

## A NOTE ON THE ELEMENTARY THEORY OF THERMAL DIFFUSION

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**ABSTRACT.** An elementary derivation of the co-efficient of thermal diffusion and its change of sign with concentration is discussed. The results have been compared with the experimental results of Grew.

The phenomena of thermal diffusion was predicted independently by Enskog and Chapman about 20 years ago, but it did not attract much attention until the work of Clusius and Dickel (1938, 1939) which has made it the most effective method for the separation of isotopes. The convection currents set up in the Clusius-Dickel vertical column progressively build up, due to thermal diffusion, the separation of the constituents, and one is reminded in this connection of Linde's method of regenerative cooling by Joule-Thomson effect which, prior to Linde's work, was only of laboratory interest. It was supposed for a long time that, unlike the case of ordinary diffusion, no elementary theory of thermal diffusion was possible and hence the recent paper of Fürth (1942) discussing thermal diffusion from elementary considerations is of some interest. As Fürth has shown, the simple treatment brings out most of the essential features of Enskog-Chapman's analysis, and in this connection it is interesting to observe that the simple theory also provides an immediate explanation of the recent experiment of Grew (1942) on the change of sign of thermal diffusion factor for a neon-ammonia mixture.

Let us consider a binary mixture in which the concentration and temperature gradients are present only along one direction, say the  $z$ -axis. If  $n_1$  and  $n_2$  denote the concentration of the two types of molecules and  $T$  the temperature, all functions of  $z$  ( $n_1, n_2$  will also be functions of time), then the pressure  $p$  will be

$$p = k(n_1 + n_2)T = \text{constant}. \quad \dots (1)$$

If  $\Gamma_1$  and  $\Gamma_2$  represent the net flow of molecules of types one and two respectively along the positive  $z$ -direction, then we have in the usual way

$$\Gamma_1 = -\Gamma_2 = -\frac{\lambda_1}{3} \frac{d}{dz} (c_1 n_1) + u n_1 = \frac{\lambda_2}{3} \frac{d}{dz} (c_2 n_2) - u n_2, \quad \dots (2)$$

where  $u$  is the velocity of mass motion,  $\lambda_1, \lambda_2$  the mean free paths and  $c_1, c_2$

the mean velocities of molecules of types one and two respectively. The mutual rate of diffusion  $q_{12}$  is defined as

$$q_{12} = \frac{V_1}{n_1} - \frac{V_2}{n_2} = V_1 \left( \frac{1}{n_1} + \frac{1}{n_2} \right) = \frac{n_1 + n_2}{n_1 n_2} V_1.$$

Substituting for  $V_1$  and  $u$  from (2), using (1) and replacing  $n_1$  and  $n_2$  by the partial concentrations  $\gamma_1, \gamma_2$  defined by

$$\gamma_1 = \frac{n_1}{n_1 + n_2}, \quad \gamma_2 = \frac{n_2}{n_1 + n_2},$$

we have

$$q_{12} = - \frac{D}{\gamma_1 \gamma_2} \left\{ \frac{d\gamma_1}{dz} + k_T \frac{d(\log T)}{dz} \right\},$$

where

$$D = \frac{1}{3} (\gamma_1 \lambda_{22} c_2 + \gamma_2 \lambda_{11} c_1),$$

and

$$k_T = \gamma_1 \gamma_2 \left\{ \frac{\lambda_{22} c_2 - \lambda_{11} c_1}{2(\gamma_1 \lambda_{22} c_2 + \gamma_2 \lambda_{11} c_1)} \right\},$$

$k_T$  is called the thermal diffusion ratio. Writing as usual

$$\frac{1}{\lambda_1} = \pi(n_1 \sigma_1^2 + n_2 \sigma_{12}^2) \quad \text{and} \quad \frac{1}{\lambda_2} = \pi(n_2 \sigma_2^2 + n_1 \sigma_{12}^2),$$

where  $\sigma_1$  is the collision diameter for mutual collision between type-one molecules,  $\sigma_2$  the same for type-two and  $\sigma_{12}$  the collision diameter for collision between type-one and type-two.

$$\text{Thus we have} \quad k_T = \frac{\gamma_1 \gamma_2}{2} \frac{a_1 \gamma_1 - a_2 \gamma_2}{b_1 \gamma_1^2 + b_2 \gamma_2^2 + b_{12} \gamma_1 \gamma_2}, \quad \dots \quad (3)$$

where

$$a_1 = m_1^{\frac{1}{2}} \sigma_1^2 - m_2^{\frac{1}{2}} \sigma_{12}^2, \quad a_2 = m_2^{\frac{1}{2}} \sigma_2^2 - m_1^{\frac{1}{2}} \sigma_{12}^2,$$

$$b_1 = m_1^{\frac{1}{2}} \sigma_1^2, \quad b_2 = m_2^{\frac{1}{2}} \sigma_2^2,$$

and

$$b_{12} = (m_1^{\frac{1}{2}} + m_2^{\frac{1}{2}}) \sigma_{12}^2,$$

$m_1, m_2$  are the molecular masses of the two components.

Let us now assume that the two components differ from one another only to a small extent, *i.e.*,  $m_1 - m_2 = \Delta m$ ,  $\sigma_1 - \sigma_2 = \Delta \sigma$  and  $\sigma_{12} - (\sigma_1 + \sigma_2)/2 = \Delta S$ , then, we have to the first order

$$k_T = \frac{\gamma_1 \gamma_2}{2} \left\{ \frac{\Delta \sigma}{\sigma} + \frac{1}{2} \frac{\Delta m}{m} - 2(\gamma_1 - \gamma_2) \frac{\Delta S}{\sigma} \right\}, \quad \dots \quad (4)$$

In the case of an isotropic mixture  $\Delta \sigma = \Delta S = 0$ , and

$$k_T = 0.5 \gamma_1 \gamma_2 \frac{\Delta m}{2m}. \quad \dots \quad (5)$$

This may be compared with the expression

$$k_T = 0.35 \gamma_1 \gamma_2 \frac{m_1 - m_2}{m_1 + m_2} = 0.35 \gamma_1 \gamma_2 \frac{\Delta m}{2m},$$

given by Furry, Clark-Jones and Onsager (1939).

Writing (4) in the form

$$\begin{aligned} k_r &= \gamma_1(1-\gamma_1) \{a + b(1-2\gamma_1)\}, \\ &= b\gamma_1(1-\gamma_1)\{(1+q) - 2\gamma_1\}, \end{aligned}$$

where 
$$a = \frac{1}{2} \left( \frac{\Delta\sigma}{\sigma} + \frac{1}{2} \frac{\Delta m}{m} \right), \quad b = \frac{\Delta S}{\sigma}, \quad \text{and } q = a/b,$$

we notice that

(1)  $k_r = 0$  for  $\gamma_1 = 0$ ,  $\gamma_1 = 1$ , and  $\gamma_1 = a_0 = (1+q)/2$ ;

and (2)  $\frac{dk_r}{d\gamma_1} = 0$  for values of  $\gamma_1$  given by

$$6\gamma_1^2 - 2(q+3)\gamma_1 + (q+1) = 0.$$

Denoting the two values of  $\gamma_1$  by  $\alpha_1$  and  $\alpha_2$  we have

$$\alpha_1 + \alpha_2 = \frac{q+3}{3} = \frac{2(a_0+1)}{3}, \quad \alpha_1\alpha_2 = \frac{q+1}{6} = \frac{a_0}{3}, \quad \dots \quad (6)$$

which gives 
$$\alpha_1 = \frac{1+a_0 - \sqrt{1+a_0+a_0^2}}{3} = \frac{1+a_0-x}{3}, \quad \dots \quad (7)$$

and 
$$\alpha_2 = \frac{1+a_0 + \sqrt{1+a_0+a_0^2}}{3} = \frac{1+a_0+x}{3},$$

where 
$$x = \sqrt{1+a_0+a_0^2}.$$

Further, denoting by  $y_1$  the value of  $k_r$  for  $\gamma_1 = \alpha_1$  and by  $y_2$  the value corresponding to  $\gamma_1 = \alpha_2$ , we have

$$y_1 = \frac{2}{27} (1+a_0-x) (2-a_0+x) (2a_0-1+x), \quad \dots \quad (8)$$

and 
$$y_2 = \frac{2}{27} (1+a_0+x) (2-a_0-x) (2a_0-1-x).$$

We reproduce the experimental curve due to Grew<sup>1</sup> for the neon-ammonia mixture. From the curve we notice that  $a_0 = 0.75$ ,  $\alpha_2 = 0.27$ ,  $\alpha_0 = 0.86$ ; and, as is reasonable, assuming the ordinates to be proportional to  $k_r$ , we have

$$y_1/y_2 = -5.2.$$

The simple theory given above requires that

$$\frac{1}{2}(\alpha_1 + \alpha_2) = \frac{1}{3} + \alpha_1\alpha_2, \quad \dots \quad (9)$$

$$\alpha_0 = 3\alpha_1\alpha_2, \quad \dots \quad (10)$$

and 
$$\frac{y_1}{y_2} = \frac{(1+a_0-x) (2-a_1+x) (2a_0-1+x)}{(1+a_0+x) (2-a_0-x) (2a_0-1-x)}, \quad \dots \quad (11)$$

Substituting Grew's values of  $\alpha_1$ ,  $\alpha_2$  (10) requires  $\alpha_0$  to be 0.74 whereas Grew's value is 0.75. Further, substituting the observed value of  $\alpha_0$  we obtain  $y_1/y_2 = -6.9$ , whereas the observed value of the ratio is about -5.2.

<sup>1</sup> The value of the separation at the bottom of the figure is given by Grew to be -2.5. This is presumably -5

In connection with the above agreement, it must be remarked that the discussion given above is crude though extremely simple. For example, at some stages of the argument, the elastic model of the molecule is assumed, whereas in taking  $\sigma_{12}$  not equal to  $(\sigma_1 + \sigma_2)/2$ , we consider the force-field model. Again, in the case of the neon-ammonia mixture  $\Delta\sigma/\sigma$  cannot really be regarded as a small quantity. However, it seems that such defects must be present in any elementary treatment of thermal diffusion.

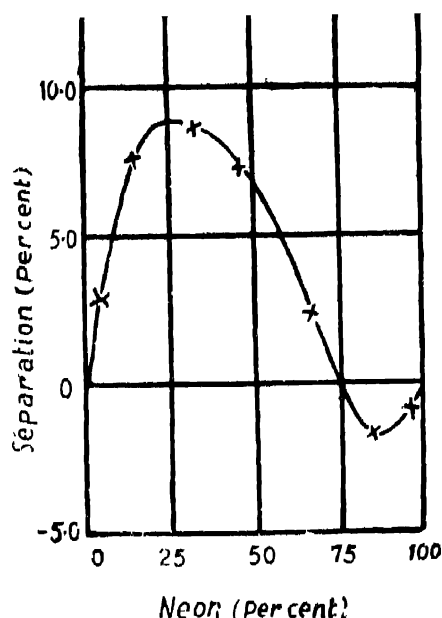


FIG. 1

It will be seen that for the existence of a reversal of sign of  $k_T$  with concentration it is necessary that  $0 < (1+g)/2 < 1$ , i.e.,  $a$  must be numerically less than  $b$ .

In the case of the neon-ammonia mixture, the value of  $a$  is contributed almost entirely by  $\sigma_1 - \sigma_2$ , the contribution due to mass difference though of opposite sign is relatively very small. The following mixtures are also expected to show reversals of the type observed by Grew : (1)  $N_2$  and  $NO$ , (2)  $A$  and  $CO_2$ .

## REFERENCES

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 Grew, K. E., 1942, *Nature*, **150**, 320.