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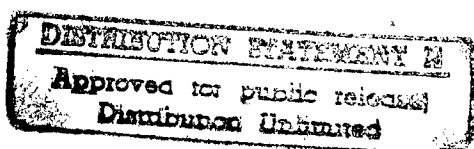
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THE ISOTOPE EXCHANGE METHOD FOR MEASURING SATURATED
VAPOR PRESSURE AND DIFFUSION COEFFICIENTS

- USSR -

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THE ISOTOPE EXCHANGE METHOD FOR MEASURING SATURATED VAPOR PRESSURE AND DIFFUSION COEFFICIENTS

I. The Effect of the Molecular Condensation Coefficients on the Rate of the Exchange Reaction

[This is a translation of an article
written by V. I. Lozgachev in Zhur. Fiz.
Khim. (Journal of Physical Chemistry),
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The interest displayed recently in the measurements of saturated steam pressures and diffusion coefficients D by means of isotope exchange is not accidental, since this exchange is the only convenient method which permits the determination of the buoyancy of the saturated vapors of alloys, where the concentration of a component during the experiment should remain constant. This method permits, at the same time, the determination of the other, not less important characteristic of the metal or alloy, its diffusion coefficient. This fact, namely that the surface layer of a specific thickness participates directly in the exchange, permits the estimation of some surface properties of the given substance if the appropriate equations are solved. The availability of convenient radioactive isotopes of almost all elements of the periodic table makes this method universally applicable to the practical study of any substance in its condensed state.

However, a broader implantation of the above method in the field of practical scientific investigation is hindered by an incomplete understanding of its theory. The theoretical data published previously (1-5) are insufficient. The author's aim is to present a full and consecutive solution (as far as possible) of a series of problems connected with the application of the proposed method in the region of low-pressure saturated vapor (less than 0.1 mm).

According to the kinetic theory, gas pressures are determined by the number of impacts of molecules per unit of

wall area, per unit of time. A dynamic equilibrium exists between the saturated vapor and solid (or liquid) phase, when the same number of molecules evaporate from the surface of a substance per unit time as are condensed on it. If the coefficient of condensation α is less than 1, the apparent rate of vaporization n ($\text{cm}^{-2}\text{sec}^{-1}$), corresponding to the buoyancy of the saturated vapor, is larger than the true evaporation rate of the given substance in vacuum n_0 ($\text{cm}^{-2}\text{sec}^{-1}$). The two rates are related by the following equation:

$$n_0 = \alpha n \quad (1)$$

The lower the coefficient of condensation, the higher the pressure of saturated vapor, at a given true evaporation rate.

Condensation is defined as a transition of molecules from a gaseous to a solid (or liquid) phase, in the course of which the condensed molecule loses its "identity," and becomes indistinguishable from the other surface molecules of the substance. At vapor pressures lower than 0.1 mm it may be apparently assumed that the real evaporation rate of the substance is independent of the buoyancy of the surrounding vapor. In other words, the evaporation rate in vacuum is the same as that in the presence of saturated vapor (6) [at less than 0.1 mm]. These postulates permit the use of isotope exchange between the gaseous and condensed phases of the given substance for the determination of saturated vapor pressures of solid and liquid substances.

It is assumed that the analyzed substance is inert to the wall of the exchange vessel and that the number of intermolecular collisions is small as compared with the number of molecular impacts on the wall of the vessel. The molecules of the substance which fall on the wall from the gaseous phase are reflected from it according to Knudsen's Cosine law and may give part of their energy to the wall or may rebound according to the law of elastic spheres. In this sense, even the surface points on which condensation does not occur are passive, and their number may be used for the determination of condensation coefficients. A certain surface layer of the substance (exchange layer), consisting of one or several monolayers (ν - number of layers), is subject to a direct effect of the exchange. This monolayer is characterized by the fact that its isotope concentration gradient is always zero. The thickness δ and density ρ of the exchange layer are constant for each given substance at a given temperature and depend apparently on its crystalline structure. On the basis of the above assumptions, it is not too difficult to visualize a simple exchange mechanism. If several samples of a given substance with different amounts

many times longer than the linear dimensions of the vessel (Table 1). Therefore, it should be noted that no noticeable changes in the substance will occur prior to the establishment of equilibrium.

Table 1*

Pressure Mm Hg	1,000°K			100°K		
	Rate of Molecular Motion 10^{-4} Cm/Sec	Evaporation Rate $\text{Cm}^{-2}\text{sec}^{-1}$	Vapor Density Cm^{-3}	Rate of Molecular Motion 10^{-4}	Evaporation Rate $\text{Cm}^{-2}\text{sec}^{-1}$	Vapor Density Cm^{-3}
10^{-2}	4.4	10^{18}	10^{14}	1.4	$3.4 \cdot 10^{18}$	$9.6 \cdot 10^{14}$
10^{-4}	4.4	10^{16}	10^{12}	1.4	$3.4 \cdot 10^{16}$	$9.6 \cdot 10^{12}$
10^{-8}	4.4	10^{12}	10^8	1.4	$3.4 \cdot 10^{12}$	$9.6 \cdot 10^8$

* The table is based on molecular weight $M = 107.9$ and condensation coefficient $\alpha = 1$.

If only one specimen is in equilibrium with its saturated vapor, the entire vapor is renewed instantaneously at pressures which are of interest to us, provided the containing vessel is not too large. This fact may be inferred from Table I. However, one may select experimental conditions in such a way that the specific activity of the vapor over the specimen (region U in Fig. 1)

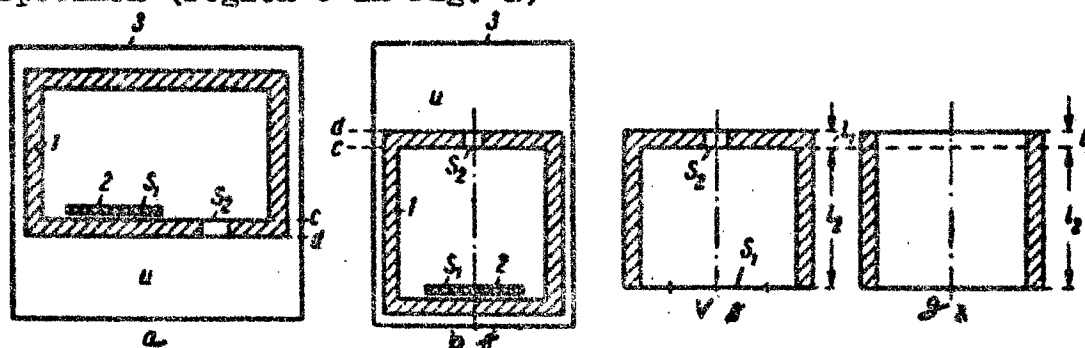


Fig. 1. Derivation of Transfer Coefficients for Molecular Transfer from Different Type of Vessels Into Vacuum: a, b - Effusion chambers with an orifice situated correspondingly in the plane of evaporizer or coaxially with it. 1 - the chamber's shell, 2 - the sample, 3 - vapor-containing vessel (specific activity α)

[cont'd]

ivity U); V - chamber b with an orifice in which the sample is replaced with an infinitely thin diaphragm, g - cylindrical tube

remains practically constant, whereas the activity of the specimen changes with time (4,5). Because of this choice, such a system may have a practical significance.

Probabilities of Transfer: The probabilities of molecular transfer from one exchange layer into another depend on the shape and size of the container, the spacing of specimens in relation to each other, and on the molecular condensation coefficients in the given layer.

We shall study a variant, in which Knudsen's effusion chamber is placed in the atmosphere of saturated vapor of constant specific activity, on the bottom of which chamber is placed a round, flat specimen of surface area, s_1 . The area of cross section of the chamber orifice is s_2 . The orifice's resistance is denoted by K (Fig. 1, a, b). The steady rate with which the gas flows from the orifice of the chamber into the vacuum shall be determined. For this reason, we shall follow the process which leads to the establishment of a steady state of gas flow.

Let us call the probability $W_1(W_2)$ that a molecule, which leaves the surface $s_1(s_2)$, according to the Cosine Law, falls always on the surface $s_2(s_1)$. On its way the molecule may collide several times with the wall of the vessel, but cannot return to the surface of the evaporator. The probabilities $W_1(W_2)$ are integral, or evenly distributed over the entire surface of the evaporator, and depend only on geometric factors. Since all molecules evaporated from the surface of the specimen are equivalent, it is sufficient to measure the increase of molecular bombardment density with time on the wall of the vessel, conditioned by only one molecule. The over-all effect, in such a case, will be equal to the sum of the effects of all molecules.

The molecule leaving surface s_1 has two possibilities of returning to it: (1) as a result of a reflection from the wall of the chamber, and when it misses the orifice with a probability $1-W_1$, and (2) as a result of reflection from the wall of orifice s_2 . Similarly, a molecule crossing the lower cut C plane of the orifice in the direction of s_1 may return to s_2 after being bounced from the wall of the chamber (probability of return is $1-W_2$), or after the reflection from the surface s_1 (if it does not undergo condensation).

One must assume that the directional distribution of molecules in the plane C , upon their exit from the orifice, occurs in accordance with the Cosine Law, otherwise the term W_2 must take into account the parameters in which

the orifice differs from the flat evaporator.

The increase of molecular bombardment density may be conveniently studied in separate consecutive cycles, taking as a basis the constant true evaporation rate independent of the surrounding pressure. The length of the cycle is determined by the time necessary for the molecule to traverse the path from the evaporator to the wall of the vessel and back. For one molecule the given process is illustrated in Table 2.

Table 2

Cy- cle	Over-all Molecular Flux, 1/Sec.					
	From Evapor- ator s_1	To Surface s_2		From Surface s_2 (as a result of bouncing off Walls of Ori- fice) B_1	Towards Evaporator $s_1 A_1$	
		From Surface s_1	From Walls of Chamber		From Walls of Orifice	From Walls of Chamber
1	1	W_1	0	$W_1(1-K)$	$B_1 W_2$	$1 - W_1$
2	$1 + A_1(1-\alpha)$	$[1 + A_1(1-\alpha)]W_1$	$B_1(1 - W_2)$	$\{[1 + A_1(1-\alpha)]W_1 + B_1 \times (1 - W_2)\}(1-K)$	$B_2 W_2$	$\{[1 + A_1(1-\alpha)] \times (1 - W_2)\}$
n	$1 + A_{n-1}(1-\alpha)$	$\{[1 + A_{n-1} \times (1-\alpha)]W_1$	$B_{n-1}(1 - W_2)$	$\{[1 + A_{n-1}(1-\alpha)]W_1 + B_{n-1} \times (1 - W_2)\}(1-K)$	$B_n W_2$	$\{[1 + A_{n-1} \times (1-\alpha)](1 - W_2)\}$

Functions A_n and B_n represent infinitely decreasing series. In the interval $n = \infty$ the recurrent formulae relating the two are transformed into a system of two equations:

$$A = [1 + A(1-\alpha)](1 - W_1) + BW_2,$$

$$B = \{[1 + A(1-\alpha)]W_1 + B(1 - W_2)\}(1 - K).$$

from which by rearrangement one obtains:

$$A = \frac{K - K(W_1 + W_2) + W_2}{Z}; \quad (3)$$

$$B = \frac{W_1(1-K)}{Z}, \quad (4)$$

where $Z = Ka + KW_1(1 - \alpha) + \alpha W_2(1 - K)$.

By substituting into appropriate expressions of fluxes for simplification the terms for A and B, according to the equations (3) and (4), and multiplying the results by $n_0 s_1$, the desired flux formulae are obtained. The expression for the total flux from a unit of surface s_1 has a form (Table 2):

$$n' = n_0 \frac{K + W_2(1 - K)}{Z}. \quad (5)$$

The number of molecules impinging on a unit of the surface s_2 of the orifice and coming from the specimen equals:

$$n_1^0 = n_0 \frac{s_1}{s_2} \frac{W_1}{Z}. \quad (6)$$

Let us introduce the notation:

$$\omega_1 = \frac{W_1 K}{Z}, \quad (7)$$

in which ω_1 represents the probability of transfer of an evaporated particle from specimen s_1 into the region U. The steady rate of gas outflow from the orifice of the effusion chamber, having the permeability* K , into the vacuum is equal to $n_0 s_1 \omega_1$.

The reverse flux from the surface s_2 is represented by the expression (Table 2):

$$n_0 s_1 \frac{W_1(1 - K)}{Z}. \quad (8)$$

The reverse flux towards the surface s_1 equals:

$$n_0 s_1 \frac{K - K(W_1 + W_2) + W_2}{Z}. \quad (9)$$

Let $K = 0$ in equation (6) (orifice of chamber is closed), then:

$$n_1^0 = \frac{n_0 s_1 W_1}{s_2 W_2}. \quad (10)$$

Since the exchange chamber is uniformly filled with molecules, the forward and reverse fluxes are equal in the sur-

* Permeability is defined as a probability of passage of the molecules through the orifice of the chamber.

rounding region U and are directly over the specimen. Therefore, in the case of equilibrium vapor, one may write:

$$W_1 s_1 = W_2 s_2. \quad (11)$$

At the same time, according to (1) from equation (10), one finds that $n_1^0 = n$. The term n represents the normal molecular bombardment density, corresponding to the saturated vapor buoyancy of the given substance, at a given condensation coefficient. This normal density will be inevitably attained in the vessel if the vapor flow outwards is stopped.

Let us now find the expression for the molecular transfer from the saturated vapor region U to the exchange layer s_1 (Fig. 1, a, b). Let us assume that the sample does not evaporate. Since part of the molecules are reflected from the surface s_1 ($\alpha \neq 1$), the surface is equivalent to an orifice of area s_1 , over which a net with a number of "eyes" is seemingly stretched. The "eyes" (cells) of the net correspond to the surface units on which condensation occurs. The reflection of molecules from the net's knots follows the Law of Cosines. In such a setup the gas enters the chamber through an orifice and leaves it through the net at a constant rate. A measured pressure drop in the vessel will thus be produced. This drop may be determined by means analogous to those used in the previous measurements. However, since the coefficient K is intrinsically the same as the coefficient of condensation α (the only difference is their numerical value), one may make formally the same deductions which interest us, from the above established equations for gas flow from the chamber into region U. To obtain this result, it is only necessary to substitute simultaneously K for α , W_1 for W_2 and correspondingly s_1 for s_2 .

Since the original number of molecules traversing the lower cross section of the orifice in one second is equal to nKs_2 , the corresponding single effects should be multiplied by nKs_2 . In such a manner, the total flux per unit area of the orifice into the chamber would be equal, according to (5), to

$$n'' = Kn \frac{\alpha + W_1(1-\alpha)}{2}. \quad (12)$$

Expression Z, as may be readily seen, does not change in case of the above rearrangement. Similarly, the number of molecules impinging on the unit area s_1 of the specimen per second is obtained from expression (6)

$$n_1^0 = n_{s_1} \frac{KW_1}{Z}. \quad (13)$$

Let us introduce the notation:

$$\omega_2 = \frac{KW_2}{Z}, \quad (14)$$

where ω_2 represents the probability of molecular transfer from the region of saturated vapor U into the exchange layer s_1 , reduced to the true evaporation rate. The steady rate of gas flow from region U through the orifice of the effusion chamber and further through the net is equal to $n_{0s_2} \omega_2 (\text{sec}^{-1})$.

According to (8), the reverse flux from the specimen s_1 is found to be

$$n_{s_1} K \frac{W_2(1-\alpha)}{Z}. \quad (15)$$

The number of molecules returning to the orifice s_2 equals, according to (9)

$$n_{s_2} K \frac{\alpha - \alpha(W_1 + W_2) + W_1}{Z}. \quad (16)$$

If the conditions at which one may neglect the collision between the molecules are fulfilled, the regular flow rates of gas from the specimen s_1 towards the outside, and the reverse flow from region U into the chamber, are established independently of each other. Therefore, upon the transfer of the chamber from vacuum into the atmosphere of saturated vapor, the two opposed fluxes are superimposed. Upon the attainment of equilibrium their sum is equal to the sum of fluxes, calculated separately for each process. In Table 3 are given the expressions for pressure in the appropriate planes, for the gas flow from specimen s_1 into vacuum (I), and from region U through the chamber and the imaginary net (II) downwards $p\downarrow$ or upwards $p\uparrow$. Saturated vapor pressure is taken as a unit.

Table 3

Plane	Type of Flux	$p \downarrow$	$p \uparrow$	Pressure Drop $\Delta p = p \downarrow - p \uparrow$
s_1	I	$1 - \frac{W_1 K}{Z}$	$\frac{K\alpha + W_2 \alpha (1 - K)}{Z}$	$\frac{K\alpha W_1}{Z}$
	II	$\frac{W_1 K}{Z}$	$\frac{KW_1 (1 - \alpha)}{Z}$	
c	I	$\frac{W_2 \alpha (1 - K)}{Z}$	$\frac{W_2 \alpha}{Z}$	$\frac{K\alpha W_2}{Z}$
	II	$\frac{K\alpha + KW_1 (1 - \alpha)}{Z}$	$1 - \frac{\alpha W_2}{Z}$	
d	I	0	$\frac{K\alpha W_2}{Z}$	$\frac{K\alpha W_2}{Z}$
	II	1	$1 - \frac{K\alpha W_2}{Z}$	

From the table it may be seen that the sum of pressures I and II in the given plane and in each direction equals one, since at equilibrium in any point of the vessel the common pressure equal to the pressure of the saturated vapor is established.

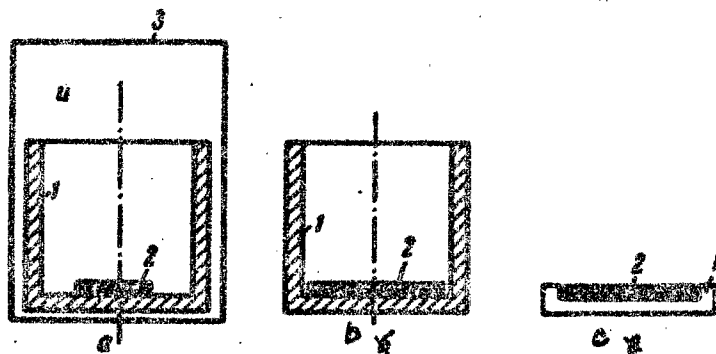


Fig. 2. The types of exchange chambers for a unidirectional exchange: 1 - Shell of chamber; 2 - Specimen, 3 - Vessel filled with the saturated vapor of a given substance with a constant specific activity.

It may be also inferred from the table that pressure drops in each plane are equal for both fluxes. This [equality] means that the passage of the substance from one phase to another follows the law of mass conservation of these phases. This law should be fulfilled at equilibrium independently

of the geometry of the vessel. Therefore, it is sufficient to know only one coefficient of transfer. The other one may be found from the equation

$$\omega_1 s_1 = \omega_2 s_2, \quad (17)$$

which follows from the mass conservation law. Equation (17) is not valid if the temperatures of the phases are different.

If one lets $K = 1$ in equations (7) and (14), the appropriate expressions for the vessels with infinitely thin diaphragm (Fig. 2,a) or altogether without the diaphragm (Fig. 2,b) are obtained:

$$\omega_1 = \frac{W_1}{\alpha + W_1(1-\alpha)}; \quad (18)$$

$$\omega_2 = \frac{W_2}{\alpha + W_1(1-\alpha)}, \quad (19)$$

If $K = W_1 = 1$ — the case of direct contact of the studied substance with the vapor of constant specific activity U (Fig. 2,c), then $\omega_1 = \omega_2 = 1$.

By definition, the probability W_1 may be replaced by a certain generalized probability P of the impingement of the molecule from an evaporator of any form on some arbitrary surface. This assumption is valid only if the molecule traveling to its destination is incapable of returning to the evaporator. In such a case, from (18) one obtains an expression for the contribution of the condensation coefficient effect:

$$\Omega(\alpha) = \frac{P}{\alpha + P(1-\alpha)}, \quad (20)$$

where $P = \Omega(1)$. The equation is valid for vessels with one or several arbitrarily shaped orifices.

Expression (20) may be used specifically for the determination of the mass of gas leaving the cylindrical tube with an evaporating surface per unit time (Fig. 1,g). The specimens of such a character are frequently employed for the measurement of gas buoyancy by Langmuir's Method, using high-frequency heating.

When $\alpha = 1$, one obtains from (7)

$$P = \omega_1(1) = \frac{W_1 K}{K + W_2(1-K)}. \quad (21)$$

If one now substitutes the above expression into equation (20), one obtains the original equation. Expression (21) represents a general formula for the passage of the rarefied

gas through a two-vessel system. One such system is represented in Fig. 1,v. The entrance orifice s_1 of the tube consists of an infinitely thin membrane, whereas orifice s_2 is represented by a tube of length l_1 .

One of the corrolaries evident from equation (21) may now be indicated. Since no limitations on the size of the vessels were imposed in the derivation of equation (7), and if one assumes $s_1 = s_2 = s$, one obtains a smooth cylinder of length $l_1 + l_2$ (Fig. 1,g). The correctness of the following equations is then apparent,

$$W_1 = W_2 = W(l_1); \quad K = W(l_2); \quad \alpha_1 = W(l_1 + l_2).$$

where $W(l)$ is the Clausing Coefficient. In such a case, equation (21) is transformed into

$$W(l_1 + l_2) = \frac{W(l_1) W(l_2)}{W(l_1) + W(l_2) - W(l_1) W(l_2)}.$$

Assuming $l_1 = l_2 = 1$, we find

$$W(l) = \frac{1}{1 + \frac{1}{W(2l)}}. \quad (22)$$

Equation (22) assumes that the directional distribution of the molecules upon their exit from the tube is subject to the law of cosines. In Table 4 the results calculated by means of equation (22) are compared with the tabular results for several values of length (radius of the tube is taken as a unit). As may be seen from the table, the smallest deviations occur when the shortest and longest tubes are used. Therefore, one may assume that in the case of short and long tubes the directional distribution of molecules in the plane of the tube orifice is the same as the one on the surface of a flat evaporator, which distribution follows the Cosine Law.

Table 4

1	W(1)	
	Calculated from Equation (22)	Tabular
0.1	0.952	0.952
0.5	0.803	0.801
1	0.677	0.672
1.5	0.592	0.681
5	0.328	0.315
10	0.203	0.197

The probabilities ω_1 and ω_2 in equations (7) and (14) are real in the case of the unidirectional transfer. In order to establish the equivalent equations for a bidirectional transfer in a closed vessel (Fig. (3)), it is sufficient to let $K = \alpha$ in equations (7) and (14). This value is possible, since the orifice of the chamber, with permeability K , is equivalent to a flat evaporator formed at the intersection of C by the surface s_2 whose condensation coefficient α equals K (restatement of an assumption made above). In such a manner the probabilities of passage in bidirectional transfer for vessels and evaporators of arbitrary shapes are expressed by the following equations:

$$\omega_1 = \frac{W_1}{\alpha + (W_1 + W_2)(1 - \alpha)}, \quad \omega_2 = \frac{W_2}{\alpha + (W_1 + W_2)(1 - \alpha)} \quad (23)$$

where the probability W_2 has one well defined meaning.

In an analogous manner one can find the dependence of molecular flux magnitudes on condensation coefficients q_1 and q_2 between discs I and II with areas s_1 and s_2 in a vacuum (Fig. 4). Let disc I be an evaporator and disc II a collector. In the absence of a collector $n_0 s_1$ molecules/second would pass from the evaporator into vacuum. If one now introduced a disc collector at the evaporator, an equilibrium will be attained in the system at some time. In such a system the total number of molecules leaving the surface I would be larger than from the original one, since a fraction of the molecules will reflect from the collector and may return again to the evaporator. The flux growth for one molecule is represented in Table 5.

Table 5

Cycle	Over-all Molecular Flux, 1/Sec			
	From Evaporator	To Collector	From Collector	To Evaporator
1	$1 = A_1$	$A_1 P_1$	$A_1 P_1 (1 - q_2)$	$A_1 P_1 (1 - q_2) P_2$
2	$1 + A_1 P_1 (1 - q_2) P_2 (1 - q_1) = A_2$	$A_2 P_1$	$A_2 P_1 (1 - q_2)$	$A_2 P_1 (1 - q_2) P_2$
...	...	...	...	...
n	$1 + A_{n-1} P_1 P_2 (1 - q_1) (1 - q_2) = A_n$	$A_n P_1$	$A_n P_1 (1 - q_2)$	$A_n P_1 (1 - q_2) P_2$

Where P_1 is an integral (evenly distributed on the disc) probability of a straight impingement of molecules I on disc II; whereas P_2 is a similar probability for the collector.

At $n = \infty$, the recurrent formula A_n is transformed into an equation with one unknown. Its solution is of the following type: $A_n = 1 / (1 - P_1 P_2 (1 - q_1) (1 - q_2))$. Therefore, the probability of the transfer of molecules from evaporator to the collector is equal to:

$$\bar{\omega}_1 = \frac{P_1 q_2}{1 - P_1 P_2 (1 - q_1) (1 - q_2)} \quad (24)$$

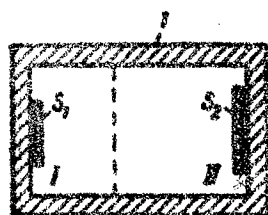


Fig. 3

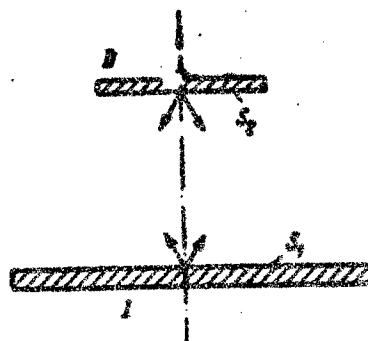
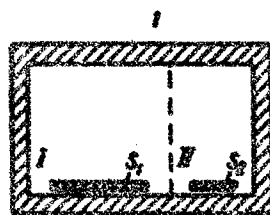


Fig. 4

Fig. 3. The types of specimen positioning in bidirectional exchange in a closed vessel. I - Shell of Exchange Chamber; I - Specimen-donor; II - Specimen-acceptor.

Fig. 4. Bidirectional exchange in a vacuum: I - Disc with an area s_1 ; II - Coaxial disc with an area s_2 .

For the reverse transfer one gets:

$$\bar{\omega}_2 = \frac{P_2 q_1}{1 - P_1 P_2 (1 - q_1) (1 - q_2)} \quad (25)$$

Interaction of Exchange Layers. Assuming that the substance has the same specific activity, α , in condensed and in gaseous phases, let us define α as a ratio of the number of active molecules to the total number of molecules in the given phase. According to this definition, one obtains:

$$\alpha = \frac{N^*}{N_{\Sigma} v} = \frac{n^*}{n_0}, \quad U = \frac{n^*}{n} \quad (26)$$

where $N_{\Sigma} v$, N^* are the total number of molecules and the number of active molecules per unit of the exchange layer

area, correspondingly; n^* , n are the numbers of active molecules, correspondingly impinging on the unit of surface area and truly evaporating from the unit surface area per unit time; U is the constant specific activity.

From now on, indices 1 and 2 will describe, correspondingly, specimen I and II in bidirectional exchange.

Let us determine the change with time of the number of active molecules in the exchange layer, in the case of unidirectional exchange (Fig. 1, a, b and 2). According to (7) and (26), the exchange layer loses $n_0 s_1 \omega_1 \alpha dt$ active molecules in time dt , at the same time gaining $n_0 s_1 \omega_1 U dt$ active molecules from the region U (Phase Conservation Law). Consequently, per unit area of the exchange layer, the following equation is valid:

$$dN^* = n_0 \omega_1 (U - \alpha) dt. \quad (27)$$

The diffusional flux inwards into the specimen did not enter into our considerations in this given case.

Considering the specific activities, a differential equation is obtained from (27) according to (26):

$$\frac{d\alpha(t)}{dt} = \frac{n_0 \omega_1}{N_s v} (U - \alpha),$$

which can be solved at conditions $\alpha(\infty) = U$, $\alpha(0) = \alpha(0)$, to give the following expression

$$\alpha = U + (\alpha(0) - U) e^{-\frac{n_0 \omega_1}{N_s v} t}, \quad (28)$$

The exponential multiplier ω_1 is defined as the transfer coefficient. In this case, it is identical with the transfer probability and may be calculated from equation (7).

Two significant cases may be inferred here:

- 1) $U = 0$, $\alpha(0) \neq 0$, in which case the analyzed substance is a donor with an original specific activity $\alpha(0)$;
 - 2) $U \neq 0$, $\alpha(0) = 0$, in which case the analyzed substance is an acceptor with an original specific activity equal to zero.
- The solution of (28) is real for any shape of the exchange chamber at an appropriate value of the transfer coefficient.

In the case of bidirectional exchange in a closed vessel of any shape, the change of the number of active molecules in layers I and II (Fig. 3) in time dt may be represented by the following relationships according to (23), (17) and (26) (per unit surface area):

$$dN_1^* = n_0 \omega_1 (\alpha_2 - \alpha_1) dt, \quad dN_2^* = n_0 \omega_2 (\alpha_1 - \alpha_2) dt. \quad (29)$$

According to (26), a system of simultaneous, simple differential equations may be obtained from (29):

$$\frac{d\alpha_1}{dt} = \frac{n_0\omega_1}{N_s v} (\alpha_2 - \alpha_1); \quad \frac{d\alpha_2}{dt} = \frac{n_0\omega_2}{N_s v} (\alpha_1 - \alpha_2). \quad (30)$$

Multiplying (30) correspondingly by s_1 and s_2 , one may prove that $s_1 d\alpha_1 = -s_2 d\alpha_2$. From which it follows that

$$\alpha_1 s_1 + \alpha_2 s_2 = \text{const.}$$

Assuming

$$\alpha_1(0) = \alpha_1(0), \quad \alpha_2(0) = \alpha_2(0), \quad \alpha_1(\infty) = \alpha_2(\infty) = U, \quad (31)$$

one finds that $U(s_1 + s_2) = \alpha_1(0)s_1 + \alpha_2(0)s_2 = \text{const.}$ Consequently,

$$\frac{\alpha_1(t)s_1 + \alpha_2(t)s_2}{s_1 + s_2} = U, \quad (32)$$

In other words, the average magnitude of specific activity of the saturated vapor in the chamber is independent of time and is equal to the activity of the given system at steady-state conditions.

The solution of the system of equations (30) at the conditions of (31) leads to:

$$\alpha_i(t) = U + (\alpha_i(0) - U) \exp \left[-\frac{n_0}{N_s v} \Omega(x) t \right], \quad (33)$$

where the transfer coefficient is determined from (23), according to the formula $\Omega(\alpha) = \omega_1 + \omega_2$, or from (20) where $P = W_1 + W_2$; $i = 1, 2$.

In such a way the character of the equation for the interaction of exchange layers does not change upon the switch from uni- to bidirectional exchange.

One may arrive at the expression for the probability (23) by studying the interaction of exchange layers with the vapors above them. The change of activity per unit surface area of the specimen may be expressed in such a case by the following equation

$$dN_1^* = n_0(\alpha^* - \alpha_1) df, \quad dN_2^* = n_0(\alpha^* - \alpha_2) dt; \quad (29')$$

where $\omega_1 = \omega_2 = 1$, α^* and α_0 are vapor activities over the donor and acceptor.

The quantities α^* and α^0 are related by equations:

$$\begin{aligned} n s_1 \alpha^* &= n_0 s_2 \alpha_2 W_2 + (n - n_0) s_2 \alpha^0 W_2 + [n_0 s_1 \alpha_1 + (n - n_0) s_1 \alpha^*] (1 - W_1), \\ n s_2 \alpha^0 &= n_0 s_1 \alpha_1 W_1 + (n - n_0) s_1 W_1 \alpha^* + [n_0 s_2 \alpha_2 + (n - n_0) s_2 \alpha^0] (1 - W_2). \end{aligned}$$

With the aid of relationships (1) and (11), the solutions of the above equations are obtained. Their substitution in (29') leads to (29) and consequently to (23). If the thickness of the exchange layers varies (the case of liquids), relationship (29) still holds, and hence may be used for the calculation of the change in the number of radioactive atoms in layers ν_1 and ν_2 in dt . Switching to the specific activities according to (26) and introducing thickness $\delta = N_0 \nu / \bar{n}$, one obtains a system of simultaneous equations from (29):

$$\frac{d\alpha_1}{dt} = \frac{n_0 \omega_1}{\delta_1 \bar{n}} (\alpha_2 - \alpha_1), \quad \frac{d\alpha_2}{dt} = \frac{n_0 \omega_2}{\delta_2 \bar{n}} (\alpha_1 - \alpha_2),$$

where $\bar{n}$ is the number of molecules per unit volume of the condensed phase. The solution of the above system of equations at conditions of (31) yields:

$$\alpha_i(t) = U + (\alpha_i(0) - U) \exp \left[-\frac{n_0}{\bar{n}} \left(\frac{\omega_1}{\delta_1} + \frac{\omega_2}{\delta_2} \right) t \right]. \quad (34)$$

The expression for the steady-state specific activity is obtained by a method analogous to the one employed for (32)

$$U = \frac{\alpha_1(t) s_1 \delta_1 + \alpha_2(t) s_2 \delta_2}{s_1 \delta_1 + s_2 \delta_2}.$$

For coaxially spaced specimens in vacuum Fig. (4), one may generally write

$$\begin{aligned} s_1 dN_1^* &= [n_2 s_2 \bar{\omega}_2 \alpha_2 - n_1 s_1 (1 - P_1 (1 - q_2) \bar{\omega}_2) \alpha_1] dt, \\ s_2 dN_2^* &= [n_1 s_1 \bar{\omega}_1 \alpha_1 - n_2 s_2 (1 - P_2 (1 - q_1) \bar{\omega}_1) \alpha_2] dt, \end{aligned}$$

where n_1 and n_2 are the evaporation rates of discs I and II (see Table 4).

If ν_1 and ν_2 are considered constant, the following system of equations is obtained:

$$\begin{aligned} \frac{d\alpha_1(t)}{dt} &= \frac{1}{N_1 \nu_1 s_1} [n_2 s_2 \bar{\omega}_2 \alpha_2 - n_1 s_1 (1 - \bar{\omega}_2 P_1 (1 - q_2)) \alpha_1], \\ \frac{d\alpha_2(t)}{dt} &= \frac{1}{N_2 \nu_2 s_2} [n_1 s_1 \bar{\omega}_1 \alpha_1 - n_2 s_2 (1 - \bar{\omega}_1 P_2 (1 - q_1)) \alpha_2]. \end{aligned} \quad (35)$$

Let us limit ourselves to two cases: 1) the temperature of the acceptor is low ($n_2 = 0$); 2) the temperatures of the discs of the same surface area are identical. If $n_2 = 0$, one obtains from (35):

$$\alpha_2(t) = \alpha_2(0) - K \frac{v_1 s_1}{v_2 s_2} (\alpha_1(t) - \alpha_1(0)), \quad (36)$$

where

$$\alpha_1(t) = \alpha_1(0) e^{-\frac{n_1 \bar{\omega}_1}{N_s v_1 K} t}, \quad K = \frac{\bar{\omega}_1}{1 - \omega_2 P_1 (1 - q_2)}.$$

If t is small and $\alpha_2(0) = 0$, then $\alpha_2(t) = \frac{n_1 s_1}{N_s v_2 s_2} \bar{\omega}_1 t$,

which means that the initial activity of the acceptor is independent of the thickness of the exchange layer of the donor.

If $n_1 = n_2 = n_0$ and $s_1 = s_2 = s$, when $v_1 = v_2 = v$, $q_1 = q_2 = q$ and $P_1 = P_2 = P$, for the initial conditions $\alpha_1(0) = \alpha_2(0) = \alpha_2(0)$, the solution of (35) is of the following form

$$\alpha_i(t) = \frac{\alpha_1(0) + \alpha_2(0)}{2} e^{-m_1 \frac{n_0}{N_s v} t} + (-1)^{i+1} \frac{\alpha_1(0) - \alpha_2(0)}{2} e^{-m_2 \frac{n_0}{N_s v} t},$$

where

$$m_1 = \frac{1-P}{1-P(1-q)}, \quad m_2 = \frac{1+P}{1+P(1-q)}, \quad i=1,2.$$

The probabilities of transfer (20) or (23) are the exchange reaction rate constants.

At $W_1 + W_2 < 1$, $\partial \omega_1 / \partial \alpha < 0$ (23). This relation means that with the increase of the condensation coefficient the probability of transfer and, consequently, the exchange rate decrease. The explanation for this apparently paradoxical conclusion is that as α increases the buoyancy of the saturated vapor decreases. Consequently, the number of collisions of the molecules with the surface of another specimen decreases. This fact has a stronger effect on the result at given vessel geometry than a simple increase of the condensation coefficient.

A condition at which α does not have any effect on the rate of exchange, namely when $W_1 + W_2 = 1$, follows from the above explanation.

The derivation of the probability (W_1 and W_2) equations and of P_1 and P_2 will be published in the future.

Conclusions

Equations were presented for the probabilities of transfer of the molecules from one specimen to another, in a closed vessel or in a vacuum, as a function of the geometry of the system and of the condensation coefficients. It has been shown that under certain geometric conditions the rate of isotope exchange through the gaseous phase is independent of the condensation coefficient.

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