A Countercurrent Gaseous Diffusion Process; Theory of the Separation at Equilibrium

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An experimental device for the obtention of a gaseous diffusion countercurrent process is proposed. The theory of the separation at equilibrium for a binary isotopic mixture is developed on the basis of the transport up the tube, the total and the desired molecules transverse transport. The solution is given for any value of the relative abundances.

Fig. 1 shows an experimental device in which a countercurrent gaseous diffusion process can be obtained. P is a pump, and M is a porous barrier. The length $h$ determines the ratio of pressures $\xi$ for each value of the velocity $v_0$ ($z=h$). The notation used follows.

- $N$: molar fraction of light molecules,
- $1-N$: molar fraction of heavy molecules,
- $N_h$: molar fraction of light molecules at $z=h$,
- $N_0$: molar fraction of light molecules at $z=0$,
- $\delta$: density of the gas,
- $p$: pressure of the gas,
- $v$: velocity of the gas,
- $w$: gap-space of the chambers,
- $\sigma$: cross-section of the chambers,
- $c_1$: mean thermal velocity of light molecules,
- $c_2$: mean thermal velocity of heavy molecules,
- $c=Nc_1+(1-N)c_2$: mean thermal velocity of the molecules of a gas of light molecular fraction $N$,
- $D$: self-diffusion coefficient,
- $\kappa$: specific free area of the porous wall,
- $h$: total length of the countercurrent, and
- $\nabla$: $\nabla x$.

![Fig. 1. Device for countercurrent gaseous diffusion.](image)

Transport up the Tube

At equilibrium, the transport up the tube of the desired molecule, — let us assume the lighter one of a binary mixture —, must be zero. In fact, there are two opposed transports, one due to the countercurrent $(\varphi_c)$, the other to ordinary diffusion $(\varphi_D)$. They are respectively

$$\varphi_c = \kappa (c \varphi N + c \varphi N')$$
$$\varphi_D = \kappa (c \varphi D + c \varphi D')$$

Now, taking into account that $c \varphi + c \varphi' = 0$; $d \varphi' = d \varphi$; $d D = d D'$, and that in all places $\nabla N = \nabla N'$, we arrive at

$$v A N - 2 D \nabla N = 0$$

where

$$A N = N - N'$$

Total Transverse Transport

To a far greater extent than is the case with the conventional countercurrent, the gaseous diffusion countercurrent is sensitive to its length. It must be remarked that the total transverse transport is zero in a conventional countercurrent. For a gaseous diffusion one it is not. On the contrary, it is even greater than the desired molecules transport itself. Consequently, the velocity of each current is a function of $z$. Let us consider the velocity of the gas in the low-pressure chamber. The variation $v \nabla v$ is due to the total transverse flow of material per unit length of column per second. Then, if there is no viscous flow through the porous barrier,

$$w d \nabla v = \kappa c (\delta' - \delta)$$
where \( z \) is a dimensionless quantity that characterizes the porous barrier.

Consequently, since \( v_{x=0} = 0 \), the velocity results

\[
v = \left( \frac{c}{w} \right) \left( \xi - 1 \right) z = \nabla v \cdot z
\]

where \( \xi = \frac{p'}{p} \).

Making \( z = h \), one obtains, obviously,

\[
v = \left( \frac{c}{w} \right) \left( \xi - 1 \right) h
\]

which gives the relation between \( \xi \), \( h \) and \( v_h \).

**Transverse Transport of the Desired Molecules**

The effects that tend to change the value of \( \Delta N \) must add to zero. There are two such effects, the change in concentration due to the countercurrent and the gaseous diffusion itself. Let \( \psi \) be the transverse transport per unit area of unit length of porous wall per second. The change in concentration per unit length per second due to the countercurrent is, for the low pressure chamber,

\[
dw \left[ \nabla (v N) - D \nabla^2 N \right]. \tag{9}
\]

We have then

\[
\psi - \delta w \left[ \nabla (v N) - D \nabla^2 N \right] = 0. \tag{10}
\]

The transport \( \psi \) is the consequence of two transports, \( \psi_+ \) due to diffusion from high pressure chamber, and \( \psi_- \) due to diffusion from low pressure chamber. They are respectively

\[
\psi_+ = \frac{\alpha c}{w} \delta' N', \quad \psi_- = \frac{\alpha c}{w} \delta N. \tag{11}, (12)
\]

Substitution of (11) and (12) in (10) then gives, neglecting \( D \nabla^2 N \),

\[
(\frac{\alpha c}{w}) \left[ N(\xi - 1) - \xi \Delta N \right] = v \nabla N + N \nabla v. \tag{13}
\]

**Consequences of the Transport Equations**

Equation (4) may now be solved for \( \Delta N \), and substitution of this value in (13) then gives

\[
N \frac{c_1 - c}{c} \nabla v = \left[ v + \frac{2 \alpha c_1}{w v} \xi D \right] \nabla N \tag{14}
\]

where, for the sake of simplicity, we have supposed the term in \( D \nabla^2 N \) to be null, in so far as it actually is much smaller than \( \nabla (v N) \).

Now, since from the definition of \( c \)

\[
c_1 - c = (1 - N) \Delta c
\]

where \( \Delta c = c_1 - c_2 \), equation (14) becomes

\[
N(1 - N) \frac{\Delta c}{c} \nabla v = \left[ v + \frac{2 \alpha c_1}{w v} \xi D \right] \nabla N \tag{15}
\]

which leads to

\[
d \ln \frac{N}{1 - N} = \frac{\Delta c}{c v} \nabla v \; \mathrm{d}z \tag{16}
\]

where

\[
\Omega = v^2 + 2 \left( \frac{\alpha c_1}{w} \right) \xi D. \tag{17}
\]

The solution of equation (16) is

\[
\ln \frac{N}{1 - N} = \frac{\Delta c}{c} \ln \Omega + C \tag{18}
\]

which leads to the separation factor

\[
q = \frac{N_h(1 - N_h)}{N_h(1 - N_h)} = \left[ 1 + \frac{v_h^2}{B} \right]^{\frac{\Delta c}{2} c} \tag{19}
\]

where

\[
B = 2 \left( \frac{\alpha c}{w} \right) \xi D \ll v_h. \tag{20}
\]

Equation (19) can also be given as a function of \( \xi \) and \( h \), \( (c_1 \sim c) \), as follows,

\[
q = \left[ 1 + \frac{\alpha c}{w} (\xi - 1)^2 h^2 \right]^{\frac{\Delta c}{2} c}. \tag{21}
\]

If one applies equation (19) to isotopic mixtures, the following approximation usually stands

\[
\Delta c/c = \ln a \tag{22}
\]

where \( a \) is the separation factor of a unit process. The equivalent number of unit processes is then, from (19)

\[
n = \frac{1}{2} \ln \left[ 1 + \frac{\alpha c}{w} (\xi - 1)^2 h^2 \right]^{\frac{\Delta c}{2} c}. \tag{23}
\]

**Interpretation of Results**

For the interpretation of the results, we shall now consider the separation of a heavy isotopic mixture treated through a barrier of \( \xi \sim 10^{-3} \), in an apparatus of \( h \sim 1 \text{ m} \) and \( w \sim 1 \text{ cm} \), with a ratio of pressures \( \xi \sim 10 \). The thermal velocities are, of course, ca. \( 10^4 \text{ cm/s} \). In such a case, the value of \( n \) results ca. 7. It must be remarked that the concept of height equivalent to a theoretical unit loses its sense. In fact, further increasings of \( h \) increase slighter and slighter the separation factor. In the practical case discussed, for example, \( n \) takes the value of 8 for \( h = 3 \text{ m} \), 9 for \( 10 \text{ m} \), and only 11 for \( 100 \text{ m} \)!

A laboratory apparatus could be made 3 m-length. In such a case, when applied to, let us say, \( ^{36} \text{A} - ^{40} \text{A} \), for which \( \alpha = 1.05 \), the total separation factor attained would be 1.48.

It obviously is possible to adjust the apparatus for continuous production. In this case, the separation factor would be smaller.