A CONTRIBUTION TO THE THERMODYNAMIC THEORY OF "STEADY" STATES OF TWO GAS VOLUMES JOINED BY A CAPILLARY

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The methods of nonequilibrium thermodynamics are used to establish a relation between the gradients of thermodynamic quantities in the quasi-steady state of a system of two gas volumes joined by a capillary.

We shall examine two volumes containing a binary gas mixture joined by a capillary. If at time zero the temperature, concentration, and pressure in the two volumes are different, then in the course of a sufficient time interval an adiabatic closed system of this kind will reach a state of thermodynamic equilibrium, characterized by maximum entropy and uniformity of all the thermodynamic parameters defining the state of the system.

It is not difficult to evaluate the relaxation time for each parameter by putting the remainder constant.

From the balance equations we obtain

$$\tau_P = \frac{4\eta lV}{\Pi r_0^4 P}, \quad \tau_C = \frac{lV}{2\Pi r_0^2 D}, \quad \tau_T = \frac{lV}{2\Pi r_0^2 \chi}. \tag{1}$$

It may be seen from (1) that $\tau_C \simeq \tau_T$, while for the ratio τ_P/τ_C, we have

$$\tau_P/\tau_C = 8\eta D/Pr_0^2.$$

For $r_0 = 0.01$ cm and normal conditions we obtain

$$\tau_P/\tau_C = 10^{-5}.$$

This means that under the conditions indicated in the system, the pressure is firstly established for practically unchanged concentration and temperature in the volumes of the system. A state of this kind is quasi-steady, or, according to the terminology of irreversible process thermodynamics, a steady state of the second order [1].

To find the connection between the thermodynamic parameter gradients in such a "steady" state, we use the methods of irreversible process thermodynamics.

The rate of entropy increase in an adiabatically closed enclosed system [2] is

$$\frac{\partial}{\partial t}\int \rho S dV = -\int (\mathbf{q} - \mathbf{i}\mu)\frac{\nabla T}{T^2} dV - \int \mathbf{i}\frac{\nabla\mu}{T} dV + \int \frac{1}{T}\sigma'_{ik}\frac{\partial v_i}{\partial x_k} dV. \tag{2}$$

The last integral in (2) may be transformed as follows:

$$\int \frac{1}{T}\sigma'_{ik}\frac{\partial v_i}{\partial x_k} dV = \int \frac{\partial}{\partial x_k}\left(\frac{\sigma'_{ik} v_i}{T}\right) dV - \int \frac{1}{T} v_i \frac{\partial \sigma'_{ik}}{\partial x_k} dV + \int \frac{1}{T^2}\sigma'_{ik} v_i \frac{\partial T}{\partial x_k}\partial V. \tag{3}$$

By transforming the first integral with respect to volume on the right of (3) into an integral over the motionless surface bounding the system, we may verify that it is equal to zero, if we neglect slip.

From the law of conservation of momentum, neglecting the convective term, we have [2]

$$\frac{\partial P}{\partial x_i} = \frac{\partial \sigma'_{ik}}{\partial x_k}. \tag{4}$$

Substituting (4) and (3) into (2), we obtain

$$\frac{\partial}{\partial t}\int \rho S \partial V = -\int \mathbf{v} n \frac{\nabla P}{nT} dV - \int \mathbf{i}\frac{\nabla\mu}{T} dV - \int (\mathbf{q} - \mathbf{i}\mu - \vec{\sigma}'\mathbf{v})\frac{\nabla T}{T^2} dV. \tag{5}$$

On the basis of (5) we may write the linear phenomenological relations

$$\mathbf{J}_i = -\sum_{k=1}^{3} L_{ik}\mathbf{X}_k, \quad \mathbf{J}_1 = \mathbf{v}n, \quad \mathbf{J}_2 = \mathbf{i}, \quad \mathbf{J}_3 = \mathbf{q} - \mu\mathbf{i} - \vec{\sigma}'\mathbf{v},$$

$$\mathbf{X}_1 = \frac{\nabla P}{nT}, \quad \mathbf{X}_2 = \frac{\nabla\mu}{T}, \quad \mathbf{X}_3 = \frac{\nabla T}{T^2}. \tag{6}$$

We shall make the following linear transformation of the fluxes and the corresponding transformation of forces:

$$\mathbf{J}'_i = \sum_{k=1}^{3}\beta_{ik}\mathbf{J}_k, \quad \mathbf{X}'_i = \sum_{k=1}^{3}\beta^*_{ik}\mathbf{X}_k. \tag{7}$$

The flux and force transform matrices are

$$\beta = \begin{Vmatrix} 1 & a & 0 \\ c & \frac{1}{m_1} & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \quad \beta^* = \begin{Vmatrix} \frac{1}{b} & -\frac{cm_1}{b} & 0 \\ -\frac{am_1}{b} & +\frac{m_1}{b} & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \tag{8}$$

$$a = (m_2 - m_1)/m_2 m_1; \quad b = (1 - acm_1).$$

The transformations (7) and (8) give $\mathbf{J}'_1$, the total molecular flux density, and $\mathbf{J}_2$, the flux density of one of the components in the fixed coordinate system.

The steady state of second order being examined is characterized by absence of over-all flux of molecules from one volume to the other, i.e.,

$$\mathbf{J}'_1 = 0, \quad \mathbf{X}'_1 + \frac{L'_{12}}{L'_{11}}\mathbf{X}'_2 + \frac{L'_{13}}{L'_{11}}\mathbf{X}'_3 = 0. \tag{9}$$

Setting $\mathbf{X}_2' = \mathbf{X}_3' = 0$ and using the Onsager relations, we obtain

$$\frac{L_{12}'}{L_{11}'} = \frac{\mathbf{J}_2'}{\mathbf{J}_1'}\bigg|_{\mathbf{X}_2' = \mathbf{X}_3' = 0}\,, \quad \frac{L_{13}'}{L_{11}'} = \frac{\mathbf{J}_3'}{\mathbf{J}_1'}\bigg|_{\mathbf{X}_2' = \mathbf{X}_3' = 0}\,. \tag{10}$$

Reverting to the former forces and fluxes, we obtain

$$\mathbf{X}_1 + \mathbf{X}_2 \frac{\mathbf{J}_2}{\mathbf{J}_1}\bigg| + \mathbf{X}_3 \frac{\mathbf{J}_3}{\mathbf{J}_1}\bigg| = 0. \tag{11}$$

The ratios of fluxes in (11) must be taken under the condition

$$\mathbf{X}_2' = \mathbf{X}_3' = 0 \text{ or } a\nabla P = n\nabla\mu,\ \nabla T = 0. \tag{12}$$

Under the above conditions, for an incompressible fluid, we have [2]

$$\mathbf{J}_1 = n\mathbf{v} = -n\frac{r_0^2}{8\bar{\eta}}\nabla P; \quad \mathbf{J}_2 = \mathbf{i} = -\rho D\nabla\mu \Big/ \left(\frac{\partial\mu}{\partial C'}\right)_{P,T}, \tag{13}$$

where $\bar{\eta}$ is some mean viscosity of the mixture.

From similar considerations we obtain, under conditions (12),

$$\mathbf{q} - \mu\mathbf{i} = -\rho D\left[k_T - T\left(\frac{\partial\mu}{\partial T}\right)_{C',P} \Big/ \left(\frac{\partial\mu}{\partial C'}\right)_{T,P}\right]\nabla\mu. \tag{14}$$

The calculations of $\vec{\sigma}'\mathrm{v}$ under conditions (12) is somewhat more complicated. If we understand v in the expression for $\vec{\sigma}'\mathrm{v}$ to be the mean velocity over the section of the capillary for an incompressible fluid, we may write

$$(\sigma' v)_z = 2\bar{\eta}\frac{\partial}{\partial z}\frac{v^2}{z}. \tag{15}$$

Allowing for dissipation of kinetic energy during viscous flow of the gas in the capillary, and averaging over the section, we obtain

$$-2\Pi r_0^2\rho v\frac{\partial}{\partial z}\frac{v^2}{2}dz = \int \sigma_{ik}'\frac{\partial v_i}{\partial x_k}dV = dz\int_0^{r_0}\bar{\eta}\left(\frac{\partial v_z}{\partial z}\right)^2 2\Pi r\,dr. \tag{16}$$

Substituting $v_z = -1/4\bar{\eta}(r_0^2 - r^2)(\Delta P)_z$ into (16) and integrating, we have

$$\frac{\partial}{\partial z}\frac{v^2}{2} = \frac{4\bar{\eta}v}{r_0^2\rho}. \tag{17}$$

From (17), (15), (14), (13), and (11), under conditions (12), it follows that

$$\left(\frac{\nabla P}{nT}\right) + \left(\frac{\nabla\mu}{T}\right)\frac{8a\bar{\eta}D\rho}{n^2 r_0^2\left(\frac{\partial\mu}{\partial C'}\right)_{P,T}} + \left(\frac{\nabla T}{T^2}\right)\times\left[\frac{8a\bar{\eta}D\rho}{n^2 r_0^2}\left(k_T - T\frac{\left(\frac{\partial\mu}{\partial T}\right)_{P,C'}}{\left(\frac{\partial\mu}{\partial C'}\right)_{P,T}}\right) - \frac{8\bar{\eta}^2}{n\rho r_0^2}\right] = 0. \tag{18}$$

Equation (18) gives the relation between gradients of the thermodynamic quantities which describe the system in the quasi-steady state under examination.

Let us examine the isothermal case, i.e., we shall assume that the two volumes contain a mixture of gases at different concentrations but at identical temperature. It then follows from (18) that

$$\nabla P = -\frac{8a\bar{\eta}D\rho}{nr_0^2\left(\frac{\partial\mu}{\partial C'}\right)_{P,T}}\nabla\mu = -\frac{8a\bar{\eta}D}{r_0^2}\frac{\rho}{n}\left[\nabla C' + \frac{k_P}{P}\nabla P\right]. \tag{19}$$

Transferring to molar concentrations C and neglecting the pressure diffusion term, we obtain, after integration with respect to concentration,

$$\Delta P = \frac{8\bar{\eta}D}{r_0^2}\ln\frac{[C + m_2/(m_1 - m_2)]_{\mathrm{II}}}{[C + m_2/(m_1 - m_2)]_{\mathrm{I}}}. \tag{20}$$

Designations I and II refer to the different volumes, and C is the molar concentration of the first gas. If there are originally pure gases in the volumes, we arrive at the well-known expression [3, 4]

$$\Delta P = 8\frac{\bar{\eta}D}{r_0^2}\ln\frac{m_2}{m_1}. \tag{21}$$

Equation (21) shows that during time τ_P a pressure drop is established in the system, even if the pressures in the two volumes were the same at time zero. Then the fluxes of individual components from one volume to the other after elapsed time τ_C will be equal neither in concentration nor in pressure. This phenomenon has been studied experimentally in [4, 5] under the name of baroeffect, in mutual diffusion of gases. If slip of the gas at the capillary wall is not allowed for, then the experimental results are described satisfactorily by (21).

Let us examine a second case, when the two volumes contain the same gas at different temperatures; then from (18) we have

$$\nabla P/\nabla T = 8\bar{\eta}^2 R/r_0^2 MP. \tag{22}$$

Equation (22) gives the thermomolecular pressure difference for small Knudsen numbers. If energy dissipation through viscosity is not taken into consideration, the thermodynamics of irreversible processes would indicate that there is no thermomolecular pressure difference at low Knudsen numbers. The thorough tests of Knudsen [6] were devoted to an experimental study of thermomolecular pressure difference. His theoretical formula, obtained by the Maxwell method, gave results at increased pressures differing from experimental values by more than a factor of two, although agreement was good in the molecular flow regime. Knudsen gives an experimental coefficient of 7.75 instead of 8 in (22), and in a later work 8.31 instead of 8. Since he assigned great weight to the data at intermediate pressure in reducing the experimental results, it must be assumed that (22) gives a sufficiently good description of Knudsen's experimental results.

A similar formula with coefficient 12.2 was obtained by Deryagin and Bakanov [7] by methods of irreversible process thermodynamics, and including the third-order approximation of the Champman and Cowling kinetic theory in calculating heat transfer.

In more complex cases, when there are gases with different concentrations and different temperatures in the two volumes, the pressure difference that develops may also be obtained from (22).

NOTATION

τ_P, τ_C, τ_T—relaxation times for pressure, concentration, and temperature; V—one of the volumes of the system; l, r_0—length and radius of capillary; η, D, χ—coefficients of viscosity and mutual diffusion, and thermal diffusivity; S, μ—entropy and chemical potential of unit mass of gas mixture; q, i—heat and diffusion flux densities; ρ—mixture density; T—absolute temperature; σ_{ik}—viscous stress tensor; v—mixture mass velocity; k_p, k_T—pressure diffusion and thermal diffusion ratio; m_1, m_2—masses of molecules of system; R—gas constant; M—molecular weight; C, C'—molar and weight concentrations. Subscripts i, k for the tensors are coordinates, and for the matrices—numbers of rows and columns.

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