An Analytical Treatment of a Reference Coordinate for the Diffusion and Sedimentation Processes

OLE LAMM

The Royal Institute of Technology, Division of Physical Chemistry, Stockholm 70, Sweden

In order to ensure a clear significance of a reference equation, which is used in certain theories of the diffusion and sedimentation processes, a general derivation and discussion of this equation is developed.

At least in fluid systems, the diffusion and sedimentation processes are generally studied under such conditions that there is no, or only a negligibly small, "bulk displacement" or flow of the mixture as a whole. Here, we will stick to the typical case of a mixture in which the *partial volumes* of the different components are practically independent of the time and the distance coordinates, either owing to very small concentration differences (differential diffusion) or due to the use of nearly ideal mixtures. Absence of flow then simply means that the system is enclosed in a diffusion or sedimentation cell.

The fundamental equations in the diffusion and sedimentation theories (*cf.* Refs.[1-3]) need a complementary equation which defines a reference frame for the flows. In this respect, an equation proposed by Onsager [4]

$$\sum \bar{v}_i J_i = \sum \bar{v}_i C_i c_i = 0 \tag{1}$$

has been used. J is the flow in moles/cm² sec, C the linear velocity of the component, c mole/cm³ the concentration of the component and $\bar{v}$ its partial molar volume. The sums in these equations have the dimension of velocity and represent the flow in bulk of the mixture. Eqn. (1) has never been deduced analytically and the underlying facts have been explained only for *two* components [5,6]. It is felt that this is disadvantageous at least from an elementary point of view, especially in a case like the sedimentation diffusion process in a centrifugal field. This proceeds in a cell of sector shape and there should be no doubt as to the applicability of eqn. (1) also in this case.

The procedure is to combine the equation of continuity with the general expression $\sum \bar{v}_i dc_i = 0$, known from the treatment of partial quantities in thermodynamics. The former gives for the (trivial) case of parallel flow

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x} \tag{2a}$$

and for the cylindrical flow in a parallel-walled cell of sector shape

$$\frac{\partial c_i}{\partial t} = -\frac{1}{x}\frac{\partial xJ_i}{\partial x} \tag{3a}$$

Combining these equations with $\sum \bar{v} \dfrac{\partial c_i}{\partial t} = 0$ gives

$$\sum \bar{v}_i \, \partial J_i = 0 \tag{2b}$$

and

$$\sum \bar{v}_i \, \partial J_i \Big/ \sum \bar{v}_i \, J_i = -\partial x/x \tag{3b}$$

or by integration

$$\sum \bar{v}_i \, J_i = C' \tag{2c}$$

and

$$\sum \bar{v}_i \, J_i = \frac{D'}{x} \tag{3c}$$

Owing to $\sum \bar{v}_i (C_i + C)c_i = \sum \bar{v}_i C_i c_i + C$, to give a certain value to the integration contants C' or D' is to define a coordinate for the velocities which is common to all the components. In eqn. (1) these constants are put equal to zero.

In order to see that $C' = 0$ and $D' = 0$ correspond to the case of a closed cell, *i. e.* absence of flow in bulk, we simply have to consider the volume change caused by the transports of ∂n_i mole in the time ∂t per cm^2 through a certain x-level. This is $\partial V = \sum \bar{v}_i \, \partial n_i = \sum \bar{v}_i \, J_i \partial t = \partial t \sum \bar{v}_i \, J_i$. Hence, $\partial V = 0$ corresponds to the validity of eqn. (1) and *vice versa*.

That $\sum \bar{v}_i J_i$ represents the velocity of the flow in bulk of the mixture is illustrated by eqn. (3c) since, in the sector shaped cell, the velocity of a flow in bulk is inversely proportional to the radius x. It is seen that $D' = 0$ is the only assumption which gives a *fixed* coordinate for the diffusion sedimentation process in a sector-shaped cell. Any other assumption defines a *local* frame, varying with x. This fixed coordinate evidently also holds for the cell itself and the measuring arrangement as a whole.

REFERENCES

1. Onsager, L. *Ann. N. Y. Acad. Sci.* **46** (1945) 241.
2. Lamm, O. *Arkiv Kemi, Mineral. Geol.* **18A** (1944) No. 2.
3. Lamm, O. *Acta Chem. Scand.* **7** (1953) 173; **8** (1954) 1120.
4. Onsager, L. and Fuoss, R. M. *J. Phys. Chem.* **36** : **2** (1932) 2689.
5. Hartley, G. S. and Crank, *J. Trans. Faraday Soc.* **45** (1949) 801.
6. Lamm, O. *Arkiv Kemi, Mineral. Geol.* **17A** (1943) No. 9.