the chamber or collisions with hydrogen nuclei) would have to be photographed and measured because of the statistical nature of the processes. The effort would be large; a whole experimental system would have to be conceived, designed, and developed. Cryogenics, thermodynamics, optics, mechanical and electronic engineering, and computer technology would be needed, with a full supply of physical insight to guide the whole program in a fruitful direction. With characteristic boldness, Alvarez returned to Berkeley and got to work, assembling the skills needed, organizing and directing, and inventing ways around numerous difficulties.



Luis Alvarez

His program was a brilliant success. Hydrogen bubble chambers of increasing size, up to the 72-inch chamber, the first large hydrogen chamber, were built and operated. Measuring instruments were developed, first the "Franckenstein," named after engineer Jack Franck, then the SMP (scanning and measuring projector), then the spiral reader. Elaborate computer programs were written. In 1957, results in particle physics began to emerge. The primary source of high-energy protons was the bevatron, a 6.2-Bev proton synchrotron; these protons were directed onto a target, where secondary particles such as pions, kaons, or antiprotons were created; these in turn traveled through a focusing and analyzing system into the chamber; the rest of the process has already been outlined.

The first resonance found in this work was reported at the 1960 Rochester Conference by Alvarez and a group of his colleagues. It is now designated by the symbol $\Sigma(1385)$, where the Greek letter Σ refers to a subfamily of particles and the number in parentheses refers to the mass, in units equal to the mass equivalent of a million electron volts. This resonance is produced by the collision of a kaon with a proton, and decays into a lambda particle and a pion. Its lifetime is so short that it cannot make a track; the production and decay appear as a single event: kaon (the incident particle) plus proton (a hydrogen nucleus) gives lambda particle plus two pions, one from decay of the $\Sigma(1385)$ and one emitted during its creation. To make things more difficult, the lambda particle does not make a track, for a different reason: it is neutral and deposits no energy along its path; its presence is deduced from its decay into two charged pions at a distance from the event in which it was made. It is clear that a single observation of this kind gives no very profound information, but a statistical study of a large number of observations shows that the particular distribution of angles and momenta can only result from the presence of an intermediate state, the $\Sigma(1385)$, and allows the determination of its mass and even of its lifetime, which in this case is 2×10^{-23} seconds. This is a truly evanescent state, but its existence is solidly established by the elaborate chain of experimental techniques and theoretical interpretation outlined here. Many other discoveries followed—at Berkeley, at other laboratories using Berkeley film, and at laboratories that built their own bubble chambers. The many "particles" or "resonances" began to form a pattern, whose interpretation is now a major effort of theorists all over the world.

Luis W. Alvarez was born in San Francisco, California, on 13 June 1911. His family moved to the Midwest, and he attended the University of Chicago, where he received the degrees of B.S. in physics in 1932, M.S. in 1934, and Ph.D. in 1936. He then returned to the University of California as a research associate at the Radiation Laboratory of Professor Ernest O. Lawrence on the Berkeley campus. He became instructor in physics in 1938 and was made assistant professor in 1939, associate professor in 1941, and professor in 1946. His research career started early and showed, from the beginning, outstanding qualities of originality, insight, and boldness of concept. While a graduate student at Chicago, he took part in experiments establishing the east-west effect in cosmic rays, which showed the sign of the incoming particles to be positive. In his early years at Berkeley he gave the first experimental demonstration of the existence of the phenomenon of orbital electron capture by nuclei. Another early development was a method for producing beams of very slow neutrons, using a cyclotron as a source. This method led Alvarez, together with Professor Pitzer, to a fundamental investigation of neutron scattering in ortho- and para-hydrogen. With Professor Bloch of Stanford, Alvarez also used neutron scattering in measuring the magnetic moment of the neutron. Just before World War II, Alvarez proposed methods of searching for the expected but undiscovered isotopes hydrogen-3 and helium-3, and, with the help of Robert Cornog, he succeeded in finding these important nuclei.

In 1941 he took leave from the University of California to join the research staff of the radiation laboratory at Massachusetts Institute of Technology, which was being established in order to develop the new field of microwave radar. There Alvarez was responsible for a number of notable advances, the best known being the GCA (ground-controlled-approach) blind landing system for aircraft, which has become a most important aid for both military and civilian flying. In 1943 he transferred his research efforts to the field of atomic energy under the Manhattan Engineer District, first for a few months at the University of Chicago and then at the Los Alamos Scientific Laboratory in New Mexico, where he stayed until the end of the war in 1945, returning then to Berkeley. While at Los Alamos he conceived the idea of a new type of linear accelerator for protons, and on his return to Berkeley he gathered together a group of able men and built such a machine. This has served as a prototype for the heavy-ion linear accelerator now in operation at Berkeley and for the proton linear accelerators used as particle injectors by the bevatron at Berkeley and other proton synchrotrons both in this country and abroad.

The next stage of his career has already been told in the early part of this account. In recent years he has, with typical flair and enthusiasm, embarked on new projects, including one to observe cosmic rays from high-altitude balloons, and one to locate hidden chambers in the Egyptian pyramids by measuring their effect on the absorption of cosmic rays. One notes a consistent thread of imagination and ingenuity in his work, an attraction to the unusual, the difficult but possible, and the adventurous, tempered by a strong insight into what is significant. His influence on science extends well beyond the field for which the Nobel prize was awarded.

Alvarez is a member of the National Academy of Sciences, the American Philosophical Society, and the American Academy of Arts and Sciences; he is now vice president of the American Physical Society and will be its president next year. In previous recognition of his various achievements, he has been awarded the Collier trophy, the Medal for Merit, the John Scott medal, the Einstein medal, the Pioneer award of the AIEEE, the National Medal of Science, and the Michelson award, and has been granted the degree of D.Sc. by the University of Chicago and the Carnegie-Mellon University.

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2. Chemistry

The Nobel prize in chemistry for 1968 has been awarded to Lars Onsager of Yale University, with the citation "for the discovery of the reciprocal relations bearing his name which are fundamental for the thermodynamics of irreversible processes."

It is a singularly appropriate coincidence that Onsager is J. Willard Gibbs Professor of Theoretical Chemistry at Yale. Gibbs was professor of theoretical physics at Yale from 1871 until 1903; his two papers on "Equilibrium of heterogeneous systems" in the *Transactions of the Connecticut Academy of Arts and Sciences* in 1876 and 1878 are fundamental for the thermodynamics of reversible processes. Gibbs based his theoretical treatment on the equilibrium principle, which derives from the two laws of thermodynamics, which Clausius so succinctly states "Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu." This principle states that at equilibrium the entropy of a system held at constant energy cannot increase. His invention of the chemical potentials, the partial derivatives of the characteristic energy functions with respect to the masses of the components of the system, permitted precise analytical description of equilibria in multiphase multicomponent systems, a formulation which is completely independent of any model to represent the system. Gibbs achieved in this way a mathematically rigorous treatment of equilibria in general, in which observable thermodynamic properties can be explicitly given in terms of the relevant independent variables which are temperature, pressure, and concentrations, plus intensity factors which describe any external forces (in addition to pressure) which may act on the system. Onsager, in his two papers on "Reciprocal relations in irreversible processes," which appeared in the *Physical Review* in 1931, accomplished for the irreversible process what Gibbs did for the reversible. The scope of the Onsager theory is, however, broader than that of Gibbs thermodynamics. The latter might well be called "thermostatics" (as in fact was done by van der Waals and Kohnstamm in the *Lehrbuch der Thermostatik* which introduced European scientists to Gibbs' treatment of equilibria). A system at equilibrium is in a sense static: all changes which could occur in a given system subjected to an arbitrary set of initial conditions have occurred when equilibrium is reached. (Actually, of course, equilibria in real systems are dynamic, in that the generalized forward and back reactions are still taking place, but at exactly compensating rates in both directions. No macroscopic change, however, is observable. But this more detailed description requires a molecular model, which is extraneous to Gibbs thermodynamics.) An irreversible process is one which occurs spontaneously; it is precisely this kind of process which must occur in order for a system in an arbitrary initial nonequilibrium state to reach its final equilibrium state. Also, it is the type of process which occurs when a system reverts to its equilibrium state after it has been displaced in any way from equilibrium. All such processes are, in last analysis, transport processes: energy, matter, electrical charge; *something must flow* so that equilibrium can be reached. And in every case, the entropy of the system increases; that is, the time derivative dS/dt of entropy is positive. Furthermore, the class of phenomena known as steady states belong to the group of irreversible processes; when a fixed potential is applied across two electrodes immersed in an electrolytic solution, for example, the current becomes constant, while anions and cations are being transported in opposite directions and energy, measured by the product of current and voltage, is being dissipated as heat. More generally, several forces may act on the system simultaneously. As in the case of the spontaneous approach to equilibrium of a nonequilibrium system, the stationary state in a transport process is always accompanied by a positive value of dS/dt. Onsager's principle of least dissipation is to the irreversible process what the equilibrium principle is to the reversible process. That the reciprocal relations, which are necessary for the precise description of irreversible processes in general, are a consequence of microscopic reversibility and that the principle of the least dissipation of free energy can be derived as a variation principle from the same hypothesis of symmetry in past and future are the discoveries whose fundamental significance was recognized by the award of the 1968 Nobel prize in chemistry to Onsager.

Lars Onsager

The development of the thermodynamics of irreversible processes began with a consideration of heat flow in an isotropic solid as a special case; then by application of the principle of microscopic reversibility, the reciprocal relations were derived for the general irreversible process. In a gas in equilibrium, for example, this principle requires that transitions from a state characterized by velocities ($\mathbf{v}_1'$, $\mathbf{v}_2'$) to one corresponding to ($\mathbf{v}_1''$, $\mathbf{v}_2''$) and those for the transition ($-\mathbf{v}_1'$, $-\mathbf{v}_2'$) to ($-\mathbf{v}_1''$, $-\mathbf{v}_2''$) which results from replacing time t in the equations of motion by $-t$ must occur equally often. More generally, the principle requires that a displacement of energy $\alpha_1 \rightarrow \alpha_1'$ in the x_1 direction, followed τ seconds later by a displacement $\alpha_2 \rightarrow \alpha_2''$ in the x_2 direction must occur just as often as $\alpha_2 \rightarrow \alpha_2''$ followed τ seconds later by $\alpha_1 \rightarrow \alpha_1'$, whence it follows that the averages of the products

$$\alpha_1(t)\ \alpha_2(t+\tau) \text{ and } \alpha_2(t)\ \alpha_1(t+\tau)$$

must be equal. From this equality, it was shown that the fluctuations satisfy the equality

$$\langle \alpha_1(t) \cdot d\alpha_2/dt \rangle = \langle \alpha_2(t) \cdot d\alpha_1/dt \rangle$$

(where the time derivatives are understood as quotients, because τ, while small in the secular sense, must be large compared to τ_0, the time interval between successive molecular collisions).

The general transport problem is described by the system of phenomenological equations

$$J_i = \Sigma_k L_{ik} X_k$$

where J_i is a generalized current and the X_k's are the conjugate driving forces: for electric fields, X_k is field intensity; for heat flow, it is temperature gradient; for diffusion, it is gradient of chemical potential. By considering fluctuations in the averages of energy densities given by the principle of microscopic reversibilty, Onsager then showed that the off-diagonal elements of the conductance matrix **L** were pairwise equal, that is,

$$L_{ik} = L_{ki}$$

These are the famous reciprocal relations. Their physical meaning can best be explained by an example. Suppose two different forces X_1 and X_2 act on a system. Each will produce a direct effect, proportional to its magnitude; these currents are $L_{11}X_1$ and $L_{22}X_2$. But there will also be present cross terms or interference effects; the force X_1 will contribute an amount $L_{21}X_1$ to the current J_2 and X_2 will generate a flux $L_{12}X_2$ as part of the total current J_1. The reciprocity lies in the equality of the conductance coefficients L_{12} and L_{21} which describe the cross terms. In the alternative formulation

$$X_j = \Sigma_k R_{jk} J_k$$

where the R_{jk}'s are generalized resistances, the coefficients R_{jk} and R_{kj} are equal, because the resistance matrix equals the inverse of the symmetrical conductance matrix. Onsager also showed that the reciprocal relations can be expressed in terms of a potential, the dissipation function Φ, which is a quadratic in the rates $d\alpha_j/dt$, by requiring that the difference between rate of production of entropy dS/dt and Φ be a maximum:

$$\delta[dS(\alpha, d\alpha/dt)/dt - \Phi(d\alpha/dt, d\alpha/dt)] = 0$$

Electrokinetic phenomena represent a typical case of coupled effects in an irreversible process. Consider two electrolytic solutions of the same concentration, at the same temperature T, separated by a porous diaphragm, and apply a potential ΔV across a pair of electrodes placed in the two compartments. The electrical current J_1 is given by

$$J_1 = L_{11}\,\Delta V/T + L_{12}\,\Delta p/T$$

where Δp is the difference in pressure which develops. The flux of matter (ionic flow) J_2 is given by

$$J_2 = L_{21}\,\Delta V/T + L_{22}\,\Delta p/T$$

The streaming potential $(\Delta V/\Delta p)_{J1=0}$ is $-L_{12}/L_{11}$, and the electro-osmosis is the ratio $(J_2/J_1)_{\Delta p=0} = L_{21}/L_{11}$. The electro-osmotic pressure is $(\Delta p/\Delta V)_{J2=0} = -L_{21}/L_{22}$ and the streaming current is $(J_1/J_2)_{\Delta V=0} = L_{12}/L_{22}$. The reciprocal relation $L_{12} = L_{21}$ predicts equality between streaming potential and electro-osmotic flow per unit current, and between electro-osmotic pressure and streaming current, experimentally verifiable relations between effects which superficially might appear to be independent. Another example of coupled effects in irreversible processes is given by the diffusion of gases through a porous wall separating two compartments held at different temperatures. Both mass flow and heat flow occur, due to the simultaneous transport of matter and energy through the diaphragm, and again the equality of the coefficients L_{12} and L_{21} relate the energy flux due to pressure difference to the material flow caused by the temperature gradient. Many biological processes involve a coupling between diffusion and chemical reactions; from the thermodynamic point of view, a living cell exists in a steady nonequilibrium state, maintaining internal concentrations different from those in the environment, against the existing gradients of chemical potential. Transport across cell membranes represents a typical irreversible process to which the reciprocal relations must apply.

Onsager has made many other contributions to theoretical chemistry and physics, in addition to the reciprocal relations. His first published work, in 1926, was a derivation of the electrophoretic term in electrical conductivity, in a form which involved no arbitrary parameters. This was followed in 1927 by a recalculation of the relaxation effect in conductance, which had previously been investigated by Debye and Hückel. Onsager's treatment of the problem included consideration of the Brownian motion of the ions; the basic equations of motion coupled diffusion due to local concentration gradients with ionic motion produced by the field due to the asymmetry in the distribution of charges surrounding a given ion. Together, the electrophoretic and relaxation effects led to an exact prediction of the limiting square-root behavior of equivalent conductance. In 1932, Onsager and Fuoss completed a comprehensive treatment of transport processes in solutions: conductance, viscosity, and diffusion were calculated for an arbitrary mixture of electrolytes at low concentrations. The reciprocal relations were used to derive the entire matrix of cross coefficients for mobility in conductance and diffusion. Another problem in electrolytes was solved by Onsager in 1934, by calculation of the effect of high fields on the dissociation of ion pairs; the observed linear increase in conductance with field strength (second Wien effect) was theoretically predicted. Later, the effects of high fields on relaxation and electrophoresis were derived, both for simple electrolytes and for mixtures; the observed increase in conductance, proportional here to the square of field strength (first Wien effect), was correctly given by the Onsager-Wilson-Kim theory. A fundamental contribution to the theory of dielectrics was provided by Onsager's recognition of the reaction field which a dipole generates in its environment; this led to the first realistic description of polar liquids. In 1944, the partition function for the two-dimensional Ising model was computed, and from this the thermodynamic properties. Logarithmic singularities similar to those later observed in real three dimensional systems were predicted. From about 1940, Onsager became active in low temperature physics: he suggested the existence of quantized vortices in liquid helium below the λ-point and theorized about their behavior. His observations on the general interpretation of the oscillatory diamagnetism in metals led to the development of a powerful method for the experimental mapping of their Fermi surfaces, particularly by D. Schoenberg. More recently, Onsager has been concerned with conductance and dielectric relaxation in ice, and with other problems in the general field of proton, electron, and ion conductance.

Onsager received the Ch.E. degree from the Norwegian Technical Institute in 1925. He was with Debye in Zurich until 1928, when he came to the Johns Hopkins University. Next, he was instructor in chemistry at Brown University, 1928 to 1933. He came to Yale as Sterling Fellow in 1933, and received the Ph.D. from Yale in 1935. He was appointed assistant professor in 1934, associate professor in 1940, and promoted to full professorship in 1945. He was elected to membership in the National Academy of Sciences in 1947. He has received honorary doctorates from Harvard (1954), the Technical University of Trondheim (1960), Rensselaer Polytechnic Institute (1962), Brown (1962), the Rheinisch-Westfachlische Technische Hochschule (Aachen, 1962), and the University of Chicago (1968). Other awards include the Rumford Medal of the American Academy of Arts and Sciences (1953), the Lorentz Medal of the Royal Netherlands Academy of Sciences (1958), the Gilbert Newton Lewis Medal of the Berkeley Section of the American Chemical Society (1962), the John Gamble Kirkwood Medal of the New Haven Section of the American Chemical Society (1962), the J. Willard Gibbs Medal of the Chicago Section of the American Chemical Society (1962), the Theodore William Richards Medal of the Northeastern Section of the American Chemical Society (1964), the Peter J. W. Debye Award in Physical Chemistry (1965), and the fifth Annual Award of the Belfer Graduate School of Yeshiva University (1966).

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