TABLE I. Contribution of electron shells to transition probabilities.

Electron	Transition probability	Ionization potential, ev
$3p$	0.60	430
$3d$	0.27	260
$4p$	0.10	45
$4d$	0.03	7
	Sum 1.00	

quantity $1/r^4$ being canceled by positive powers arising from the wave functions), to rise to a maximum, and to become negligibly small for values of r greater than about 0.2A, so that the effect depends on the behavior of the wave function for small values of r. The required integrals have been computed numerically. For transitions from the bound s wave functions to the continuum, the probabilities prove to be negligibly small, for a rather trivial reason: the integrand is partly positive, partly negative in the range of integration on account of the innermost node of the s functions, and the contributions almost cancel. For the transitions from the p and d electrons, in the free atom, the relative contributions to the internal conversion, as computed, are given in Table I. These values are to be regarded as very rough approximations, on account of the very crude numerical integration which has so far been used to approximate the wave functions. In Table I we give also very rough approximations to the ionization potentials of the various shells, obtained by interpolation between known x-ray term values.

In the metal or in $KTcO_4$, as contrasted to the free atom, these probabilities will be affected only as the charge density of the various electronic shells is altered at distances less than 0.2A, which alone contribute to the transition probabilities. A rough estimate indicates that the $3p$ and $3d$ electrons will not be affected to a significant extent. The $4p$ shell, which certainly does not contribute to binding, will be somewhat squeezed, and very rough estimates indicate that it might increase its charge density in the required region by a few percent of its total density, giving an increase of probability of a few tenths of a percent over all. The change in the $4d$ shell is less easy to estimate. These electrons doubtless take part in the binding, both in the metal and the $KTcO_4$. In the metal, they are certainly somewhat squeezed as compared with the free atom. In the $KTcO_4$, an ionic picture, regarding the $(TcO_4)^-$ ion as being made up of $Tc^{+7}(O^=)_4$, would lead to a large removal of $4d$ electrons from the neighborhood of the Tc, piling them up around the oxygens. No one, however, supposes that this really happens, and the writer suspects that the actual density of valence electrons near the Tc atom is not very different in $KTcO_4$ from what it is in the free atom or the metal. In other words, it is uncertain whether the contribution 0.03 of the $4d$ electrons in the free atom would be increased or decreased in the crystals. These considerations, in other words, lead to the order of magnitude of a fraction of a percent for the total change, as has been observed, probably arising mostly from the $4p$ wave functions.

As to why the probability of internal conversion is greater in $KTcO_4$ than in the metal, the most straightforward explanation seems to be that the Tc atom is squeezed more in the $KTcO_4$. The Tc—Tc distance in the metal is about 2.7A.[2] The distance has not been measured in $KTcO_4$, but an interpolation between similar tetrahedral ions indicates a probable distance from Tc to O of about 1.7A. Discussion of the sizes of the atoms shows that this indicates a much greater squeezing in the $KTcO_4$, on account of the close distance of approach of the O atoms. This effect would probably be felt on the $4p$ electrons as well as on the $4d$'s; the effect would also be strong on the $5s$'s, but would not appear in the internal conversion probability on account of the small contribution of these electrons.

Of course, it is to be realized that the wave functions of the valence electrons surrounding the Tc, in the ion $(TcO_4)^-$, will be quite different from what they are in the isolated atom, and work is under way to investigate the actual form of wave functions in ions of this sort. It will not be possible to make real calculations of the effect of chemical combination on internal conversion probability until such wave functions have been studied.

I am much indebted to Dr. Bainbridge and Dr. Goldhaber for pointing out to me the interesting relations of this problem to the electronic wave functions in molecules and solids. Similar experiments may well be able to throw considerable light on the electronic distributions in compounds of various sorts.

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* Research carried out under contract with AEC.

† On leave from Massachusetts Institute of Technology, Cambridge, Massachusetts.

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Proton-Proton Scattering at 240 Mev by a Magnetic Deflection Method*

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(Received October 22, 1951)

PROTON-PROTON scattering at 240 Mev has been observed for eight angles ranging from 171.3° to 108.1° center of mass. The cross section has the previously observed isotropic behavior down to about 15° (referring to the more commonly used supplementary scattering angle for the conjugate proton) and then increases sharply by a factor of 3.5 at 8.7°. This increase at the small c.m. angle, caused in part by Coulomb effects, has the same general trend observed by Chamberlain, Segrè, and Wiegand[1] at 11.3° for 345-Mev protons. The average value of the cross section (excluding the value at 8.7°) is 4.66 ± 0.39 mb/sterad., based on a $C^{12}(p, pn)C^{11}$ cross section of 49 ± 3 mb. The error in the average value includes the statistical error, the 6 percent error in the C^{11} cross section, a 4 percent error in the beta-counter calibration, and other estimated errors.

The apparatus has been described briefly before.[2] The detectors were photographic plates placed in the tank of the Rochester cyclotron near the lower pole tip. The protons scattered by protons in a hydrocarbon $(CH_2)_n$ target arrive at a given position on a plate in a nearly collimated group which corresponds to a well-defined angle of proton-proton scattering, while the protons scattered by the carbon nucleons arrive uncollimated. The angles at which the protons entered the plates were measured with a protractor eyepiece attached to a microscope. Entrance angle distributions were obtained for both hydrocarbon and carbon targets of suitable thicknesses, the incident beam being monitored by the C^{11} activity induced in each target. The number of protons scattered by protons was determined by subtracting the carbon target distribution from the hydrocarbon target distribution. As a result of energy loss in the thinnest carbon targets that could be used, thin polystyrene $(CH)_n$ targets were used to check the distribution of protons scattered by the carbon nucleons in the polyethylene $(CH_2)_n$ targets for the laboratory angles 83.1° and 85.4°.

The center-of-mass cross sections obtained are presented in Table I and Fig. 1. The indicated errors are the statistical errors in the number of tracks in the proton-proton peak and carbon background.

TABLE I. Experimental differential scattering cross section.

$\pi-\theta_{c.m.}$	$d\sigma/d\Omega$, mb/sterad.
71.9°	4.33 ± 0.22
45.2°	4.81 ± 0.25
36.6°	4.90 ± 0.28
28.3°	4.43 ± 0.21
27.2°	4.38 ± 0.38
18.6°	4.59 ± 0.31
13.0°	5.16 ± 0.39
8.7°	$15.8\ \pm1.6$

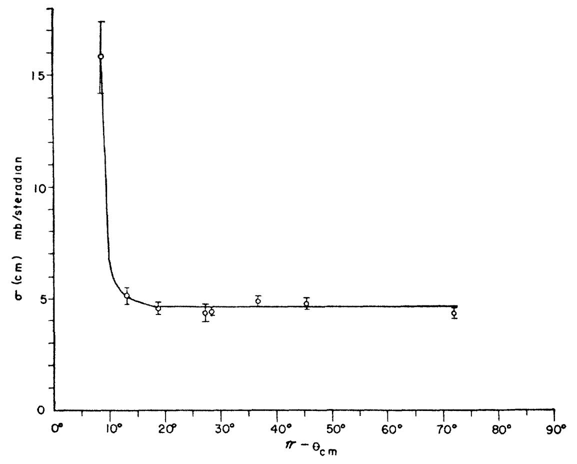

FIG. 1. Differential cross section for proton-proton scattering at 240 Mev.

These results agree with those of Oxley and Schamberger[3] of this laboratory, who obtain an average cross section of 4.97±0.42 mb/sterad from 27.5° to 90° cm. The relative error in both of these experiments is 0.22 mb/sterad, since the errors in the C^{11} cross section and the beta-counter calibration are mutual. The combined value of the two experiments gives 4.81±0.38 mb/sterad for the isotropic part of the cross section.

These measurements are about 30 percent higher than those published by Chamberlain *et al.*[1] The cause of this discrepancy is not clear at the present time.

Details of this experiment will be published at a later date. I wish to thank Professor C. L. Oxley for many suggestions during the course of this work.

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* Assisted by the joint program of the ONR and AEC.

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Thermodynamic Functions on the Generalized Fermi-Thomas Theory

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(Received July 30, 1951)

RECENTLY, equations of state of the elements[1] based on the generalized Fermi-Thomas theory have been developed. It has been shown[2] that exchange effects may be neglected for high temperatures, and they will not be considered here. In the past, the pressure has been obtained by calculating the rate of flow of momentum through the surface of the atom, which is assumed to be a sphere of radius a. It is also possible to find the pressure from the free energy or the logarithm of the partition function.[3] The purpose of this note is to show that the pressure calculated from the free energy using the generalized Fermi-Thomas model for arbitrary temperatures agrees with that found by mechanical considerations based on the same model, and, in addition, one obtains expressions for the entropy and the specific heat.

Our model leads to the kinetic energy density[4]

$$E_K(r)=(4\pi/h^3)(2m)^{3/2}\beta^{-5/2}I_{3/2}[\eta+\beta eV(r)], \tag{1a}$$

and the electron number density

$$\rho(r)=(4\pi/h^3)(2m)^{3/2}\beta^{-3/2}I_{1/2}[\eta+\beta eV(r)], \tag{1b}$$

where $V(r)$ is the total potential, V_N+V_e, and $\beta=(kT)^{-1}$. Here V_N is the nuclear potential Ze/r, and $-V_e$ satisfies Poisson's equation with the charge density $e\rho(r)=\rho_e$. The boundary conditions are the vanishing of the total potential and the electric field at the surface of the atom. The volume integral of (1a) is the kinetic energy E_{kin} and that of (1b) is Z, the nuclear charge. The potential energy E_{pot} is

$$E_{\text{pot}}=-\tfrac{1}{2}\int_0^a \rho_e V_e d\tau-\int_0^a \rho_e V_N d\tau=E_{e,e}+E_{e,N}, \tag{2}$$

where $d\tau$ is $4\pi r^2 dr$. By mathematical manipulation, one finds the virial theorem

$$E_{\text{kin}}=\tfrac{3}{2}pv-\tfrac{1}{2}E_{\text{pot}}. \tag{3}$$

The difference between our calculation and previous ones is that the pressure is obtained by macroscopic rather than microscopic considerations.

The pressure p and the entropy S are found from the free energy $F=E_{\text{tot}}-TS$, where T is the absolute temperature, by means of the thermodynamic relations,

$$p=-(\partial F/\partial v)_T, \tag{4a}$$

$$S=-(\partial F/\partial T)_v. \tag{4b}$$

The basis of our work is the Gibbs-Helmholtz equation in the form,

$$E_{\text{tot}}=(\partial/\partial\beta)[\beta F], \tag{5}$$

of which we obtain the indefinite integral. This is done by integrating the various terms of E_{tot} by parts and using the relations between the derivatives of $E_K(r)$ and ρ_e obtained by differentiating (1a) with respect to a, β, and r, including the cross derivatives. Employing Green's theorem, one finds

$$F=-\tfrac{2}{3}E_{\text{kin}}-E_{e,e}+ZkT\eta. \tag{6}$$

From the relations (4a) and (4b) it follows that

$$p=\tfrac{2}{3}E_K(a), \tag{7a}$$

$$S=T^{-1}\{(5/3)E_{\text{kin}}+2E_{e,e}+E_{e,N}\}-Zk\eta. \tag{7b}$$

The first of these is the value obtained from mechanical considerations. Consideration of the Fermi factor shows that there is a maximum value of the momentum, $p_m(r)$, given by

$$P_m^2(r)/2m=eV(r)+\eta kT, \tag{8}$$

in the sense that in the limit as T tends to zero the Fermi factor is one for $p<p_m(r)$ and is zero for $p>p_m(r)$. Integrating Eq. (8), which is the same as the last equation of Sec. IV of reference 1, over the phase space at absolute zero yields

$$(5/3)E_{\text{kin}}=-2E_{e,e}-E_{e,e}+ZkT\eta. \tag{9}$$

This shows that $\lim_{T\to 0} S=0$, as it should.

The specific heat at constant volume, C_v, given by the relation,

$$C_v=-\beta(\partial S/\partial\beta)_v, \tag{10}$$

may be expressed in the form,

$$\frac{4}{3}TC_v=\frac{5}{2}pv+\frac{7}{6}E_{e,e}+\frac{1}{6}E_{e,N}-Z\left\{\frac{\partial\eta}{\partial\beta}+e\beta\frac{\partial V_e(0)}{\partial\beta}\right\}+T\left(\frac{\partial p}{\partial T}\right)_v v. \tag{11}$$

This may be shown to agree with that given in reference 1 as T tends to zero. The expression derived in reference 1 is based upon relationships valid at $T=0$, whereas our relations are valid at an arbitrary temperature.

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[2] H. Jensen, Z. Physik **111**, 373 (1938).

[3] Marshak, Morse, and York, Astrophys. J. **111**, 214 (1950).

[4] The notation is the same as that of reference 1, except that our $\rho=-\rho_e$ of it.

The Near Infrared Spectrum of Lightning*

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(Received October 25, 1951)

ON September 18, 1951, a spectrum of lightning in the wavelength range 7100–9100 angstroms was secured on an Eastman spectroscopic plate type $1N$. The instrument used was one