

studies and the latter in studying atmospheric ionization at ground level. These increases in ionization are considered to be due to radioactive matter brought down with the rain. Between 0935 and 1900 hr. GMT on November 29 at Ottawa precipitation was falling. The precipitation started as snow and changed to rain about 1400 hr. Compared with the results of Doan and Wait and McNish the 35 percent increase in the soft component registered at Ottawa by counters seems too high to be explained in the same way, unless there was an exceptionally high density of radioactive matter in the atmosphere at the time. An alternative, but not very likely explanation, might be that there was a burst of hard gamma-rays or some other radiation which would increase the number of soft shower particles without any appreciable effect on the hard component.

An interesting feature of the November 19 increase is the difference between the measurements at the various stations, particularly between Resolute and Godhaven (geomagnetic latitude 80°). These two stations are about 900 miles apart and the differences confirm previous indications that sudden increments in cosmic-ray intensity occur over a limited area. The lack of a sudden decrease after the increment is unusual, since a decrease has been reported on previous occasions.

The cooperation of the Department of Transport of the Government of Canada is appreciated for supplying facilities at Resolute and for weather information.

<sup>1</sup> A. Dauvillier, *Comptes Rendus* **229**, 1096 (1949).

<sup>2</sup> Forbush, Stinchcomb, and Schein, *Bull. Am. Phys. Soc.* **25**, No. 1, 15 (1950).

<sup>3</sup> I. L. Chakraborty and S. D. Chatterjee, *Ind. J. Phys.* **23**, 525 (1949).

<sup>4</sup> Forbush, Gill, and Vallarta, *Rev. Mod. Phys.* **21**, 44 (1949).

<sup>5</sup> R. L. Doan, *Phys. Rev.* **49**, 107 (1936).

<sup>6</sup> G. R. Wait and A. G. McNish, *Monthly Weather Rev.* **62**, 1 (1934).

### An Identity in Quantum Electrodynamics

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IT has been recently proved by Dyson<sup>1</sup> that all divergencies in the  $S$ -matrix of electrodynamics may be removed by a renormalization of mass and charge. Dyson defines certain fundamental divergent operators  $\Gamma_\mu$ ,  $S_{F'}$ ,  $D_{F'}$  and gives a procedure for the calculation of their finite parts  $\Gamma_{\mu 1}$ ,  $S_{F'1}$ ,  $D_{F'1}$  by a process of successive approximation. It is then shown that

$$\Gamma_\mu = Z_1^{-1} \Gamma_{\mu 1}(e_1), \quad S_{F'} = Z_2 S_{F'1}(e_1), \quad D_{F'} = Z_3 D_{F'1}(e_1), \\ e_1 = Z_1^{-1} Z_2 Z_3^{1/2} e,$$

where  $Z_1$ ,  $Z_2$ , and  $Z_3$  are certain infinite constants and  $e_1$  is the renormalized electronic charge. Dyson conjectured that  $Z_1 = Z_2$ , and it is proposed here to give a formal proof of this relation.

In the first place, with any proper electron self-energy part  $W$ , may be associated a set of proper vertex parts  $V^i$  obtained by inserting a photon line in one of the electron lines of  $W$ . Now consider the operators  $\Lambda_\mu(V^i, \not{p}, \not{p})$  in which the two external electron momentum variables  $\not{p}$  have been set equal, and the external photon variable made to vanish. Then  $\Lambda_\mu(V^i, \not{p}, \not{p})$  may be obtained from  $\Sigma(W, \not{p})$  by replacing  $S_F$  by  $S_{F'} \gamma_\mu S_{F'}$  at one electron line of  $W$ . Because of the identity

$$-(1/2\pi) \partial S_{F'} / \partial \not{p}_\mu = S_{F'} \gamma_\mu S_{F'},$$

on summing  $\Lambda_\mu(V^i, \not{p}, \not{p})$  over all vertex parts  $V^i$  associated with  $W$ , one finds

$$\Sigma_{V^i} \Lambda_\mu(V^i, \not{p}, \not{p}) = -(1/2\pi) (\partial \Sigma(W, \not{p}) / \partial \not{p}_\mu).$$

(One can verify that any closed loop in  $W$  gives zero total effect.) Finally summing over all proper electron self-energy parts  $W$ , one finds

$$\Lambda_\mu(\not{p}, \not{p}) = -(1/2\pi) (\partial \Sigma^*(\not{p}) / \partial \not{p}_\mu).$$

Now substitute this identity into Eqs. (91) and (95) of reference 1. One finds

$$\Lambda_\mu = Z_1^{-1} [(1 - Z_1) \gamma_\mu + \Lambda_{\mu C}], \quad \Sigma^* = Z_2^{-1} [(Z_2 - 1) S_{F'}^{-1} + S_{F'}^{-1} S_C / 2\pi].$$

We have

$$-(1/2\pi) Z_2^{-1} \{ (Z_2 - 1) 2\pi \gamma_\mu + \gamma_\mu S_C + (\gamma_\lambda \not{p}_\lambda - iK_0) (\partial S_C / \partial \not{p}_\mu) \} \\ = Z_1^{-1} \{ (1 - Z_1) \gamma_\mu + \Lambda_{\mu C}(\not{p}, \not{p}) \}.$$

Now put

$$\gamma_\lambda \not{p}_\lambda = iK_0, \quad (\not{p}_\lambda)^2 = -K_0^2.$$

The convergent parts of these equations then vanish and there is left the relation

$$-(1/2\pi) Z_2^{-1} (Z_2 - 1) 2\pi \gamma_\mu = Z_1^{-1} (1 - Z_1) \gamma_\mu$$

which reduces immediately to  $Z_1 = Z_2$ .

<sup>1</sup> F. J. Dyson, *Phys. Rev.* **75**, 1736 (1949).

### The Partial Molal Entropy of Superfluid in Pure He<sup>4</sup> below the $\lambda$ -Point

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IN a recent article<sup>1</sup> (the notation of which is retained here, except that subscripts  $4n$  and  $4s$  refer to normal fluid and superfluid, respectively, in place of 1 and 2), I have considered the thermodynamics of liquid helium on the two-fluid theory, taking account of the fact that if two "phases" or "components," the normal fluid and the superfluid, exist together they must be in equilibrium with each other. On this basis, using the assumed relation<sup>2</sup> which states that the total molal entropy  $S$  at any temperature is the mole fraction  $x_{4n}$  of normal fluid times the molal entropy  $S_\lambda$  at the  $\lambda$ -point

$$S = x_{4n} S_\lambda = (1 - x_{4s}) S_\lambda, \quad (1)$$

using the empirical relation for  $S$  as a function of temperature

$$S = S_\lambda (T/T_\lambda)^r \quad (2)$$

(with  $r \sim 5.6$ ), and assuming that the partial molal enthalpy of superfluid,  $\bar{H}_{4s}$ , is independent of temperature (at essentially constant pressure), and independent of  $x_{4s}$  (i.e., there is no heat of mixing), I derived the equation for the partial molal entropy of superfluid

$$\bar{S}_{4s} = S_\lambda x_{4n} / (r + 1). \quad (3)$$

However, as I remarked in reference 1, there are some approximations involved in this procedure. Equation (1) is based on the assumption that below  $T_\lambda$  the entropy is contributed solely by the normal fluid, whose molal entropy is always set equal to the constant  $S_\lambda$ , thus neglecting any temperature dependence. Furthermore, there is an implied inconsistency, since Eq. (1) assumes no entropy of mixing while Eq. (3) implies that there is a mixing entropy. In fact, in the following letter we shall show that we may derive a somewhat different expression for  $S$  from Eq. (3). We shall, therefore, discard Eq. (1) and turn to a consideration of the enthalpies.

If  $\bar{H}_{4s}$  is independent of  $x_{4s}$ , then  $\bar{H}_{4n}$  must be also, and we have  $\bar{H}_{4n} = H_{4n}$ , where  $H_{4n}$  is the enthalpy of pure normal helium. We can write for the total molal enthalpy<sup>3</sup>

$$H = x_{4n} H_{4n}. \quad (4)$$

We will now proceed to derive an expression for  $\bar{S}_{4s}$ , in a somewhat more direct way than in reference 1, using Eq. (4) in place of Eq. (1). Since  $F = H - TS$  and  $\mu_{4s} = \bar{H}_{4s} - T\bar{S}_{4s} = -T\bar{S}_{4s}$ , the condition for internal equilibrium,  $F = \mu_{4s}$ , gives

$$\bar{S}_{4s} = S - H/T. \quad (5)$$

Equation (2) implies, from the relation between  $S$  and  $H$  (see footnote 10 of reference 1) that

$$H/H_\lambda = (T/T_\lambda)^{r+1}, \quad (6)$$

with

$$H_\lambda = rS_\lambda T_\lambda / (r+1). \quad (7)$$

Using Eq. (4)

$$x_{4n} = (H_\lambda/H_{4n})(T/T_\lambda)^{r+1}. \quad (8)$$

From Eqs. (2), (5)–(7),

$$\tilde{S}_{4s} = S_\lambda (T/T_\lambda)^r / (r+1). \quad (9)$$

This equation, of course, holds only at equilibrium. However, if  $H_{4n}$  were independent of  $T$  (hence equal to  $H_\lambda$ ) we could write, using Eq. (8)

$$\tilde{S}_{4s} = [S_\lambda / (r+1)] x_{4n}^{r/(r+1)}, \quad (10)$$

which expresses  $\Delta_{4s}$  as a function of  $x_{4n}$  independent of  $T$ . If  $H_{4s}$  is temperature independent, then  $(\partial S_{4s} / \partial T)_{x_{4n}} = 0$  (at constant pressure), so  $\tilde{S}_{4s}$  cannot depend explicitly on  $T$ . Equation (10), since it gives  $\tilde{S}_{4s}$  at all equilibrium concentrations, must thus be the correct general form for  $\tilde{S}_{4s}$ , if  $H_{4n}$  is constant. If  $H_{4n}$  depends on  $T$  the proper equation for  $\tilde{S}_{4s}$  can still be obtained by eliminating  $T$  between Eqs. (8) and (9).

The determination of  $H_{4n}$  as a function of  $T$  offers some difficulty. I have suggested that the superfluid appeared above the  $\lambda$ -point in the form of globules, and below the  $\lambda$ -point principally in a sort of fibroid form. The fibroid form would not occur at all above  $T_\lambda$  but there would be some persistence of the globules below  $T_\lambda$ . The fibroid form only is actually included in the mole fraction  $x_{4s}$  below  $T_\lambda$ . Below the  $\lambda$ -point then the globules should be considered as part of the normal fluid, and they will alter its properties. However, it is unlikely that the globules are important at temperatures appreciably below  $T_\lambda$ , and it seems reasonable to suppose that we can get a good idea of the temperature dependence of  $H_{4n}$  by extrapolating the specific heat from above the temperature ( $\sim 2.5^\circ\text{K}$ ) of appearance of the  $\lambda$ -anomaly.<sup>4</sup> If we do this we conclude that  $H_{4n}$  certainly does not vary much more rapidly than  $T$  itself, and the dependence of  $\tilde{S}_{4s}$  on  $x_{4n}$  probably lies somewhere between proportionality to  $x_{4n}^{r/(r+1)}$  and  $x_{4n}^{r/(r+1)}$ . Equation (3), then, should give an approximation which may be used without fear of serious error.

<sup>1</sup> O. K. Rice, Phys. Rev. **76**, 1701 (1949). C. J. Gorter, Physica **15**, 523 (1949) has independently stated the basic principles, but we differ in subsidiary assumptions and in method.

<sup>2</sup> L. Tisza, Phys. Rev. **72**, 838 (1947).

<sup>3</sup> Compare W. Band and L. Meyer, Phys. Rev. **74**, 386 (1948), Eqs. (10) and (11).

<sup>4</sup> O. G. Engel and O. K. Rice, Phys. Rev. **78**, 55 (1950).

## Thermodynamics of He<sup>3</sup>–He<sup>4</sup> Solutions

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IN a recent letter Gorter and de Boer<sup>1</sup> have discussed mixtures of He<sup>3</sup> and He<sup>4</sup>, modifying somewhat the earlier views of de Boer.<sup>2</sup> Their new formulation is in accord with the ideas of Rice,<sup>3</sup> but differs in one respect from what is found by a logical extension of his treatment of pure He<sup>4</sup>.

Equation (3) of the preceding letter leads to the following expression for the total entropy of  $m_{4n} + m_{4s}$  moles of pure He<sup>4</sup> below the  $\lambda$ -point.

$$S = m_{4n} S_{4n} - m_{4n} S_\lambda (r+1)^{-1} \ln [m_{4n} / (m_{4n} + m_{4s})]. \quad (1)$$

Here  $m_{4n}$  and  $m_{4s}$  are the number of moles of normal and superfluid, respectively.  $S_{4n}$ , the molal entropy of pure normal helium, cannot be directly determined below the  $\lambda$ -point, where pure normal He<sup>4</sup> is unstable, but its magnitude can be estimated.

Equation (1) yields Eq. (3) of the preceding note by partial differentiation with respect to  $m_{4s}$ . It has the correct form (it is consistent with the Gibbs-Duhem relation for entropy) and fulfills the correct boundary condition for  $m_{4s} = 0$ . It is thus uniquely determined by Eq. (3) of the preceding note.

Below the  $\lambda$ -point He<sup>3</sup> appears to be soluble only in the normal part<sup>4</sup> of He<sup>4</sup>. There is therefore an entropy of mixing,  $S_{34}$ , which can be supposed to be independent of  $m_{4s}$ . Assuming Raoult's law

$$S_{34} = -m_{4n} R \ln [m_{4n} / (m_{4n} + m_3)] - m_3 R \ln [m_3 / (m_{4n} + m_3)]. \quad (2)$$

However, there is still a superimposed entropy of mixing,  $S_{ns}$ , of normal and superfluid. Rice's suggestion of a separation of normal superfluid in ordinary space makes it seem reasonable to suppose that  $S_{ns}$  will not depend on the relative amounts of He<sup>3</sup> and He<sup>4</sup> in the normal fluid. We simply substitute  $m_{4n} + m_3$  for  $m_{4n}$  in the mixing term in Eq. (1):

$$S_{ns} = -(m_{4n} + m_3) S_\lambda (r+1)^{-1} \times \ln [(m_{4n} + m_3) / (m_{4n} + m_3 + m_{4s})]. \quad (3)$$

$S_\lambda$  has the same constant value; it is the entropy of pure He<sup>4</sup> at its  $\lambda$ -point. For the total Gibbs free energy of  $m_{4n} + m_{4s}$  moles of He<sup>4</sup> and  $m_3$  moles of He<sup>3</sup> we write

$$F = m_{4n} F_{4n} + m_3 F_3 - TS_{34} - TS_{ns}, \quad (4)$$

where  $F_3$  and  $F_{4n}$  are molal free energies of pure He<sup>3</sup> and pure normal He<sup>4</sup> respectively;  $F_{4s}$  is zero. The terms  $m_3 F_3$  and  $-TS_{34}$  are essentially like corresponding terms of Gorter and de Boer. However, these authors would make  $(m_{4n} F_{4n} - TS_{ns}) / m_{4n}$  (equivalent to their  $G_4$ ) a function of  $T$  and  $m_{4n} / (m_{4n} + m_{4s})$  instead of  $T$  and  $(m_{4n} + m_3) / (m_{4n} + m_3 + m_{4s})$ .

From Eq. (4) with (2) and (3), we get the chemical potentials  $\mu_{4n}$ ,  $\mu_{4s}$ , and  $\mu_3$  by partial differentiation with respect to  $m_{4n}$ ,  $m_{4s}$ , and  $m_3$ , respectively. The  $\mu$ 's can be expressed as functions of  $T$  and the mole fractions  $x_{4n}$ ,  $x_{4s}$ , and  $x_3$ , provided  $F_3$  and  $F_{4n}$  are known as functions of  $T$ .  $F_{4n}$  cannot be obtained directly, but can be found if the specific heat of pure normal He<sup>4</sup> can be estimated (see preceding note). The values of  $x_{4n}$  and  $x_{4s}$  in an equilibrium mixture at any given  $T$  and  $x_3$  can then be found by setting  $\mu_{4n} = \mu_{4s}$  (or, alternatively,<sup>1</sup> by minimizing  $F$ ), together with  $x_{4n} + x_{4s} + x_3 = 1$ . Thus the  $\mu$ 's become functions of  $T$  and  $x_3$  only. The partial vapor pressures of He<sup>3</sup> and He<sup>4</sup> can then be found, provided the vapor pressures of pure He<sup>3</sup> and He<sup>4</sup> and the equations-of-state of their vapors are known.

A solution with properties determined by Eqs. (2)–(4) we shall call a "quasi-ideal" solution, since the mixture of He<sup>3</sup> and normal He<sup>4</sup> follows the ideal solution law, while the superimposed mixture of normal and superfluid follows the same law as pure He<sup>4</sup>. If deviations occur in practice<sup>5</sup> it would seem reasonable to try first to explain them as deviations in the terms other than  $TS_{ns}$ . We may add terms

$$m_3 RT \ln \gamma_3 + m_{4n} RT \ln \gamma_{4n}$$

to Eq. (4), where  $\gamma_3$  and  $\gamma_{4n}$  (activity coefficients for He<sup>3</sup> and normal He<sup>4</sup>) depend only on  $\rho = x_3 / x_{4n}$ , where  $\gamma_3 \rightarrow 1$  and  $d\gamma_3/d\rho \rightarrow 0$  as  $x_{4n} \rightarrow 0$ , and  $\gamma_{4n} \rightarrow 1$  and  $d\gamma_{4n}/d\rho \rightarrow 0$  as  $x_3 \rightarrow 0$ , and where

$$m_3 d \ln \gamma_3 / d\rho + m_{4n} d \ln \gamma_{4n} / d\rho = 0.$$

Such terms will not affect  $\mu_{4s}$ , but will change the equilibrium between normal and superfluid He<sup>4</sup> because of the effect on  $\mu_{4n}$ . However, this equilibrium would not be changed in sufficiently dilute solutions of He<sup>3</sup> and He<sup>4</sup> where He<sup>4</sup> obeys Raoult's law ( $\gamma_{4n} = 1$ ) even though He<sup>3</sup> obeys Henry's rather than Raoult's law. If there is heat of mixing of He<sup>3</sup> and He<sup>4</sup> it will be reflected in the temperature coefficients of  $\ln \gamma_3$  and  $\ln \gamma_{4n}$ .

<sup>1</sup> C. J. Gorter and J. de Boer, Phys. Rev. **77**, 569 (1950).

<sup>2</sup> J. de Boer, Phys. Rev. **76**, 852 (1949).

<sup>3</sup> O. K. Rice, Phys. Rev. **76**, 1701 (1949); **77**, 142 (1950).

<sup>4</sup> Taconis, Beenakker, Nier, and Aldrich, Phys. Rev. **75**, 1966 (1949); Physica **15**, 733 (1949).

<sup>5</sup> Weinstock, Osborne, and Abraham, Phys. Rev. **77**, 400 (1950).