

## LETTERS TO THE EDITOR

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Communications should not in general exceed 600 words in length.

### Note on the Mathematical Foundation of the Thermodynamical Equation of State

Starting from the resolution of the differential equation for the volume deviation  $\Delta v$

$$T\left(\frac{\partial(\Delta v)}{\partial T}\right)_p - \Delta v = \varphi(T, p)$$

we shall show that the thermodynamical equation of state may be given in the general form

$$vp = RT + pT \left\{ \int \frac{\varphi}{T^2} dT + \theta \right\},$$

where  $\varphi(T, p)$  denotes the function of the Joule-Thomson effect and  $\theta$  depends on pressure alone.

Any equation of state can be represented in the form

$$vp = RT + p\Delta v \quad (1)$$

where  $\Delta v$  (the "volume deviation") may be regarded as a definite function of the independent variables: pressure  $p$  or volume  $v$  and absolute temperature  $T$ ;  $R$  is the gas constant.

The thermodynamical expression for the Joule-Thomson effect  $\mu_y$  as a function of  $T$  and  $p$  gives

$$\varphi(T, p) = \frac{\mu_y C_p}{A} = T \left( \frac{\partial v}{\partial T} \right)_p - v, \quad (2)$$

where  $C_p$  and  $A$  are, respectively, the specific heat at constant pressure and the thermal equivalent of mechanical energy.

Substituting  $(\partial v / \partial T)_p$  and  $v$  in Eq. (2) from Eq. (1), we get

$$T(\partial(\Delta v) / \partial T)_p - \Delta v = \varphi(T, p). \quad (3)$$

From the differential Eq. (3), there follows the equation for  $\Delta v$  in the integral form

$$\Phi(p)\Delta v - T \exp \left( \int \frac{\varphi}{\Delta v} \frac{d\psi}{\psi} \right) = 0, \quad (4)$$

which can be resolved in the following way. From Eq. (4) we get

$$\lg \frac{\Phi(p)\Delta v}{T} = \int \frac{\varphi}{\Delta v} \frac{dT}{T}$$

or differentiating and simplifying

$$\left( \frac{\partial(\Delta v / T)}{\partial T} \right)_p = \frac{\varphi}{T^2}. \quad (5)$$

Hence integrating

$$\Delta v = T \left\{ \int \frac{\varphi}{T^2} dT + \theta \right\}, \quad (6)$$

where  $\theta$  is the arbitrary function of pressure  $p$  alone.<sup>1</sup>

Eq. (3) can be therefore regarded as a satisfactory mathematical foundation for finding the exact and general form of the thermodynamical equation of state.

But while the function  $\varphi$  of the Joule-Thomson effect is not yet satisfactorily known for any body, nevertheless the general resolution (6) and especially (4) are of great importance in limiting the arbitrariness of functional constructions of equations of state and in finding the adequate form by concrete mathematical operations.

The volume  $v$  satisfies the same Eq. (2). Hence analogously,

$$v = T \left\{ \int \frac{\varphi}{T^2} dT + \theta, (p) \right\}. \quad (7)$$

From Eq. (7) in connection with Eq. (1) and Eq. (6) follows

$$\theta_1 = \theta + R/p, \quad (8)$$

where  $\theta$  is due to the expression for the volume deviation alone.

Eq. (8) shows that for finding the equation of state the consideration of the volume deviation  $\Delta v$  is more convenient than the direct operation with the volume  $v$ , since thus the large and regularly varying term  $RT/P$  is eliminated from the calculations.

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<sup>1</sup> The Eq. (3) may also be resolved otherwise. For the case that  $\varphi = 0$ , we have  $T\partial(\Delta v_1) / \partial T - \Delta v_1 = 0$  and  $\Delta v_1 = T\omega(P)$ .

The application of Lagrange's method of variation of arbitrary function suggests the resolution of the Eq. (3) where  $\varphi \neq 0$ , in the form

$$\Delta v = T\Omega(T, p) \quad (a)$$

with the new unknown function  $\Omega$ . Thus

$$\partial(\Delta v) / \partial T = \Omega + T\partial\Omega / \partial T \quad (b)$$

and substituting in Eq. (3) from Eq. (a) and Eq. (b) we get

$$T^2\partial\Omega / \partial T = \varphi.$$

Hence  $\Omega = \int \frac{\varphi}{T^2} dT + \phi(p)$  and finally  $\Delta v = T \left\{ \int \frac{\varphi}{T^2} dT + \theta \right\}$ .

The application of Lagrange's method in the case is due to Professor R. O. Kuzmin in Leningrad.

### On the Nuclear Transformation with the Absorption of the Orbital Electron

According to the present theory of  $\beta$  disintegration, the nucleus of atomic number  $Z$  transforms into its isobar  $Z-1$  with the emission of a positron and a neutrino, if the difference  $\Delta W$  of proper energies of these isobars is larger than  $mc^2 + \mu c^2$ , where  $m$  and  $\mu$  are the masses of the electron and the neutrino, respectively. On the contrary, the isobar

TABLE I.

Z	$\alpha Z$	$\tau$ (Fermi)	$\tau$ (K-U)
1	1/137	2740 $(\Delta w + 1)^{-2}$ years	1860 $(\Delta w + 1)^{-4}$ years
2	2/137	170 $(\Delta w + 1)^{-2}$ years	120 $(\Delta w + 1)^{-4}$ years
14	0.1	200 $(\Delta w + 1)^{-2}$ days	130 $(\Delta w + 1)^{-4}$ days
27	0.2	25 $(\Delta w + 1)^{-2}$ days	16 $(\Delta w + 1)^{-4}$ days
69	0.5	12 $(\Delta w + 0.87)^{-2}$ hours	8 $(\Delta w + 0.87)^{-4}$ hours

$Z-1$  transforms into  $Z$  with the emission of an electron and an antineutrino, if  $\Delta W$  is smaller than  $-mc^2 - \mu c^2$ . The isobar  $Z$  can transform into  $Z-1$  also by absorbing one of the orbital electrons and emitting a neutrino at the same time, if  $\Delta W$  is larger than  $-E + \mu c^2$ , where  $E$  is the total energy of the orbital electron.

Thus, two isobars with consecutive atomic numbers are both stable, only if  $\Delta W$  lies between  $-mc^2 - \mu c^2$  and  $-mc^2 + \mu c^2$ . This condition can be fulfilled very rarely, if the neutrino mass is small compared with the electron mass. Since the existence of several such pairs of stable nuclei was confirmed by experiment recently,<sup>1</sup> it will be worthwhile to give a brief account of the results of our previous calculations on this subject.<sup>2</sup> It will be interesting, moreover, to determine the ratio of the probabilities of the positron emission and the electron absorption above considered, when  $\Delta W$  is larger than  $mc^2 + \mu c^2$ .

First, the mean lifetime  $\tau$  of the nucleus  $Z$  due to the absorption of either of two  $K$  electrons with  $E = mc^2(1 - \alpha^2 Z^2)^{1/2}$  was calculated for the allowed transition, where  $\alpha$  was the fine structure constant. If the neutrino mass is assumed to be zero,  $\tau$  is approximately proportional to

$$(\alpha Z)^{2\gamma+1}/(\Delta w + \gamma)^2 \quad \text{or} \quad (\alpha Z)^{2\gamma+1}/(\Delta w + \gamma)^4,$$

according as the coupling scheme of Fermi or Konopinski-Uhlenbeck is adopted, where

$$\Delta w = \Delta W/mc^2, \quad \gamma = (1 - \alpha^2 Z^2)^{1/2}.$$

The numerical values for several cases are shown in Table I.<sup>3</sup>

The apparent discrepancy between these results and the existence of stable pairs of heavy nuclei can be removed, only if we assume (i) the difference of nuclear spins to be large in every case, or (ii) the neutrino mass to be comparable with the electron mass, or (iii) the wave functions of the electron in the neighborhood of the nucleus to be much smaller than those calculated by Dirac's theory.

The extreme case  $Z=1$  in Table I, which corresponds to the transformation of the hydrogen atom into the neutron, will not occur actually according to the recent data of mass defects, whereas the case  $Z=2$  has some practical impor-

TABLE II.

Z	$\alpha Z$	$\Delta w$	$\sigma$ (Fermi)	$\sigma$ (K-U)
14	0.1	2	2.9	0.15
14	0.1	5	250.	36.
27	0.2	2	0.2	0.022
27	0.2	5	21.	3.1
82	0.6	2	$0.8 \times 10^{-3}$	$2.5 \times 10^{-5}$
82	0.6	5	0.1	0.016

tance indicating the spontaneous transformation of He<sup>3</sup> into H<sup>3</sup> by absorbing one of the  $K$  electrons.

Next, the ratio  $\sigma$  of the probabilities of the positron emission and the  $K$  electron absorption was calculated on similar assumptions as above, when  $\Delta W$  is larger than  $mc^2 + \mu c^2$ , the numerical results for  $\mu=0$  being summarized in Table II.

Thus, for ordinary radio elements emitting positrons, for which  $Z$  is small and  $\Delta w$  is about 5 or more, the ratio  $\sigma$  is so large that the order of the mean lifetime calculated by assuming the positron emission alone is not changed by the additional contribution of the absorption of the orbital electron. On the contrary, for large values of  $Z$ , the latter process will occur far more frequently than the former as long as  $\Delta w$  is not too large compared with 1. It will be possible to test these conclusions by experiment.

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<sup>1</sup> Brainbridge and Jordan, Phys. Rev. 50, 282 (1936).

<sup>2</sup> Proc. Phys.-Math. Soc. Japan 17, 467 (1935); 18, 128 (1936). Extension of the calculation to the case of forbidden transitions was made by Lamb, Phys. Rev. 50, 388 (1936). (Abstract). See also Bethe and Bacher, Rev. Mod. Phys. 8, 82 (1936). Similar calculations were made recently by Møller, Phys. Rev. 51, 84 (1937).

<sup>3</sup> For the numerical calculation in the case of K-U, the same coupling constant as that of Bethe and Bacher (reference 2, p. 193) was employed.

#### On the Nature of the Superconducting State

Most attempts to explain superconductivity encounter the difficulty that they have to introduce an enormous number of different quantum states in order to represent the infinite number of possible currents, different as to their direction and intensity; it seems difficult to explain how the interaction between these electronic states and the lattice could be sufficiently weak for no transitions between them to be possible and no energy and velocity of the electrons to be dissipated over the lattice.

It has recently been shown,<sup>1</sup> however, that quantum kinematics furnishes a possibility of describing superconductivity in such a manner, that for a simply connected superconductor even one single electronic state is sufficient for representing the electromagnetic behavior of a superconductor with all its various possible currents. It would be sufficient to show that this state has the following properties:<sup>2</sup>

(1) Its energy is separated by a finite interval from that of the ordinary Bloch states and lies lower than those.

(2) Its eigenfunction is nondegenerate and in a weak magnetic field it undergoes no stronger perturbation than one proportional to  $H^2$ .

$$\psi = \psi_0 + H^2 \psi_1 \quad (\psi_0 = \text{eigenfunction for } H=0).$$

There may be several states of this kind below the Bloch states. Transitions between them would not produce a dissipation of current.

The properties (1) and (2) characterize the electromagnetic behavior of the superconductor as being the same as that of a single big diamagnetic atom. The variety of currents which can be produced in the one ground state of a diamagnetic atom by suitably varying the orientation and intensity of the external magnetic field corresponds, in