

Stempel, Phys. Rev. May, 1922). Rock-salt is of course not suited to fine structure work.

In general no crystal should be used for fine structure observation until its tolerance angle has been determined. Many specimens of calcite give quite wide rocking

curves and are unsuited to this type of experiment.

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The Third Law of Thermodynamics

R. H. Fowler admits the practical utility of the concept of absolute entropy but maintains that no theoretical significance is to be attached to the concept. This viewpoint seems at variance with the one in vogue at the present time in physics.

If we treat absolute entropy as an operational concept the only question that needs to be considered in connection with the Third Law, is whether it is ever necessary to assume the entropy of the pure stable crystalline form of a substance different from zero at 0°K in order to calculate the correct value of the entropy from the thermal data. Difficulties might be anticipated in the case of elements in which the atoms have j values different from zero where it might prove necessary to add a term $R \ln (2j+1)$ to the value obtained from the thermal data. In the case of the sodium atom (Rodebush, Proc. Nat. Acad. **13**, 185 (1927)) and the oxygen molecule (Giauque and Johnstone, Jour. Am. Chem. Soc. **51**, 2300 (1929)) it has been shown that the thermal data alone lead to the correct value, so that apparently no correction factors are likely to be needed for electronic moments.

In the case of nuclear spins the situation is otherwise. Here theoretically the thermal data alone should still give the correct value of the entropy but practically only in the case of hydrogen (Rodebush, Proc. Nat. Acad. **15**, 678 (1929)) can the correct value of the en-

trophy be obtained in the customary manner. For all hydrogen compounds we shall presumably have to add arbitrarily the quantity $R \ln 2$ per gram atom of hydrogen to the thermal entropy. In the case of other elements having nuclear spins the term $R \ln (2s+1)$ may be omitted from the entropy of elements and compounds alike for all thermodynamical calculations.

It is not to be doubted that in the case of an element such as sodium which has a nuclear spin of several half units, that a heat effect due to the change in orientation of the nuclear spins will appear at low temperatures, but the heat effect will be so small and the temperature so low that it will probably elude observation, although the corresponding entropy change is, of course, not negligible. The more or less prevalent idea that no appreciable entropy changes occur at very low temperatures is evidently not justified.

The only other case that needs to be noticed is that of elements which are isotopic mixtures. If we consider the separation of isotopes as a process which is realizable thermodynamically then we shall have to consider the isotopic mixture as a solution and solutions together with supercooled liquids are unstable forms of matter at 0°K and the Third Law does not apply to them.

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Note on Hartree's Method

Hartree's method of self-consistent fields, for determining atomic models, has seemed to many persons to stand rather apart from the main current of quantum theory; in spite of the papers of Gaunt and the writer, showing its connection with Schrödinger's equation, it has seemed to contain arbitrary and empirical elements. It appears, however, that it has a very close relation to the variation method. That principle states that, if one has an approximate wave function con-

taining arbitrary parameters or arbitrary functions, one will have the best approximation to a solution of Schrödinger's equation if one chooses the parameters or functions so that the energy is stationary with respect to slight variations of them. Suppose one sets up an approximate wave function for a general problem of the motion of electrons among stationary nuclei, by assuming a product of functions of the various electrons: $u = u_1(x_1) \cdots u_n(x_n)$; suppose further that

one apply the variation principle by varying separately each of the functions u_i , leaving the others constant. The n variation equations so obtained prove to be those for the motion of the n electrons, each in a separate electrostatic field; and the field for each electron is obtained by adding the densities u_i^2 for all the other electrons, and finding by electrostatics the field of this charge and of the nuclei. Thus this field is self-consistent in the sense of Hartree; the result is a generalization of his method to more complicated problems than atomic ones.

For atoms, Hartree's procedure differs in the one detail that instead of taking the field so obtained (which would not be quite spherically symmetrical), he averages over all directions, to get a real central field for each electron to move in. This process also can be partly, although not entirely, justified by variation methods. If one demands that the functions u_i be solutions of a central field problem—that is, that they be products of spherical harmonics of the angles, by functions of r —and vary only the function of r , then one finds that the potential should be averaged over all orientations; but with a certain weighting function, not used by Hartree, depending on the spherical harmonic occurring in the wave function of the electron for which we are finding the potential. That is, Hartree's method could be slightly changed in this matter, with slight improvement of the results; but, except for this, it is definitely the best method, in the sense of variation principle, using central fields.

Closer examination shows that the potential we have found differs from Hartree's merely in being slightly dependent on the m , as

well as the n and l , of the electron one considers. As a result, the energy levels of the different electrons of the same n and l , but different m , will differ slightly, an effect without physical meaning. In an earlier paper of the writer (Phys. Rev. **32**, 343, 1928), it is shown that essentially this same dependence on m results in only a small error, and further, that this effect has a very close connection with the resonance terms, and that by considering these also, the energy again becomes independent of m . It would therefore not be sensible to make this slight improvement in Hartree's method without at the same time making the more important one of considering resonance. If one wished to do this, one could again use variation methods, to derive a new method similar to self-consistent fields: one would demand that the wave function be written not as $u_1(x_1) \cdots u_n(x_n)$, but as a linear combination of such functions with permuted indices, so arranged as to have proper symmetry relations; and one would then vary the u_i 's to make the energy a minimum. This would give a method similar to Hartree's, but really an improvement on it. Some preliminary calculations by Drs. Zener and Guillemin indicate that it may really be feasible to carry through this improvement. Their method differs from that sketched here only in that they represent the u_i 's by simple analytic forms containing parameters, which they vary, instead of determining them by numerical solutions of a differential equation.

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An X-Ray Study of Molecular Orientation in the Kerr Effect

Perhaps the most successful theory of the Kerr effect for liquids is that which assumes a tendency toward definite orientation of the molecules under the influence of an electric field. Such a tendency towards uniform orientation should affect the x-ray diffraction pattern of the liquid by increasing the intensity of the x-rays observed at the peak of the diffraction curve. It is the purpose of this experiment to investigate the existence of such an effect.

Since, in observing the Kerr effect, the light beam is at right angles to the applied field it was thought best to arrange the path of the

x-ray beam as nearly at right angles to the applied field as possible. In order to accomplish this the following method was devised. The liquids used were placed in a cylindrical glass cell one end of which was covered by a thin window of cellophane on whose inner side thin aluminum leaf was fastened. A beam of unfiltered x-rays from a molybdenum tube operated at 35 K.V. was reflected from this face, the cell replacing the crystal of an ordinary Bragg spectrometer. Measurements of the intensity of the reflected beam were made in the ordinary manner used in crystalline reflection, namely by turning the cell through