THERMAL DIFFUSION OF CESIUM VAPOR IN HELIUM

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An examination is made of thermal diffusion of cesium vapor in helium. Calculations of the diffusion coefficients and the thermal diffusion ratio are made from an evaluation of the thermal diffusion flux during condensation of cesium from a mixture containing helium.

It is well known that in gases, in addition to concentration diffusion, which is proportional to the gradient of relative concentrations or the partial pressures, there occurs thermal diffusion, proportional to the temperature gradients. The kinetic theory of transport phenomena in rarefied gases has been developed by Enskog and Chapman [1, 2]. This theory leads to the following expression for the flux g_1 (in mass units) of one component of a two-component mixture of ideal gases:

$$g_1 = -\frac{M_1 P D_{12}}{RT}\,\frac{M_2}{(M_1 - M_2)\frac{p_1}{P} + M_2} \times \left[\operatorname{grad}\frac{p_1}{P} + \frac{k_T}{T}\operatorname{grad} T\right]. \qquad (1)$$

The first term on the right of (1) describes concentration diffusion, and the second thermal diffusion. At not too low temperatures the thermal diffusion ratio k_T for mixtures of all ordinary gases (nonionized) is positive, if the subscript 1 denotes molecules with the larger mass or having the larger dimensions [2, 3]. These molecules then move because of thermal diffusion in the direction of lower temperatures. The thermal diffusion displacement of molecules of the second component is in the opposite direction. When the mixture temperature is lowered, k_T decreases, and a point of inversion may be reached when the sign of k_T changes.

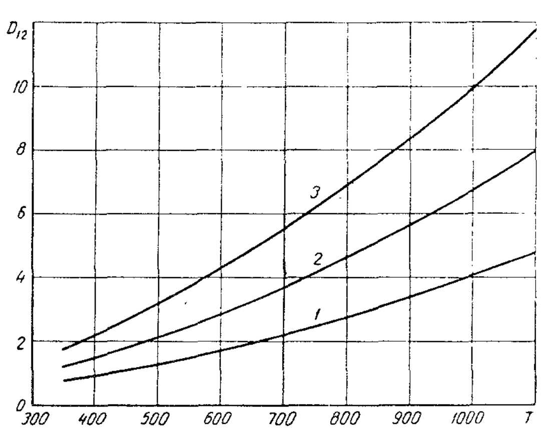

Fig. 1. The diffusion coefficient D_{12}, cm^2/sec for a mixture of cesium and helium: 1) for $P = 10^5$ N/m^2; 2) $0.6 \cdot 10^5$; 3) $0.4 \cdot 10^5$.

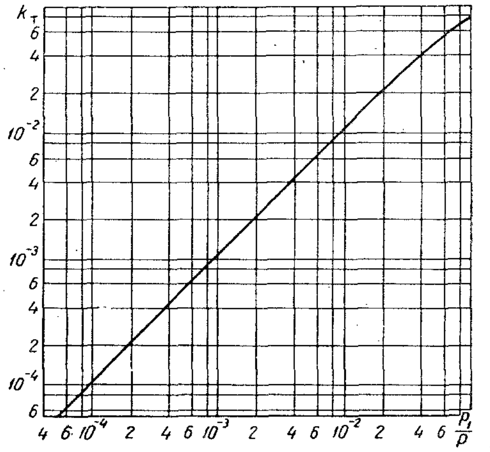

Fig. 2. Thermal diffusion ratio k_T for a mixture of cesium and helium.

The flux g_2 of the second component of the two-component mixture is equal in magnitude to the flux g_1, and oppositely directed.*

The theory of Enskog and Chapman leads also to relations determining the coefficients D_{12} and k_T. The specific formulas may be found in [2]. In calculations the Lennard-Jones potential

$$\varphi_{12}(r) = 4\varepsilon_{12}\left[(\sigma_{12}/r)^{12} - (\sigma_{12}/r)^6\right] \qquad (2)$$

is ordinarily used for the potential energy of interaction of nonpolar molecules.

The parameter ε_{12} determines the depth of the potential well, while the parameter σ_{12} is proportional to the distance between molecules at which the potential energy reaches a minimum ($r = \sqrt[6]{2}\sigma_{12}$).

The quantities ε_{12} and σ_{12} are usually determined with the aid of the combination rules

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}, \qquad (3)$$

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2, \qquad (4)$$

where the quantities ε_{11}, ε_{22}, σ_{11}, and σ_{22} refer to the components of the mixture. Use of the combination

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*In elementary treatments it is usually assumed that the opposing molar fluxes are equal in absolute magnitude, and not the mass fluxes, as follows from the strict theory. However, when the differences in the molecular weights are not large, this does not lead to important differences.

rules leads to comparatively good results, if the corresponding parameters for the mixture components do not differ substantially from one another.

Later in this paper we shall consider a mixture of cesium vapors and of cesium and helium vapor. In this case the parameters ε_{11} (for cesium) and ε_{22} (for helium) are markedly different, and the calculation according to formula (3) is evidently unreliable. However, direct data on the parameters ε_{12} and σ_{12} are available for a mixture of cesium and helium. Robinson [4] has shown that calculations based on the shift of hyperfine structure of spectral lines of cesium in a mixture with helium are in agreement with test data if it is assumed that $\varepsilon_{12}/k = 40.8°$ K and $\sigma_{12} = 3.39$ Å. These values are also used in our calculations.

The values of the coefficient D_{12} and k_T were calculated from the first approximation. The second and subsequent approximations usually give very small changes in the values of D_{12}, but can lead to more substantial change for the values of K_T [2]. However, for the purposes of the following analysis, it will be adequate to restrict ourselves to the first approximation. It should be noted that the value of k_T is very sensitive to a difference in the molecular weights in the mixture. For cesium $M_1 = 132.9$ and for helium $M_2 = 4$. We should therefore expect comparatively large values of k_T.

In the calculations of k_T, besides the values of ε_{12} and σ_{12}, we also require the values of ε_{11}, σ_{11}, ε_{22}, and σ_{22}. For helium the values assumed were $\varepsilon_{22}/k = 10.22°$ K and $\sigma_{22} = 2.58$ Å [2]. For cesium, according to estimates from the boiling temperature $\varepsilon_{11}/k = 1108°$ K, and according to measurements of the volume of the molecule in the solid phase $\sigma_{11} = 5.4$ Å [5]. Robinson [6], from calculations using the above value of σ_{12}, obtained for cesium $\sigma_{11} = 4.55$ Å and $\varepsilon_{11}/k = 4.49°$ K (in [6] this is given in error as 4490° K). The difference in the values of ε_{11} is substantial, but, in the case of small content of cesium in the helium, this has, in fact, little influence on the calculations of k_T.

The values found for D_{12} (for several pressures) and of k_T (for a low content of cesium in helium) are shown graphically in Figs. 1 and 2.

The theory of Enskog and Chapman was developed relative to rarefied gases. However, the corrections for dense gases at pressures of the order of several atmospheres are still not substantial, and the theory of Enskog and Chapman is valid. The reservation should be mentioned, however, that the theory in question, while giving good results in calculations of diffusion coefficient and other similar transport coefficients, is not sufficiently accurate for calculation of thermal diffusion. Particularly large deviations may occur in the vicinity of the inversion temperature [7]. However, the temperatures of interest to us are remote from the inversion temperature, which corresponds to a value $kT/\varepsilon_{12} = 0.95$. With the assumed value of ε_{12}/k, the inversion temperature for a mixture of cesium and helium is equal to ~39° K. Calculation shows that for the temperature region 400°–1000° K and above, the thermal diffusion ratio $k\Delta$ depends very little on the temperature. Figure 2 therefore gives only one line corresponding to the temperature range indicated. Within the framework of the theory considered, k_T does not depend on pressure.

It is noteworthy that for small values of p_1/P (up to 0.04–0.06) $k_T \approx p_1/P$ (Fig. 2). At larger values of p_1/P, $k_T < p_1/P$. Usually the thermal diffusion constant $\alpha_T = [k_T/(p_1/P)](1 - p_1/P)$ for mixtures of various gases is markedly less than unity [2, 8], i.e., $k_T < (p_1/P)(1 - p_1/P)$. With increasing difference in the molecular weights (masses) of the molecules of the mixture α_T increases. For $M_1 \gg M_2$ (when $(M_1 - M_2)/(M_1 + M_2) \approx 1$) and in the case when the interaction of the molecules obeys a Lennard-Jones potential, α_T is somewhat less than 0.4 for $p_1/P = 0.5$ and $kT/\varepsilon_{12} > 10$ [8].* Our calculations whose results are shown in Fig. 2, show that for small $p_1/P = 0.5$, the values of α_T for a mixture of cesium and helium are close to unity for $kT/\varepsilon_{12} > 10$, since $k_T \approx p_1/P$. Estimates that we made for a mixture of cesium and argon $[(M_1 - M_2)/(M_1 + M_2) = 0.54]$ for the case $p_1/P = 0.02$ and $kT/\varepsilon_{12} > 10$ gave $k_T \approx 8 \cdot 10^{-3}$ and $\alpha_T \approx 0.4$. Thus, for a reduction in the difference in the masses of the molecules the value of α_T was markedly reduced.

Using the values of D_{12} and k_T found, we shall determine the fluxes of concentration diffusion and thermal diffusion for the case of condensation of small additions of cesium in helium at the surface of a cooled tube.** The only other thing to be allowed for is that when there is condensation (or evaporation and other processes with change of volume of any component in the gaseous phase) an additional mass diffusion flux arises, usually called the Stefan flux [3]. The diffusion flux of the first (condensing) component may be written as

$$g_1 = -\frac{M_1 P D_{12}}{RT} \frac{M_2}{(M_1 - M_2)\, p_1/P + M_2} \times \left[\operatorname{grad} \frac{p_1}{P} + \frac{k_T}{T} \operatorname{grad} T \right] + W_M \frac{M_1 p_1}{RT}. \qquad (5)$$

The last term on the right of (5) describes transfer of material with a mass flux whose velocity is W_M.

The flux of the second component (inert gas), allowing for the mass flux $W_M M_2 (P - p_1)/RT$, must be equal to zero, since the condensation surface is impermeable for this component, while the total pressure must be the same everywhere. The condition that the flux of the second component must be zero gives

$$W_M = g_1' RT / M_2 (P - p_1), \qquad (6)$$

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*The calculations were made for a Lennard-Jones potential. Calculations for simpler interaction potentials (for example, taking into account only collison forces which fall off according to a power law with distance) may give smaller values of the thermal diffusion diffusion constant α_T.

**We shall consider a case with such small concentrations of cesium in helium that the cesium vapor in the boundary layer at the condensation surface will not become oversaturated anywhere and no formation of mist will begin.

where g_1' is the flux of the first component without the Stefan flux, given by formula (1).

Substituting the value of W_M into (5), we obtain

$$g_1 = -\frac{M_1 P D_{12}}{RT}\frac{1}{1-p_1/P}\left[\operatorname{grad}\frac{p_1}{P}+\frac{k_T}{T}\operatorname{grad}T\right].$$

Allowance for the Stefan flux leads to a contraction of the quantity $[(M_1 - M_2)p_1/P + M_2]$ in the formula for g_1, but a correction factor $1/(1 - p_1/P)$ has appeared. In the case when the contribution of the condensing component is small, the factor $1/(1 - p_1/P)$ is close to unity and may be omitted. But this still does not mean that the mass flux is very small. From the relation presented it may be found that the fraction of material transported with the mass flux is $(M_1p_1/P)/[(M_1 - M_2)p_1/P + M_2]$. For a mixture of cesium and helium with a cesium content of $p_1/P = 0.02$, this fraction is approximately equal to 0.4, while $1/(1 - p_1/P) \approx 1.02$. If $p_1/P = 2 \cdot 10^{-4}$ (as will be assumed in the subsequent calculations), the fraction of material transferred with the Stefan flux will be small (of the order 0.01). If the first term in (5) is expressed in terms of W_M by means of (6), we obtain

$$g_1 = \frac{M_1p_1 + M_2(P - p_1)}{RT} W_M = \rho W_M,$$

where $\rho = [M_1\rho_1 + M_2(P - \rho_1)]/RT$ is the mass density of the mixture.

To simplify calculations of condensation in tubes allowing for thermal diffusion, we make use of the concept of the reduced film [3] instead of the boundary layer. This is a nominal motionless film of gas encircling the tube, in which the processes of transport are accomplished by molecular action. Outside the film turbulent transfer considerably exceeds molecular and leads to equilibrium of temperatures or partial pressures (concentrations). If we neglect the influence of surface curvature, the thicknesses of the thermal δ_T and diffusion δ_D reduced films may be expressed by the following formulas:

$$\delta_T = \lambda/\alpha = d/\mathrm{Nu},$$

$$\delta_D = D_{12}/\alpha_D = d/\mathrm{Nu}_D.$$

In the absence of thermal diffusion, the transfer diffusion coefficient is introduced by the relation

$$g_1 = \frac{M_1\alpha_D P}{RT}\left[\left(\frac{p_1}{P}\right)_V - \left(\frac{p_1}{P}\right)_S\right],$$

where $(p_1/P)_V$ and $(p_1/P)_S$ are the relative partial pressures of cesium in the gas volume and at the tube surface. The cesium pressure at the tube surface may be considered equal to the saturation pressure at the surface temperature T_S, i.e., at the temperature assumed by a film of condensed cesium, which is a good conductor of heat. The temperature in the denominator of the quantity $M_2\alpha_D P/RT$ may be taken to be equal to the mean temperature, or even to the temperature T_V in the gas volume. It should be noted that $\lambda \sim T^{1/2}$ and $D_{12}/T \sim T^{1/2}$, approximately. Therefore, when λ is regarded as a constant as temperature changes, it is reasonable to consider the ratio D_{12}/T to be constant also [3], i.e., the quantity $M_1(\alpha_D P/RT) = M_1[(\mathrm{Nu}_D/d)(D_{12}P/RT)]$.

Because of the analogy between phenomena of heat transfer and diffusion, we may use a single parametric relation $\mathrm{Nu} = f(\mathrm{Re}, \mathrm{Pr})$ for both processes. In determining Nu_D the thermal Prandtl number $\mathrm{Pr} = \nu/a$ in the parametric relation should be replaced by the diffusion parameter $\mathrm{Pr}_D = \nu/D_{12}$. The relation [9]

$$\mathrm{Nu} = A\,\mathrm{Pr}^{0.35}\mathrm{Re}^n,$$

may be taken as a calculation relation, where the coefficient A and the exponent n are different in different ranges of Re. For example, for Re = 100–5000, A = 0.665 and n = 0.47.

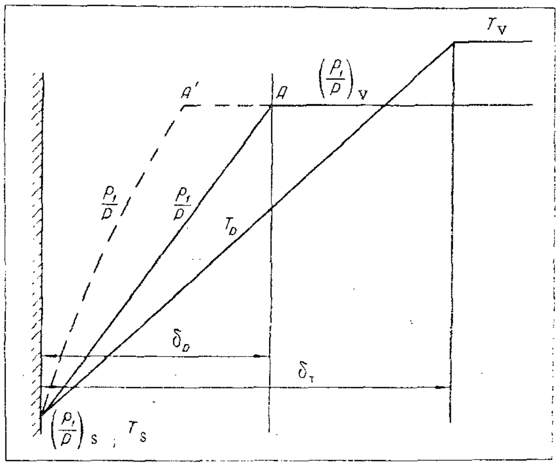

Fig. 3. Schematic of reduced films near the tube surface.

In the case of small molar additions of cesium to helium, the coefficient λ, ν and a may be reduced to those for pure helium. Because of the comparatively small values of D_{12}, it turns out that $\mathrm{Pr}_D > \mathrm{Pr}$, i.e., at $\mathrm{Nu}_D > \mathrm{Nu}$ for identical values of Re number. Therefore, $\delta_D < \delta_T$ (Fig. 3). The diffusion flux due to concentration diffusion (without thermal diffusion) is equal to

$$g_{1\mathrm{conc}} = \frac{M_1\alpha_D P}{RT_V}\left[\left(\frac{p_1}{P}\right)_V - \left(\frac{p_1}{P}\right)_S\right] = \frac{M_1D_{12}P}{RT_V}\frac{(p_1/P)_V - (p_1/P)_S}{\delta_D}.$$

The temperature drop is localized in the thermal reduced film. At the outer boundary of the diffusion film the temperature is

$$T_D = T_S + (T_V - T_S)\delta_D/\delta_T.$$

The thermal diffusion flux entering the diffusion reduced film may be estimated as

$$g_{1\mathrm{th}} = \frac{M_1D_{12}P}{RT_V}\frac{k_T}{T_D}\frac{T_V - T_S}{\delta_T},$$

k_T corresponding to the original concentration of cesium in the gas volume.

The given thermal diffusion flux must reach the walls, although, as we approach the wall and as p_1/P is reduced, the thermal diffusion ratio k_T falls off.

But the Stefan flux which is created takes part in the transport of cesium. Moreover, with decrease of the thermal diffusion flux inside the reduced film, the gradient p_1/P increases, and so does the concentration diffusion flux. The result, in fact, is a decrease in the thickness of the diffusion reduced film and an increase of the gradient in it (the broken line in Fig. 3). We may consider it to be approximately true that the total diffusion flux g_1 of cesium to the tube surface is equal to the sum of the fluxes that have been found, $g_{1\text{conc}}$ and $g_{1\text{th}}$.

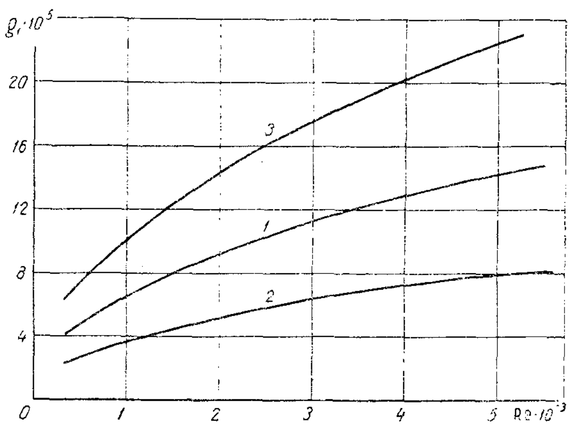

Fig. 4. Diffusion flux of cesium g_1, kg/m$^2 \cdot$ sec, to the tube surface during condensation from a mixture with helium ($P = 9.81 \cdot 10^4$ N/m^2, $(p_1/P)_V = 2 \cdot 10^{-4}$, $T_V = 873°$ K, $T_S = 373°$ K: 1) for $g_{1\text{conc}}$; 2) $g_{1\text{th}}$; 3) g_1.

The calculated values of diffusion fluxes are shown in Fig. 4. It may be seen from the figure that the thermal diffusion flux constitutes about 55% of the concentration diffusion flux and about 35% of the total diffusion flux. Of course, the results obtained are particularly tentative in nature. Nevertheless, it follows from them that in the case of condensation of cesium vapor from a mixture of cesium and helium, we must take account of thermal diffusion (for large temperature differences).

When we make a strict examination of heat transfer in the gases, in addition to the thermal flux proportional to the temperature gradient, we must also take into account the heat flux proportional to the concentration gradient (the Dufour effect). Moreover, we must take into account heat transfer due to flow of molecules of the gas [1–3]. The full expression for the heat flux q (allowing for the Stefan flux during condensation) has the form

$$q = -\lambda \operatorname{grad} T + RTk_T \frac{g_1}{(p_1/P) M_1} + \frac{5}{2} RT \frac{g_1}{M_1}. \qquad (7)$$

The second and the third terms simply express the above heat fluxes. The third term has been written down for the case of the monatomic gas helium proceeding to the wall, the specific heat of 1 mole of the helium being 5R/2 (at constant pressure).

Estimates for a mixture of cesium and helium show that in this case, when strong thermal diffusion is possible, only the first term in expression (7) is appreciable. Even for $p_1/P = 0.02$, the second and third terms together constitute less than 3% of the first term.

NOTATION

g_1 and g_2 are the diffusion fluxes of the components; M_1 and M_2 are their molecular weights; P and P_1 are the total pressure and partial pressure of the first component; D_{12} is the diffusion coefficient for a two-component mixture; R is the universal gas constant; T is the temperature; k_T is the thermal diffusion ratio; r is the distance between molecules; ε and σ are the parameters of Lennard-Jones potential function; k is the Boltzmann's constant; W_M is the Stefan mass velocity; ρ is the mass density of mixture; δ_T and δ_D are the thickness of thermal and diffusion reduced films; λ is the thermal conductivity; α and α_D are the heat transfer and diffusion transfer coefficients; d is the tube diameter; $Nu = \alpha d/\lambda$ and $Nu_D = \alpha_D d/D_{12}$ are the thermal and diffusion Nusselt numbers; $Re = Wd/\nu$ is the kinematic viscosity; $Pr = \nu/a$ and $Pr_D = \nu/D_{12}$ are the thermal and diffusion Prandtl numbers; a is the thermal diffusivity; q is the specific heat flux.

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