

TABLE I. Classified argon lines.

INT.	$\lambda(\text{VAC.})$	$\nu(\text{CM}^{-1})$	STAGE OF IONIZ.	CLASSIFICATION
3	596.69	167,590	VI	$3s^2 3p \ ^2P_{3/2} - 3s 3p^2 \ ^2S_{1/2}$
2	588.93	169,800	VI	$\ ^2P_{1/2} \ ^2S_{1/2}$
2	555.65	179,970	VI	$\ ^2P_{3/2} \ ^2P_{1/2}$
10	551.36	181,370	VI	$\ ^2P_{3/2} \ ^2P_{1/2}$
6	548.91	182,180	VI	$\ ^2P_{1/2} \ ^2P_{1/2}$
3	544.72	183,580	VI	$\ ^2P_{1/2} \ ^2P_{3/2}$
4	527.70	189,500	V	$3s^2 3p^2 \ ^3P_2 - 3s 3p^3 \ ^3S_1$
0	526.87	189,800	VIII	$3p \ ^2P_{3/2} - 3d \ ^2D_{3/2}$
4	526.45	189,950	VIII	$\ ^2P_{3/2} \ ^2D_{3/2}$
2	524.19	190,770	V	$3s^2 3p^2 \ ^3P_1 - 3s 3p^3 \ ^3S_1$
1	522.08	191,540	V	$\ ^3P_0 \ ^3S_1$
3	519.43	192,520	VIII	$3p \ ^2P_{1/2} - 3d \ ^2D_{3/2}$
10	479.39	208,600	VII	$3s 3p \ ^3P_2 - 3s 3d \ ^3D_3$
6	475.65	210,240	VII	$\ ^3P_1 \ ^3D_2$
3	473.93	211,000	VII	$\ ^3P_0 \ ^3D_1$
4	260.33	384,130	VIII	$3d \ ^2D_{3/2} - 3f \ ^2F_{7/2}$
2	260.25	384,250	VIII	$\ ^2D_{3/2} \ ^2F_{7/2}$
4	250.95	398,480	VII	$3s 3p \ ^3P_2 - 3s 4s \ ^3S_1$
2	249.89	400,170	VII	$\ ^3P_1 \ ^3S_1$
1	249.38	401,000	VII	$\ ^3P_0 \ ^3S_0$
4	230.86	433,160	VIII	$3p \ ^2P_{3/2} - 4s \ ^2S_{1/2}$
2	229.43	435,860	VIII	$\ ^2P_{1/2} \ ^2S_{1/2}$
5	192.63	519,120	VII	$3s 3p \ ^3P_2 - 3s 4d \ ^3D_3$
3	192.04	520,720	VII	$\ ^3P_1 \ ^3D_2$
2	191.76	521,490	VII	$\ ^3P_0 \ ^3D_1$

from 30A to 680A. Twenty thousand sparks (at the rate of about 100 sparks per minute) gave a very satisfactory spectrogram.

In the argon spectra lines arising from argon IV, V, VI, VII, and VIII have been identified. Preliminary results for some of the stronger lines in the spectra are listed in Table I. In all cases the frequencies agree very closely with those predicted from the laws governing isoelectronic sequences.

A more complete report on the argon spectra and one on the neon and krypton spectra will be ready soon.

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<sup>1</sup> J. C. Boyce, Phys. Rev. **48**, 396 (1935).

<sup>2</sup> J. C. Boyce, Phys. Rev. **47**, 718 (1935).

<sup>3</sup> F. W. Paul, Phys. Rev. **56**, 1067 (1939).

<sup>4</sup> J. C. Boyce, Phys. Rev. **46**, 378 (1934).

### Concentration of Isotopes by Thermal Diffusion: Rate of Approach to Equilibrium

The purpose of this note is to make some additions and corrections to an article<sup>1</sup> of the same title which appeared in a recent issue of this journal. The equation numbers given below refer to this article.

(1). In Eq. (10) we used the expression for the transport,  $\tau_1$ , which was derived by Furry, Jones and Onsager<sup>2</sup> for the stationary condition. The detailed justification for its use in the nonequilibrium case follows. We want a solution of Eq. (4), which may be written in the form

$$\frac{\partial(\rho c_1)}{\partial t} = -\rho v \frac{\partial c_1}{\partial z} + \rho D \frac{\partial^2 c_1}{\partial z^2} + \frac{\partial}{\partial x} \left[ \rho D \left( \frac{\partial c_1}{\partial x} - \frac{\alpha c_1 c_2}{T} \frac{\partial T}{\partial x} \right) \right], \quad (4')$$

subject to the boundary conditions (5) and (6):

$$c_1 v_{1z} = -D \left[ \frac{\partial c_1}{\partial x} - \frac{\alpha c_1 c_2}{T} \frac{\partial T}{\partial x} \right] = 0 \quad (5')$$

at  $x=0$  and  $x=d$ , and

$$\int_0^d \rho v(x) dx = 0. \quad (6)$$

Let us integrate Eq. (4) with respect to  $x$  from  $x=0$  to  $x=d$ . Making use of (5), we find:

$$\int_0^d \rho \frac{\partial c_1}{\partial t} dx = \int_0^d \rho D \frac{\partial^2 c_1}{\partial z^2} dx - \int_0^d \rho v \frac{\partial c_1}{\partial z} dx. \quad (a)$$

In the integral on the left-hand side and in the first integral on the right-hand side we may replace  $c_1$  by its mean value across the column without appreciable error. The fractional variation of  $c_1$  with respect to  $x$  is of the order  $\alpha \Delta T/T$ , so that the error involved is certainly less than this amount. The last integral would vanish on account of (6) if  $c_1$  were independent of  $x$ , so that it is not possible to use the mean value here. It is, of course, just the variation of the concentration across the column which gives rise to the transport.

The integral may be evaluated as follows. Let<sup>3</sup>

$$G(x) = \int_0^x \rho v dx; \quad (b)$$

then

$$G(0) = G(d) = 0. \quad (c)$$

An integration by parts gives:

$$-\int_0^d \rho v \frac{\partial c_1}{\partial z} dx = \int_0^d G(x) \frac{\partial^2 c_1}{\partial x \partial z} dx. \quad (d)$$

The value of  $\partial^2 c_1 / \partial x \partial z$  may be obtained from Eq. (4) which, after integration with respect to  $x$ , may be written

$$\rho D \frac{\partial c_1}{\partial x} = \rho D \frac{\alpha c_1 c_2}{T} \frac{\partial T}{\partial x} + \int_0^x \left\{ \rho' v' \frac{\partial c_1'}{\partial z} + \rho' \frac{\partial c_1'}{\partial t} - \rho' D' \frac{\partial^2 c_1'}{\partial z^2} \right\} dx'. \quad (e)$$

The prime indicates that the various quantities in the integrand are functions of  $x'$ . Differentiating (e) with respect to  $z$ , we find

$$\frac{\partial^2 c_1}{\partial x \partial z} = \frac{\alpha}{T} \frac{\partial T}{\partial x} \frac{\partial}{\partial z} (c_1 c_2) + \frac{1}{\rho D} \int_0^x \left\{ \rho' v' \frac{\partial^2 c_1'}{\partial z^2} + \rho' \frac{\partial^2 c_1'}{\partial z \partial t} - \rho' D' \frac{\partial^3 c_1'}{\partial z^3} \right\} dx'. \quad (f)$$

The transport equation is obtained by substituting (f) into (d) and then (d) into (a). After multiplying through by the mean circumference,  $B$ , the resulting equation may be expressed in the following form:

$$B \int_0^d \rho \left( \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial z^2} \right) \left( 1 - I(x) \frac{\partial}{\partial z} \right) c_1 dx = -\frac{\partial}{\partial z} \left( H c_1 c_2 - K \frac{\partial c_1}{\partial z} \right), \quad (g)$$

where  $I(x)$  is introduced by an integration by parts;

$$I(x) = \int_0^x \frac{G(x')}{\rho' D'} dx', \quad (h)$$

and  $H$  and  $K$  are the constants designated by the same letters by Furry, Jones and Onsager.<sup>4</sup>

$$H = -B \int_0^d \frac{G(x)}{\alpha} \frac{\partial T}{\partial x} dx, \quad (i)$$

$$K = B \int_0^d \frac{[G(x)]^2}{\rho D} dx. \quad (j)$$

Eq. (g) is the same as Eq. (10) except for the term  $I(x)\partial/\partial z$ . We will now estimate the magnitude of this term. In the actual operation of the column, the maximum value of  $\partial \log c_1/\partial z$  will be of the order  $H/K$ . The fractional error involved in the neglect of the term will therefore be of the order

$$(H/Kd) \int_0^d I(x) dx = (H/Kd) \int_0^d [\times G(x)/\rho D] dx. \quad (k)$$

With the substitution of the expressions (i) and (j) for  $H$  and  $K$ , it can be seen that the error is of the order  $\alpha \Delta T/T$ . In most cases this will be a fraction of one percent.

Strictly, we have shown only that the derivative

$$\frac{\partial \tau_1}{\partial z} \cong \frac{\partial}{\partial z} (\tau_1)_{\text{FJO}}$$

By an analysis similar to that given above it can be shown that the error involved in the use of the stationary value for  $\tau_1$  itself is of the same order of magnitude.

(2). The discussion of the roots of the equation  $F(p)=0$  (Eq. (38)) is not very clear in the article. The roots are most easily obtained in terms of  $\gamma$ :

$$p_k = -(AH/2\rho a)(1 - \gamma_k^2),$$

where the  $\gamma_k$  are roots of Eq. (47). In deriving (47) from (38) we have, among other things, multiplied through by  $\gamma$ . The root  $\gamma=0$  is therefore not to be included. If  $\gamma_k$  is a root of (47), so is  $-\gamma_k$ . These two roots correspond to a *single* root  $p_k$  of Eq. (38). Only one of them should be included in the sum in Eq. (49).

(3). There are two misprints in Eq. (49). The correct equation is:

$$c_1/c_1^0 = Ke^{2Az} + \sum_k \frac{2(R + (H/Mp_k))(e^{AL} - \gamma_k \sinh \gamma_k AL - \cosh \gamma_k AL) - 4 \cosh \gamma_k AL}{(1 - \gamma_k^2)(\gamma_k^{-1} R \sinh \gamma_k AL + \gamma_k^{-2} \cosh \gamma_k AL - AL \gamma_k^{-1} \operatorname{csch} \gamma_k AL)} \times [\gamma_k^{-1} \sinh \gamma_k A(z-L) + \cosh \gamma_k A(z-L)] \exp [A(z-L) + p_k t]. \quad (49)$$

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<sup>1</sup> J. Bardeen, Phys. Rev. **57**, 35 (1940).

<sup>2</sup> W. H. Furry, R. C. Jones, and L. Onsager, Phys. Rev. **55**, 1083 (1939). This paper will be referred to as FJO.

<sup>3</sup> Our  $G(x)$  differs from the function  $G$  introduced by FJO by a factor  $\rho D/Q^2 \lambda$ .

<sup>4</sup> Cf. Eqs. (24) and (25) of FJO. Their expression for the transport,  $\tau_1$ , is given by (23). Our treatment justifies the method used by FJO for the inclusion of the effect of longitudinal diffusion.