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Einstein, Specific Heats, and the Early Quantum Theory

Einstein's quantum theory of specific heat first showed the power of the new concept of energy quanta.

Martin J. Klein

During the month of June 1911 some 25 of Europe's most eminent physicists received invitations to take part in a select international conference whose purpose it would be to confront the scientific crisis provoked by the quantum theory (*1*). The invitations were sent by Ernest Solvay, the Belgian industrial chemist who had made a fortune with his new process for manufacturing sodium carbonate and who used his millions to support a variety of worthy causes. Solvay had an amateur's interest in the basic questions of physics, but it must have been apparent to the recipients of his letter that not even the most devoted amateur could have planned the agenda, chosen the membership, or indeed realized the urgency of the problems for which the meeting was to be convened. It did not take much searching to locate the origin of the force that had directed Solvay's enthusiastic philanthropy, since Solvay's letter asked that all replies be addressed to Professor Walther Nernst in Berlin. Among those who immediately recognized the role of the famous German physical chemist was Albert Einstein, then professor at Prague, who wrote to Nernst accepting the invitation with pleasure. "The whole enterprise is unusually appealing to me," he wrote, "and I hardly doubt that you are its soul" (*2*).

The opening lines of Solvay's letter, based on a draft by Nernst (*3*), stated some of the difficulties facing physics.

> According to all appearances, we are now in the midst of a new development of the principles on which the classical kinetic-molecular theory of matter was based. The systematic development of this theory leads, on the one hand, to a radiation formula that disagrees with all experimental results; from this same theory are deduced, on the other hand, assertions on the subject of specific heats . . . that are likewise refuted by many measurements. It has been shown, especially by Planck and Einstein, that these contradictions disappear if one sets certain limits on the motions of electrons and atoms oscillating about an equilibrium position (the principle of energy quanta); but this interpretation in turn departs so much from the equations of motion used up to now that its acceptance would necessarily and indisputably entail a vast reform of our current fundamental theories.

A decade had already gone by since Max Planck had introduced energy quanta into physics in his successful attempt to derive the correct description of the measured black-body radiation spectrum (*4*). It had taken much of that decade for even the initiates to experience the impact of Planck's radical departure and for them also to realize the impossibility of getting along by means of halfway measures. Planck himself was a conservative thinker, but he was completely convinced that physicists would have to accept and incorporate into their future theories a fundamental discontinuity of the energy, even though it meant giving up something as basic as the Hamiltonian differential equations of motion (*5*). He was by no means sure, however, that the time was quite ripe for a general acceptance of this idea of quanta. Somewhat bitter personal experience had taught him that the partisans of a scientific theory are not so easily convinced by rational argument as they ought to be, and that his own estimate of the importance of a problem was not always widely shared (*6*). This attitude had prompted his negative response to Nernst's first tentative proposal for such a meeting the previous year. In Planck's view the necessary precondition for the conference was a widespread feeling that the current defective state of physical theory was "*intolerable*—for every true theorist," a feeling that would draw these true theorists to seek counsel together. But in 1910, at least, he doubted that such sharp feelings were widely enough shared as yet; he thought, in fact, that only a few others—like Einstein, Lorentz, Wien, and Larmor—saw the urgency of these questions. He had no question about the urgency in his own mind, of course. "For I can say without exaggeration," he wrote to Nernst, "that for ten years, without interruption, basically nothing in physics has so stimulated me, agitated me, and excited me as these quanta of action" (*7*).

Planck's Radiation Formula

Einstein was surely the one physicist about whom Planck did not have to worry. Einstein, early and independently, had recognized the real inevitability of the hopelessly incorrect radiation formula that followed from classical

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physics, and he had seen further, by far, into the implications of Planck's correct radiation formula than anyone else, including Planck himself (*8*, *9*). It is not quite true to say that Planck did not have to worry about Einstein: Einstein's views did concern him, but that was because Planck thought they went much too far. Planck had no doubt that his own new constant *h*, and the discreteness of the energy that its introduction implied, would be incorporated into the fundamental theory of the future, but he was not at all ready to accept the startling conclusions that Einstein claimed to have drawn from the radiation formula.

For Einstein had argued, as early as 1905, that the observed form of the spectral distribution of black-body radiation forced a radical revision of accepted ideas on the nature of radiation (*10*). Even without having a real theory of radiation, and guided only by his incomparable insight into the statistical meaning of the second law of thermodynamics, he asserted that electromagnetic radiation must show a granular structure. Despite all the evidence for the wave theory of light there were circumstances when light would have to be considered as made up of a collection of independent particles of energy—light quanta. Einstein's first arguments were essentially independent of Planck's theory of the radiation spectrum, and even of Planck's radiation formula, since Einstein used only the experimentally well established form of the high-frequency spectrum (the Wien distribution). In later papers Einstein generalized this work and showed in several ways that the Planck radiation spectrum implied that light must show both wave and particle properties—what we now call the wave-particle duality. He was convinced that the future theory of radiation would have to be a fusion of wave and corpuscular theories (*11*).

Planck was not prepared to give up the description of radiation as a continuous phenomenon in space and time, the description provided by the electromagnetic wave theory of light. He could argue, somewhat vaguely, against assumptions tacitly made by Einstein, but their disagreement was not sharp enough for an experimental test. Einstein had, to be sure, made detailed predictions about a good many phenomena, but the experiments were difficult and had not yet been performed in 1911. His views on the corpuscular properties of radiation were sufficiently heretical that there was no great rush of attempts to put them to the test of experiment.

When the list of subjects to be treated at the Solvay conference was drawn up, probably by Nernst and Planck with revisions by H. A. Lorentz, who was to preside, Einstein's ideas on the structure of radiation were not on the agenda. Solvay's letter of invitation listed the principal subjects to be discussed, and appropriate individuals were asked to prepare written reports on them. These reports would be distributed to all members of the conference well in advance of the meeting and were intended to provide a basis for the discussions to take place at Brussels. The plans for the meeting called for reports on both the classical theory of the key problems and their modifications according to the ideas of the new quantum theory. Thus Lorentz was to discuss the application of the equipartition theorem to radiation with its disastrous implication of the Rayleigh-Jeans distribution, and Planck would report on his own radiation theory. In a similar pairing, James Jeans was asked to discuss the classical theory of specific heat (some of whose consequences had led to puzzles of longer standing than those in the theory of radiation), and Einstein, whose extreme ideas on radiation were not specifically called for, was invited to report on the quantum theory of specific heat.

Einstein's first paper on the quantum theory of specific heat had appeared in 1907 (*12*). It was his earliest work on the quantum theory of matter, in contrast with the quantum theory of radiation. This theory of specific heat, less radical in its consequences and easier to grasp than his attempts to understand radiation, clearly had to be reckoned with. For, by 1911, it already had considerable experimental support, both direct and indirect, and this support had come in large part from Walther Nernst's laboratory in Berlin. The obvious power of Einstein's ideas in accounting for Nernst's data had made Nernst into an enthusiastic proponent of the quantum theory and probably played no small part in his drive to organize the Solvay Congress. It is this important role played by Einstein's quantum theory of specific heat that I propose to describe here.

Einstein's View of Quanta

Einstein's attitude toward the concept of quanta differed sharply from Planck's. Planck had quantized the energy of a charged oscillator interacting with electromagnetic radiation in order to justify, to derive, the radiation formula he had proposed, a formula he already knew to be in agreement with experiment. The energy quanta, whose magnitude had to be proportional to the frequency of the oscillator for thermodynamic reasons, gave Planck a first suggestion of what the constant *h* in his radiation formula might signify. (He had been convinced from the outset that this constant would take its rightful place with the velocity of light, the gravitational constant, and the electronic charge as the fundamental natural constants.) (*13*). Planck saw the quantization of the oscillator's energy as the way to achieve the radiation law; he would have avoided even that radical step if he could have, but he certainly did not want to abandon any more of the established structure of theory than he absolutely had to.

Einstein, on the contrary, had argued *from* the empirically confirmed radiation law *to* the existence of energy quanta. Where Planck saw quantization as a sufficient condition for obtaining the radiation law, Einstein claimed that the radiation law demanded the existence of quanta as a necessary consequence. And to Einstein quanta represented a basic aspect of the structure of radiation, rather than just a particular property of oscillators of a certain type. Once Einstein had recognized the significance of what his friend Paul Ehrenfest would later call the Rayleigh-Jeans catastrophe (*14*), and he recognized it very early, he never stopped probing and pondering the implications of Planck's radiation law, searching for a clue that might suggest the ideas that could replace classical theory. The paper entitled "Planck's theory of radiation and the theory of specific heat" (*12*), which Einstein sent to the *Annalen der Physik* in November 1906, reported an entirely new set of connections that he had found in the course of his probing.

He had been reworking Planck's derivation of the expression for the average energy of one of the oscillators that absorb and emit electromagnetic radiation. Planck, a novice in statistical mechanics in 1900 despite his 20 years of work in thermodynamics, had adapted an old illustrative argument of Boltzmann's to his purposes. Planck's line of reasoning did not, however, really bring out the fundamental way in which he had deviated from Boltzmann's basic assumptions. Einstein began his paper with a new derivation of this equation for the average energy, going back to the fundamentals of statistical mechanics as he had independently redeveloped them a few years earlier. He showed again that a consequent treatment by the classical methods gave the equipartition result for the average energy $\bar{E}$ of an oscillator,

$$\bar{E} = (R/N_0)T, \qquad (1)$$

where R is the universal gas constant; N_0 is Avogadro's number, the number of molecules in a gram molecular weight of any substance; and T is the temperature. This result had its roots in the basic classical assumption that equal regions of phase space should be given equal weights in the averaging process. In Einstein's own way of interpreting the probabilities used in statistical mechanics this meant that the system spent equal fractions of any long time interval in regions of equal phase volume. To avoid the equipartition result and to arrive at Planck's expression for the average energy of an oscillator one had to drop this assumption and replace it with another: only those regions of phase space in which the energy took on the discrete values $0, \epsilon, 2\epsilon, \ldots, n\epsilon, \ldots$ were to have non-zero weights, and these integral multiples of the unit energy ϵ of the oscillator were to be weighted equally. On this new assumption the average energy could readily be calculated and had the value

$$\bar{E} = \epsilon\,[\exp\,(N_0\epsilon/RT) - 1]^{-1}. \qquad (2)$$

If the quantum of energy, ϵ, is set equal to $(R/N_0)\beta\nu$, where β is the constant h/k and ν is the frequency of the oscillator, in order ultimately to satisfy the displacement law, the average energy can be written in the form

$$\bar{E} = (R/N_0)\,\beta\nu\,[\exp\,(\beta\nu/T) - 1]^{-1}. \qquad (3)$$

The frequency spectrum of black-body radiation, $\rho\ (\nu, T)$, could then be obtained by using a result Planck had derived from classical electromagnetic theory, expressing the proportionality of the spectral distribution and the average energy $\bar{E}$ of the oscillators in equilibrium with the radiation,

$$\rho(\nu,T) = (8\pi\nu^2/c^3)\,\bar{E}, \qquad (4)$$

where c is the velocity of light. If we change to the notation introduced by Planck, where k is used to denote (R/N_0) and h is used instead of $(R/N_0)\beta$, the result is the usual form for the Planck distribution law,

$$\rho(\nu,T) = (8\pi\nu^2/c^3)\,(h\nu)[\exp\,(h\nu/kT) - 1]^{-1}. \qquad (5)$$

Einstein proceeded to comment on this argument and its implications. It indicated, above all, the point at which the kinetic theory of heat had to be modified in order that it be in accord with the radiation law. This, in turn, raised a major point of principle (*12*, pp. 183-4):

> While up to now molecular motions have been supposed to be subject to the same laws that hold for the motions of the bodies we perceive directly (except that we also add the postulate of complete reversibility), we must now assume that, for ions which can vibrate at a definite frequency and which make possible the exchange of energy between radiation and matter, the manifold of possible states must be narrower than it is for the bodies in our direct experience. We must in fact assume that the mechanism of energy transfer is such that the energy can assume only the values $0, h\nu, 2h\nu, \ldots, nh\nu, \ldots.$

This was by no means all, for Einstein went on to write:

> I now believe that we should not be satisfied with this result. For the following question forces itself upon us: If the elementary oscillators that are used in the theory of the energy exchange between radiation and matter cannot be interpreted in the sense of the present kinetic-molecular theory, must we not also modify the theory for the other oscillators that are used in the molecular theory of heat? There is no doubt about the answer, in my opinion. If Planck's theory of radiation strikes to the heart of the matter, then we must also expect to find contradictions between the present kinetic-molecular theory and experiment in other areas of the theory of heat, contradictions that can be resolved by the route just traced. In my opinion this is actually the case, as I try to show in what follows.

These remarks show how inadequately this paper of Einstein's is described by those who refer to it as simply an application of the quantum theory to solids. It would be more to the point to say that the paper was written to show that there was, or would have to be, a quantum *theory*, and that the range of phenomena which could be clarified by such a theory included the properties of matter as well as those of radiation. Einstein was showing in a new way how deeply the foundations of classical physics had been undermined.

Specific Heats of Solids

The contradictions to which Einstein referred in the passage quoted above concerned the violations of the equipartition theorem that were exhibited in the specific heats of solids. The early calorimetric measurements of Dulong and Petit had shown that the heat capacities of the elements in the solid state had a common value, if these heat capacities were always taken for a gram atomic weight. This Dulong-Petit rule provided a rough method for estimating atomic weights and generally served as one of the few early indications that a kinetic-molecular theory of solids might also be possible. The Dulong-Petit rule found a simple explanation if the thermal motions of the atoms in the solid were taken to be simple harmonic oscillations about positions of equilibrium. Each atom would have three independent vibrations of this type, and, since the average energy of such a simple harmonic oscillation is just $(R/N_0)T$ from the equipartition theorem (see Eq. 1), the total energy of one mole of the solid would be $3N_0(R/N_0)T$. The heat capacity per mole is the temperature derivative of this expression, $3R$, or about 6 calories per degree.

So far there is no contradiction, of course. But this explanation of the Dulong-Petit rule proved too much, since the rule is only a rule and a number of elements have heat capacities much smaller than the Dulong-Petit value. These exceptions occur particularly among the lightest elements such as beryllium, boron, and carbon. It was also well known before 1900 that these same elements had heat capacities that varied rapidly with temperature and that approached the Dulong-Petit value at temperatures well above room temperature (*15*). The difficulty was to find "some escape from the destructive simplicity of the general conclusion," as Rayleigh expressed it in a very similar connection (*16*).

The situation was, however, even more disturbing, as Einstein pointed out after describing the facts I have just summarized. By 1906 there were good reasons to believe that atoms had an internal structure and that they contained, in some way, electrons. Einstein referred in particular to Drude's work on dispersion which indicated that, while the infrared-absorption frequencies of solids could be assigned to ionic vibrations, ultraviolet-absorption frequencies seemed to be associated with electronic vibrations. But if this were the case then once again the equipartition theorem would demand too much, since it would require a full contribution of (R/N_0) from each electronic vibration, and the heat capacity would have to be far greater than the Dulong-Petit value.

Einstein had displayed the contradictions; he now proceeded to resolve them with one stroke. For if his view of the universality of the quantum hypothesis was correct ("if Planck's theory strikes to the heart of the matter"), then the average energy of any oscillator is not given by the equipartition value, $(R/N_0)T$, but rather by the expression of Eq. 3. In this case, however, the energy and specific heat depend on the frequencies of the atomic vibrations in the solid. Einstein made the simplest possible assumption here, recognizing explicitly that he was probably oversimplifying: he took all atomic vibrations to be independent and of the same frequency ν. The energy, U, of 1 mole of the solid would then be given by the equation

$$U = 3R\beta\nu\,[\exp\,(\beta\nu/T) - 1]^{-1}; \qquad (6)$$

the specific heat follows at once by differentiating U with respect to the temperature. If the specific heat is plotted as a function of temperature, or rather of $(T/\beta\nu)$, one obtains a curve that rises smoothly and monotonically from zero at the origin and approaches the equipartition value, $3R$, asymptotically when $(T/\beta\nu)$ becomes large. Roughly speaking, the heat capacity is negligibly small when $(T/\beta\nu)$ is less than 0.1, and has about the equipartition value when $(T/\beta\nu)$ is appreciably greater than one. Since light atoms would be expected to vibrate at higher frequencies than heavier ones, other things being equal, this result already gave a qualitative insight into why the light elements had anomalously low heat capacities at room temperature.

The implications of Einstein's specific heat equation went much further than these qualitative remarks. Einstein took it for granted that the vibrations which contribute to the heat capacity included those whose frequencies could be measured by a study of the optical absorption of the solid, at least in certain cases (*17*; see also *9*, p. 34). From the known value of the constant β, he readily estimated that unless the optical absorption occurred at wavelengths greater than several microns, the corresponding vibration would make no contribution to the heat capacity at room temperature. Only when the wavelength absorbed was greater than about 50 microns (well into the infrared) would the full equipartition value of the specific heat be observed at room temperature. The data available to Einstein were consistent with these results, and his estimates of infrared-absorption frequencies from specific heat values were remarkably good, considering how oversimplified a model of the solid he had used.

Even more striking than this unexpected new relationship between optical and thermal properties was the general theorem implied by Einstein's equations: the specific heat of all solids must become vanishingly small at sufficiently low temperatures. The exceptions to the Dulong-Petit rule were not to be considered as exceptional at all; they were just substances that exhibited the universal decrease of specific heat with decreasing temperature at relatively high temperatures, because of their light atoms and correspondingly high vibrational frequencies. Diamond, for example, had a specific heat that did not approach the Dulong-Petit value until it was heated to temperatures over 1000°C, and its specific heat fell off to almost a tenth of that value when it was cooled to only −50°C. A test of the theory for other materials, particularly for the large class that did obey the Dulong-Petit rule, would, however, require experiments at low temperature. Just such experiments were even then being planned and would soon be carried out at Berlin, but not for the purpose of testing Einstein's ideas.

A New Law of Thermodynamics

The zero of the absolute temperature scale introduced by Kelvin is the only temperature with an absolute significance, but the absolute zero seemed to have no particular interest for physicists prior to 1905. In December of that year Walther Nernst proposed a new theorem, which eventually took on the enviable status of a new law of thermodynamics, that established an essential relation between the thermal behavior of matter at temperatures near absolute zero and problems of pressing and even practical interest to chemists (*18*). I do not intend to review Nernst's reasoning here, but I must point out that Nernst was concerned with chemical equilibria in gases at high temperatures. Thermodynamics left one without a method for calculating the essential constant in the condition for equilibrium, and Nernst found that this gap could be filled if he postulated that entropy differences between all states of a system disappear at absolute zero. Evidence available to Nernst made this look plausible, but much work had to be done before "the new heat theorem" would rest on secure foundations.

Nernst discussed this theorem in his Silliman Lectures at Yale in the fall of 1906 and remarked on its implications for calorimetry (*19*):

> For the specific heats of liquids or solids at the absolute zero, our hypothesis requires that every atom shall have a definite value for the atomic heat, independent of the form, crystallized or liquid (i.e. amorphous), and of whether it is in chemical combination with other atoms. Numerous measurements by different experimenters have shown, in full agreement with each other, that the atomic heats in the solid state decrease greatly at low temperatures, but at the present time it is impossible to calculate the limiting value toward which they tend. For want of a better assumption I believe we can set for the present the value of the atomic heats at absolute zero for all elements equal to 1.5. Of course it is somewhat unsatisfactory to calculate with such a doubtful value; but on the one hand we are obliged for the sake of the following calculations to make some assumption, and on the other hand it makes little difference for the following purposes what value the atomic heat has between the limits 0 and 2.

This uncertainty in the behavior of the specific heats at low temperatures had to be removed in order to test the theorem and then to use it freely. As Nernst pointed out in a paper read to the Prussian Academy a month later (*20*), it would be enough to follow the specific heats down to the boiling point of hydrogen, or in many cases only to the boiling point of oxygen, in order to observe the limiting behavior.

These measurements presented a major experimental problem. Earlier workers had been content to measure average values of the specific heat over wide temperature intervals (*21*), and Nernst had to develop new methods in order to determine the specific heat at definite temperatures, a particularly delicate job at low temperatures where the magnitudes are small. It was not until February 1910 that Nernst began to report his results (*22*). He and his co-workers had studied a wide variety of elements and compounds from room temperature down to liquid air temperatures; all had shown a marked decrease in specific heat as the temperature was lowered. Nernst remarked that "one gets the impression that the specific heats are converging to zero as required by Einstein's theory." This seems to be Nernst's first reference to Einstein's work: he reported qualitative agreement with Einstein's equation, and announced that his co-workers F. A. Lindemann and A. Magnus were in the process of examining the degree to which there was also quantitative agreement.

Nernst had more to say about this quantitative agreement a month or so later when he lectured on his work to the French Physical Society (*23*). This time he quoted Einstein's equation, described its connection with "that old enigma," the Dulong-Petit rule (an especially relevant connection to note when lecturing in France), and reported that the data so far obtained agreed very well with Einstein's specific heat formula. The support that Einstein's result gave to the new heat theorem did not escape Nernst's attention, either. But he admitted freely that Einstein's theory gave to specific heat measurements an intrinsic interest that he himself had not been aware of when he planned his experimental program. What is most striking in Nernst's remarks about Einstein's work is the glaring omission of any reference to the quantum theory. In April 1910 Nernst was obviously convinced of the importance of Einstein's result, but he was not ready yet to accept or at least to comment on the theory that had led to this result.

This reluctance did not persist much longer. Nernst apparently turned his attention almost immediately to the twin problems of extending his measurements to liquid hydrogen temperatures and acquiring a full grasp of the quantum theory behind the specific heat formula.

Vibrational Frequency

One key aspect of the situation was taken up by Frederick Lindemann, the young English physicist who was Nernst's student and collaborator during this period. The single parameter in Einstein's equation for the specific heat of a solid was the vibrational frequency; once this was fixed the value of the specific heat was determined for all temperatures. Einstein had already argued (*12*) that this vibrational frequency must be identical with the optical absorption frequency as determined by the method of "residual rays." He had also pointed out that not all thermal vibrations are optically active, since the vibrating particle could be a neutral atom rather than a charged ion (*24*). Einstein had not, however, given a general way of relating the vibrational frequency, which determined the thermal behavior, to other measurable properties of the solid. In June 1910 Lindemann submitted a paper to the *Physikalische Zeitschrift* which offered a method of filling this gap (*25*). His reasoning was based on a very simple and plausible physical assumption. At the melting point of the solid its structure is disrupted, and so Lindemann assumed that the amplitude of atomic vibrations at the melting temperature must be some definite fraction of the interatomic distance in the crystal. This assumption allowed him to express the vibrational frequency simply in terms of the melting temperature, the molecular weight, and the density. He was led to results that agreed well with optical absorption frequencies where they had been measured, and also with the frequencies deduced from the specific heat data by means of Einstein's formula. This work was done with Nernst's "constant helpful interest"; Lindemann's results surely served in turn to fortify Nernst's growing belief in Einstein's work.

The new data that Nernst obtained on specific heats down to liquid hydrogen temperatures had the same effect. All the materials measured behaved in accordance with theoretical expectations; even lead, whose specific heat had not fallen more than 10 percent in going from room temperature down to liquid air temperature, showed almost a 50-percent drop in the additional 60 degrees of cooling down to liquid hydrogen temperature. Nernst's experimental curves had the shape and structure required by Einstein's theory, and they departed from the theory only at very low values of the specific heat, where the theoretical predictions were definitely below the measured values.

Nernst described these results in several papers written early in 1911 (*26*). He was now thoroughly convinced not only that Einstein's result was essentially correct, but also that its verification was a strong argument for the quantum theory that lay behind it. He wrote,

> I believe that nobody who has acquired, by long years of practice, a reasonably reliable sense for the experimental test of a theory (never by any means a simple matter) will be able to contemplate these results without becoming convinced of the mighty logical power of the quantum theory, which immediately clarifies all the essential features.

His lecture, "On modern problems in thermodynamics," delivered to the Prussian Academy of Sciences on 26 January 1911, gave Nernst the opportunity to discuss the matter at greater length and also to become even more eloquent on the subject of the quantum theory (*27*). He now described Planck's introduction of the hypothesis of energy quanta as an innovation in the same class as those due to Newton and to Dalton. The quantum theory, he said, was, to be sure, still only a rule for calculation—"a very odd rule, one might even say a grotesque one"—but it had so proven its fruitfulness in Planck's work on radiation and Einstein's on molecular mechanics that it was the duty of science to take it seriously and investigate it from as many sides as possible.

Nernst did more than declare himself a supporter of the quantum theory: he took it seriously enough to try to apply it to new problems and to develop it further. He sketched out the way in which the quantum theory might account for the old problem of the specific heats of diatomic gases by quantizing the rotational motion, and he argued that the basic qualitative features of Einstein's result ought also to apply to the specific heats of liquids. Nernst's best known venture into the quantum theory was the paper he wrote with Lindemann in July 1911 offering a revision of Einstein's theory of specific heats (*28*). The revision was called for because of the discrepancy, already mentioned, between the theory and experiment at the lowest temperatures. Nernst and Lindemann proposed that Einstein's result for the molar heat capacity at constant volume, C_v,

$$C_v = 3R \frac{(\beta\nu/T)^2 \exp(\beta\nu/T)}{[\exp(\beta\nu/T) - 1]^2}, \qquad (7)$$

be replaced by the equation

$$C_v = \frac{3R}{2}\left[\frac{(\beta\nu/T)^2 \exp(\beta\nu/T)}{[\exp(\beta\nu/T) - 1]^2} + \frac{(\beta\nu/2T)^2 \exp(\beta\nu/2T)}{[\exp(\beta\nu/2T) - 1]^2}\right]. \qquad (8)$$

The predictions of this new specific heat formula did not differ qualitatively from Einstein's, but the Nernst-Lindemann formula accounted for the data in a much more satisfactory way, without the introduction of any new parameters.

While Nernst and Lindemann originally arrived at their result empirically, they attempted to give it a theoretical significance by associating the term apparently containing "half-quanta" with the potential energy, and the term in "whole quanta" with the kinetic energy of the vibrating atoms in the crystal. The details need not concern us here, but it is quite clear that Nernst now looked upon himself as something of a quantum theorist.

A Review of the Problem

By this time, the summer of 1911, the invitations to the Solvay Congress had been received and, for the most part, accepted. Einstein, in Prague, was preparing his review on "The current status of the problem of specific heats" (*1*, pp. 407–435). He had not devoted any large fraction of his efforts to this problem in the 4½ years since his first paper on the subject had been written. Having once established the basic point, the necessity of applying the quantum hypothesis to the vibrational motions in solids, he had turned his attention back to matters he considered more fundamental—the quantum structure of radiation and the deepening implications of his relativity theory. Einstein saw no likelihood that the theory of the specific heat of solids would point the way toward the new foundations that physicists would have to construct for their science.

He did not, however, ignore the subject completely, but returned to it in two papers published early in 1911. In the first of these (*29*) he followed up a connection, originally suggested by William Sutherland (*30*), between the elastic constants of a solid and the vibrational frequencies responsible for optical absorption. Neither Sutherland nor Madelung (*31*), who had independently proposed essentially the same idea, discussed the relationship between these vibrational frequencies and the specific heat, but Einstein naturally seized upon this additional relationship. On the basis of an admittedly crude model of the interactions within the solid, Einstein could calculate the vibrational frequency from the compressibility and other data. The agreement, for the one case where Nernst's specific heat data permitted Einstein to compare the frequency determined from his own specific heat equation, was "really surprising."

In the second of these two papers (*32*) Einstein emphasized that his theory could not be expected to account fully for the measured specific heats because in reality the vibrations in a crystal were not monochromatic, as he had originally assumed for the sake of simplicity. He attempted to do something with a model of interacting atoms, taking into account the rapid transfer of vibrational energy from one atom to its neighbors, but he could not bring this to any positive result. While he was "tormenting himself" with this calculation, he received from Nernst the proof sheets of the first report on the Nernst-Lindemann formula (*33*). Einstein immediately recognized this as a valuable empirical equation, but he was evidently unconvinced by the theoretical foundations that the authors had proposed for it. Instead Einstein interpreted the Nernst-Lindemann formula in line with his own view that there was a whole spectrum of vibrational frequencies in the solid: Nernst and Lindemann had, in effect, assumed a very simple form for this spectrum, with equal numbers of vibrations at only two frequencies, ν and $\nu/2$. Einstein was sure that the true spectrum was more complex, even though he could not see how to determine it (*34*).

The divergent views held by Nernst and Einstein on the significance of the Nernst-Lindemann formula were aired at the congress in Brussels, where both men discussed the subject of specific heats. But this difference of opinion between two leading proponents of the quantum theory was very minor compared to the fundamental disagreements that were expressed and discussed at Brussels.

The Solvay Conference

For 5 days the 21 physicists talked. Solvay's staff had seen to it that the group was handsomely housed at the Hotel Métropole, where the meetings also took place; they had no need to concern themselves with anything less weighty than the pressing problems of physics. The presiding officer at all sessions was H. A. Lorentz, who needed all his brilliant insight, encyclopedic knowledge, and linguistic fluency to keep the discussions focused and to keep the participants in real contact with each other. The formal papers ranged from James Jeans's attempt to explain all of the apparent failures of the classical theory without any recourse to the ideas of quanta to Einstein's arguments for the absolute inevitability of the quantum structure of radiation. Discussion of the papers was intense and often very pointed. Poincaré dismissed Jeans's attempts with the remark: "That is not the role of physical theories. They ought not introduce as many arbitrary constants as there are phenomena to be explained" (*1*, p. 77). Einstein complained that Planck's use of the Boltzmann relation was "a bit shocking," and that his way of proceeding deprived the relation of any physical content (*1*, p. 115).

One thing this first Solvay Congress certainly did accomplish was to sharpen the issues. Planck's fear that hardly anyone would feel the "intolerability" of the unresolved problems could now be dismissed. At the final session in Brussels such a thoughtful observer as Marcel Brillouin expressed his own conclusions, granting that they might seem "pretty timid" to the younger and bolder spirits present: "It seems certain that from now on we will have to introduce into our physical and chemical ideas a discontinuity, something that changes in jumps, of which we had no notion at all a few years ago" (*1*, p. 451). And Langevin remarked that the power of the quantum theory to discover totally unexpected relationships among phenomena as apparently distinct as optical absorption frequencies and specific heats had to be acknowledged.

The indirect effects of such a meeting are incalculable. How significant was it, for example, that Niels Bohr heard a first-hand and enthusiastic account of the proceedings from Ernest Rutherford when Bohr visited him in Manchester a few weeks after Rutherford's return from Brussels? (*35*). We do know that the 19-year-old Louis de Broglie, whose older brother Maurice de Broglie was one of the scientific secretaries of the Congress, read the discussions as the manuscript was being prepared for publication. "With all the ardor of my youth," he has written, "I was swept away by my enthusiasm for the problems discussed and I resolved to devote all my efforts to understanding the true nature of the mysterious quanta that Max Planck had introduced ten years earlier" (*36*).

There is no doubt about the enormous impression that Einstein made on his colleagues at Brussels. Frederick Lindemann, who accompanied Nernst to Brussels as a scientific secretary to the Congress, wrote home to his father the day after the meeting (*37*). Lindemann, the future Viscount Cherwell and scientific adviser to Winston Churchill, was still a very impressionable young man. He described Solvay, for example, as "a very nice man, unfortunately though with rather liberal views." He went on to write:

> I got on very well with all the people here, even with Mme. Curie who is quite a good sort when one knows her. I got on very well with Einstein who made the most impression on me except perhaps Lorentz. . . . He says he knows very little mathematics, but he seems to have had a great success with them. (*37*)

A year and a half after the first Solvay Congress the four physicists from Berlin who had attended—Planck, Nernst, Rubens, and Warburg—joined forces to recommend that the Prussian Academy of Sciences take an unusual step. They proposed that the Academy elect to full membership and award a research professorship to Albert Einstein, only 34 years old at the time. The document in which they set forth their reasons, properly described by Théo Kahan as being "of unusual interest for the history of modern ideas" in science, shows clearly that it was Einstein's work on the quantum theory of matter, and on specific heats in particular, in addition to the theory of relativity, that proved influential, and also shows what even this eminent group still thought of his ideas on the structure of radiation at that date (*38*). After a brief description of the special theory of relativity the report went on in this vein:

> Fundamental as this idea of Einstein's [relativity] has proved to be for the development of physical principles, its applications are, for the present, still close to the limits of the measurable. His study of other questions which are now at the center of interest has proved to be much more significant for practical physics. Thus, he was the very first to show the importance of the quantum hypothesis for the energy of atoms and molecular motions by his deduction of a formula for the specific heats of solids from this hypothesis. Although this formula has not been confirmed in full detail, it nevertheless correctly suggested the foundations for the further development of the new kinetic-atomic theory. He has also related the quantum hypothesis to the photoelectric and photochemical effects by establishing new and interesting relationships which can be checked experimentally, and he was one of the first to point out the close connections between the elastic constants and the optical properties of crystals.
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> In sum, one can say that there is hardly one among the great problems, in which modern physics is so rich, to which Einstein has not made some remarkable contribution. That he may some-

Photograph by Benjamin Couprie, Brussels, courtesy of Solvay et Cie., Brussels.

Participants at the first Solvay Conference, 1911. Seated, left to right: Nernst, Brillouin, Solvay, Lorentz, Warburg, Perrin, Wien, Mme. Curie, Poincaré. Standing: Goldschmidt, Planck, Rubens, Sommerfeld, Lindemann, De Broglie, Knudsen, Hasenohrl, Hostelet, Herzen, Jeans, Rutherford, Kamerlingh Onnes, Einstein, Langevin.

times have missed the target in his speculations, as, for example, in his hypothesis of light quanta, cannot really be held too much against him, for it is not possible to introduce really new ideas, even in the most exact sciences, without sometimes taking a risk.

References and Notes

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2. This letter is quoted in full in an unpublished manuscript by J. Pelseneer, "Historique des Instituts Internationaux de Physique et de Chimie Solvay." I should like to thank John Heilbron of the project, "Sources for History of Quantum Physics," for the loan of this manuscript, and Prof. Pelseneer for permission to quote from it.
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39. This work was supported in part by the National Carbon Company, a division of Union Carbide Corporation.

Miocene Mammals and Central American Seaways

Fauna of the Canal Zone indicates separation of Central and South America during most of the Tertiary.

Frank C. Whitmore, Jr., and Robert H. Stewart

The fossil mammal faunas of North and South America indicate that the two continents were separated from Paleocene or earlier time until the late Pliocene (*1*, *2*). Unfortunately our almost complete ignorance of the Tertiary land mammals of Central America, together with incomplete knowledge of the geology of this large area, makes reconstruction of the Tertiary zoogeography of the region between the continents an exercise involving considerable speculation. While the differences between the faunas of the two continents, resulting from complete and long separation, prove the existence of one or more straits of some size between North and South America, we are uncertain as to the number of straits, their location, and the time of their existence. It is almost certain that there were straits across the Isthmus of Panama (*3*), and the distribution of Tertiary marine deposits indicates a major seaway in northwestern Colombia, the Bolivar Trough (Fig. 1). Thus, the separation of North from South America did not depend on the opening of a single strait. In Central America as a whole, however, the distribution of land and water during Tertiary time can be only approximately delineated, because geologic observations, as well as fossil finds, are relatively few and scattered over a large tropical region where there are few rock outcrops. A difficulty that faces the paleogeographer studying the isthmian portion of Central America is

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