ENRICHMENT CALCULATIONS IN GASEOUS DIFFUSION: Large Separation Factor

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A general method has been devised for calculating gaseous-diffusion-stage requirements to separate gases of widely differing molecular weights. For such a mixture the actual separation factor is shown to be less than the ideal separation factor, depending on the undiffused-gas composition and the ratio of absolute pressures on each side of the barrier. The equilibrium relationship between the compositions of the diffused- and undiffused-gas streams leaving any stage is also derived by means of the Rayleigh concept. Application of the method is illustrated with a diagram, like that of McCabe and Thiele for distillation, on which are stepped off the required number of theoretical stages to separate a particular hydrogen-nitrogen mixture.

Enrichment in gaseous diffusion results from the preferential effusion of the low-molecular-weight component through a barrier whose pore diameter is small with respect to the molecular mean free paths. A cascade of stages in series is used to enrich the mixture repeatedly until desired terminal compositions are achieved. In spite of inherent low thermodynamic efficiencies, the successful separation of uranium isotopes by gaseous diffusion has demonstrated the large-scale workability of the process for cases where product worth or other special considerations justify its use. Outside the field of isotope separation, gaseous diffusion might compete with low-temperature processes particularly for the separation of hydrogen from heavier gases. In such a case a high separation factor might reduce plant-size and energy requirements sufficiently to make the process economically attractive. It is to investigate such possibilities that the work of this paper was done.

In connection with their work on rubber and plastic membranes, Weller and Steiner(*4, 5*) have presented an exact and an approximate method for calculating membrane or barrier area and enriched-gas composition for a single stage when permeability coefficients and undiffused exit-gas composition are known. Although the method herein presented does not include determination of barrier area, it is believed to be a somewhat simpler and more general approach to calculation of stage requirements. Benedict(*1, 2*), Cohen(*3*), and others have developed the cascade enrichment calculations for isotope separation where the ideal separation factor is very close to unity so that certain approximations are permissible to gain simplification in the cascade calculations. Furthermore, with the relatively slight enrichment per stage and the consequent large number of stages in an isotope-separation cascade, it is permissible to treat the composition at any point in the cascade as a continuous function of stage number. Analytical methods involving conventional integration are then used to calculate the number of stages in the stripping and enriching sections of the cascade. This paper presents a method for enrichment calculations where the separation factor is considerably greater than one and the approximations of the isotope cascade are therefore not applicable.

The ideal separation factor for perfect effusion of a gas mixture into a total vacuum is given by

$$\alpha^* = \sqrt{\frac{m_H}{m_L}} \qquad (1)$$

Benedict(*2*) has shown that for the case of isotope separation the actual separation factor is independent of concentration, but it is lower than the ideal separation factor because of finite back pressure. The relationship is

$$\alpha - 1 = \left(\sqrt{\frac{m_H}{m_L}} - 1\right)\left(1 - \frac{P''}{P'}\right) \qquad (2)$$

For an ideal separation factor considerably greater than one, the actual separation factor is shown below to depend on composition as well as on the pressure ratio. Then by use of the Rayleigh concept to handle changes in composition across a stage, a relationship is derived between the composition of the two streams leaving any stage. The required number of theoretical stages is found by using a diagram like that of McCabe and Thiele for distillation. The method is illustrated by determining the number of theoretical stages necessary to separate a feed of 25 mole% hydrogen in nitrogen into an overhead of 99 mole% hydrogen and a bottoms of 99 mole% nitrogen.

ACTUAL SEPARATION FACTOR

For effusive flow through a barrier the pore size of which is small with respect to the molecular mean free path, the molar flow rate is defined by Knudsen's law of molecular effusion:

$$N = \sqrt{\frac{g}{2\pi m\, RT}}\left(\frac{\lambda d}{W}\right)(P' - P'') \qquad (3)$$

For a particular barrier at a certain operating temperature, the barrier permeability may be defined by

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$$\phi = \sqrt{\frac{g}{2\pi RT}}\left(\frac{\lambda d}{W}\right) \qquad (4)$$

By use of the appropriate mole fractions, Knudsen's law may be written for each component of a mixture as follows:

$$N_L = \frac{\phi}{\sqrt{m_L}}\,[P'x - P''y] \qquad (5)$$

$$N_H = \frac{\phi}{\sqrt{m_L}}[P'(1-x) - P''(1-y)] \qquad (6)$$

Dividing (5) by (6); substituting α^*, the ideal separation factor, for $\sqrt{\frac{m_H}{m_L}}$; and letting $P = \frac{P''}{P'}$ give:

$$\frac{N_L}{N_H} = \alpha^*\left[\frac{x - Py}{(1-x) - P(1-y)}\right] \qquad (7)$$

The actual separation factor is defined by

$$\alpha = \frac{y/1-y}{x/1-x} \text{ or } y = \frac{\alpha x}{1+(\alpha-1)\,x} \qquad (8)$$

Consideration of the flow reaching the low-pressure side of the barrier shows

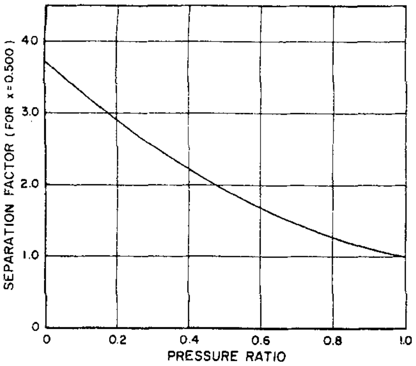

FIG. 1. VARIATION OF SEPARATION FACTOR WITH PRESSURE RATIO FOR EQUIMOLAR H_2-N_2 MIXTURE.

$$\frac{N_L}{N_H} = \frac{y}{1-y} \qquad (9)$$

Substituting (9) through (8) into (7) and solving for α gives †

$$\alpha = \frac{\alpha^*\left(\frac{1-x}{1-y}\right)}{\left(\frac{1-x}{1-y}\right) + P\,(\alpha^*-1)} \qquad (10)$$

Using (8) to eliminate y from (10) and then solving for α give‡.

$$\alpha = \frac{\alpha^*+1}{2} - \frac{P\,(\alpha^*-1)}{2x} - \frac{1}{2x} + \sqrt{\left(\frac{\alpha^*-1}{2}\right)^2 + \frac{(\alpha^*-1) - P\,[(\alpha^*)^2-1]}{2x} + \left[\frac{P\,(\alpha^*-1)+1}{2x}\right]^2} \qquad (11)$$

CHOOSING PRESSURE RATIO FOR H_2-N_2 CASCADE

For the case of H_2-N_2

$$\alpha^* = \sqrt{\frac{m_H}{m_L}} = \sqrt{\frac{2(14.008)}{2(1.008)}} = 3.7284 \qquad (12)$$

and so (11) becomes

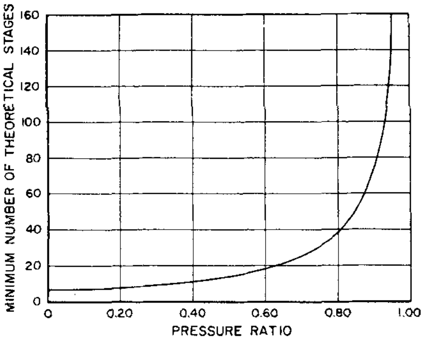

FIG. 2. MINIMUM NUMBER OF THEORETICAL STAGES VS. PRESSURE RATIO, BASED ON α FOR $x = 0.500$ IN THE H_2-N_2 EXAMPLE.

$$\alpha = 2.364 - 1.3642\,\frac{P}{x} - \frac{1}{2x} + \sqrt{1.860 + \frac{2.728 - 12.897\,P}{2x} + \left(\frac{1+2.728\,P}{2x}\right)^2} \qquad (13)$$

To examine the effect of the pressure ratio on the separation factor, x in (13) is fixed at 0.500. This is equivalent to assuming that the separation factor corresponding to $x = 0.500$ at any pressure ratio is a reasonable average value for the entire concentration span. Making this substitution in (13) reduces that equation to

$$\alpha_{(x=0.500)} = 1.364 - 2.7284\,P + \sqrt{7.442\,P^2 - 7.442\,P + 5.588} \qquad (14)$$

The curve of Figure 1 represents Equation (14). For the case of effusion into a perfect vacuum, $P = 0$ and α becomes α^*, the ideal separation factor; when the back and fore pressures are equal and P is unity, α falls to 1, indicating no enrichment.

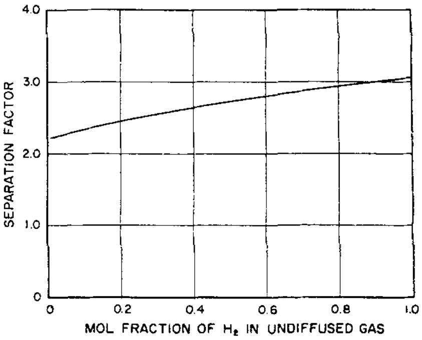

FIG. 3. VARIATION OF SEPARATION FACTOR WITH MOLE FRACTION H_2 IN UNDIFFUSED GAS FOR $P = 1/4$.

The Fenske equation for the minimum number of theoretical stages at total reflux is

$$S_{min} = \frac{\ln\left[\frac{y_D\,(1-x_B)}{x_B\,(1-y_D)}\right]}{\ln\alpha} \qquad (15)$$

The effect of the pressure ratio on the length of the cascade may be judged by plotting the ratio against the minimum number of theoretical stages required to span the concentration range from $x_B =$

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† For isotope separation where (α^*-1) is much less than unity and $\left(\frac{1-x}{1-y}\right)$ is nearly unity because enrichment per stage is small, (10) becomes identical with (2), which was derived by Benedict (2).

‡ Numerical work shows that the positive root must be used.

0.010 to $y_D = 0.990$. Figure 2 is such a plot for the H_2N_2 cascade of the example as calculated from Equations (14) and (15). The nearly horizontal portion of this curve serves to indicate the range of P values in which a cascade might economically be operated. Other engineering considerations, such as the type of compressors and the actual fore pressure to be used, will aid in fixing the particular value of P for cascade operation. For further calculations of the example H_2N_2 cascade, $P = 0.25$ has been chosen. This lies toward the upper end of the nearly level portion of the curve and represents a compression ratio of four, which is attainable with single-stage compressors.

The selected value of P may be substituted into Equation (13) to get the relationship of separation factor to mole fraction of H_2 for the system operating at a back-to-fore pressure ratio of 0.25:

$$\alpha = 2.364 - \frac{0.84105}{x} + \sqrt{1.860 - \frac{0.2481}{x} + \frac{0.70728}{x^2}} \qquad (16)$$

Figure 3 represents Equation (16) graphically; α varies from 2.222 for $x = 0.010$ upward toward a limit of 3.046 as x approaches unity.†

RELATION OF x AND y

Figure 4 is a schematic sketch of a gaseous-diffusion stage. It is evident that to achieve any enrichment some, but not all, of the entering stream must pass through the barrier; and there must be a concentration gradient between the undiffused gas entering and leaving the stage. If the stage is designed to give complete turbulence so that all the undiffused gas in the stage is of the same composition as that leaving, the situation becomes analogous to that assumed in conventional distillation calculations for a small column, where liquid mixing by the rising vapor negates any effect of liquid gradient on the plate. For such a case compositions of the effluent streams from the stage are correctly related by Equation (8) by use of separation factors from (11) or, for the example cascade, from (16). However in gaseous diffusion the undiffused gas must travel along the barrier while undergoing continual depletion of the light component. Good stage design to minimize film thickness at the barrier requires turbulence at any cross section of the axis of flow, but because there is a gradual composition gradient along the axis of flow, which is analogous to the liquid composition gradient observed in large distillation columns, it is proper to assume constant composition only within an element like that of Figure 4. A material balance around the element is

$$\frac{dq}{q} = \frac{dx}{y-x} \qquad (17)$$

For such an element Equation (8) correctly relates the compositions across the barrier. Substituting ϵ for (α-1) allows (17) therefore to be rewritten as

$$\frac{dq}{q} = \left[\frac{1 + \epsilon x}{\epsilon\, x(1-x)}\right] dx \qquad (18)$$

Although the separation factor has been shown to vary with composition, it is assumed that the variation across any *one* stage is small enough that ϵ may be treated as a constant between x_1 and x_0. If the value of α corresponding to x_0 is used, the error may be taken on the conservative side and thus made to compensate in part for errors from depletion of the film adjacent to the barrier. Under the assumption of constant separation factor, (18) may be integrated from the element of Figure 4 to the exit:

$$q = [(1-\theta)Q]\left[\left(\frac{x}{x_o}\right)^{1/\epsilon}\left(\frac{1-x_o}{1-x}\right)^{\sigma}\right] \qquad (19)$$

In (19) θ, the cut, represents the fraction of the gas entering the stage which passes through the barrier, and σ is the ratio α/ϵ or $\alpha/(\alpha\text{-}1)$.

The composition of the enriched stream leaving any stage may be written

$$y_o = \frac{\int_{x_1}^{x_o} y\,d\,q}{\int_{x_1}^{x_o} d\,q} = \frac{1}{\theta\,Q}\int_{x_1}^{x_o} y_{dq} \qquad (20)$$

The term ydq may be written in terms of x by multiplying the right-hand sides of Equations (8), (18), and (19). Making this multiplication, canceling, rearranging, and noting that Q, (1-θ), and x_0 are constant permit writing (20) as

$$y_o = -\sigma\left(\frac{1-\theta}{\theta}\right)\frac{(1-x_o)}{x_o^{\,1/\epsilon}} \int_{x_1}^{x_o} \frac{x^{\,1/\epsilon}}{(1-x)^{\sigma+1}}\,dx \qquad (21)$$

Integrating (21) after appropriate changes of variables and canceling and rearranging give

$$y_o = x_o^{\,-1/\epsilon}\left(\frac{1-\theta}{\theta}\right) \left[(1-x_o)^{\sigma}\left(\frac{x_1}{1-x_1}\right)^{\sigma} - x_o^{\,\sigma}\right] \qquad (22)$$

With reference again to Figure 4, a material balance around the stage is

$$\theta\, y_o + (1 - \theta)\, x_o = x_1 \qquad (23)$$

Since conventional enrichment calculations deal with the compositions of streams leaving a stage, Equation (23) may be used to eliminate x_1, from (22), and the subscripts are then no longer neces-

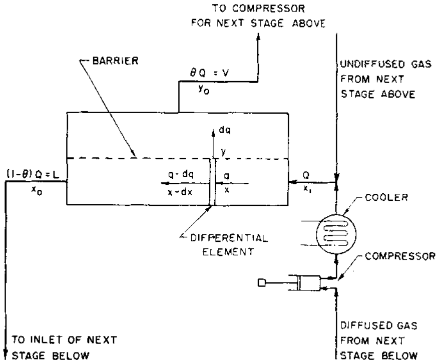

FIG. 4. SCHEMATIC SKETCH OF A GASEOUS-DIFFUSION STAGE.

TABLE 1.—EQUILIBRIUM DATA FOR THE H_2-N_2 EXAMPLE CASCADE

	α	y	
x	(P=1/4)	θ=0.3471	θ=0.5833
0.010	2.222	0.029	
.025	2.241	.070	
.035	2.253	.098	
.050	2.270	.136	
.075	2.298	.197	
.100	2.326	.252	
.150	2.374	.351	
.200	2.437	.438	0.507
.250	2.490	.512	.579
.300	2.542	.579	.639
.400	2.641		,735
.500	2.730		.807
.600	2.809		.863
.700	2.880		.907
.800	2.942		.944
.900	2.985		.974
.950	3.022		.988

From Equations (16) and (27)

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†Numerical data for Figure 3, calculated from (16), are included in Table 1.

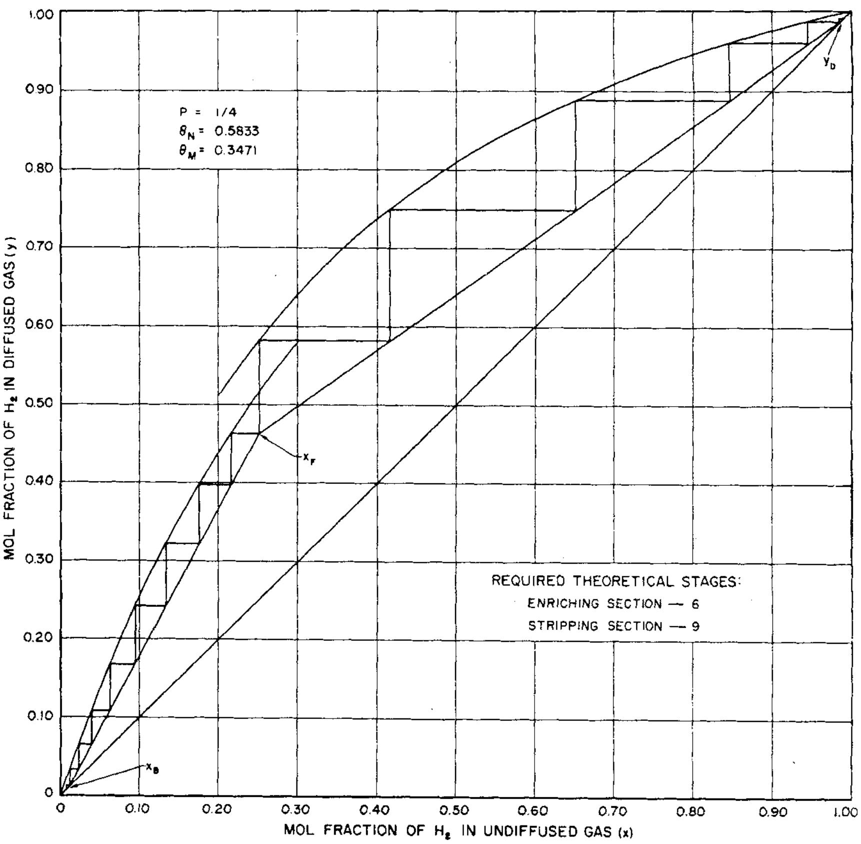

FIG. 5. ENRICHMENT DIAGRAM FOR THE H_2-N_2 CASCADE OF THE EXAMPLE.

sary. Thus the x-y relationship for any stage is

$$y = x^{-1/\epsilon}\left(\frac{1-\theta}{\theta}\right)\left\{(1-x)^{\sigma}\left[\frac{\theta\, y + (1-\theta)\, x}{1-(\theta\, y + (1-\theta)\, x)}\right]^{\sigma} - x^{\sigma}\right\} \tag{24}$$

Once the cut is fixed for each section of the cascade and the separation factor is fixed as a function of the undiffused-gas composition, Equation (24) may be used to construct an x-y diagram to permit making enrichment calculations by the method of McCabe and Thiele for distillation. It should be noted that (24) is divergent for the purpose of iteration. Therefore a result calculated from a first approximation should not be used as a second approximation in the trial-and error solution, because the computed result is farther from the actual root than is the assumed value of y.

SELECTION OF CUT

From Figure 4 it is evident that for any stage

$$\frac{L}{V} = \frac{1-\theta}{\theta} \tag{25}$$

Thus for total reflux where $L = V$ the cut must be 1/2 ; and for any finite product rate it must be greater than 1/2 in the rectifying section and less than 1/2 in the stripping section of the cascade. If the L/V ratio for either section or the V/D ratio for the cascade is known, then θ is fixed and the x-y curve may be calculated. A reasonable approximation of the continuously tapered ideal cascade which minimizes total flow may be made by using Equation (24) with $\theta = 1/2$ and the appropriate equations of Benedict(*2*). Economics would probably dictate squaring off the rectifying and stripping sections of the optimum cascade into several parts each operating at a constant L/V to achieve standardization of equipment. Once this is done Equation (24) may be used to determine the x-y curve appropriate to each part of the cascade.

With separation factors as great as those for H_2N_2, a square cascade having constant L/V ratios throughout the stripping and enriching sections would probably be chosen. For the continuation of the H_2-N_2 example a *square* cascade has been chosen with $V/D = 3.5$ for the rectifying section. From material balances and Equation (25) the cut for the rectifying section is calculated to be 0.5833. For a square cascade the following material balances may be written:

$$y_n = x_{n+1}\left(\frac{L}{V}\right)_N + y_D\left(\frac{D}{V}\right)_N \tag{26a}$$

$$y_m = x_{m+1}\left(\frac{L}{V}\right)_M - x_B\left(\frac{B}{V}\right)_M \tag{26b}$$

$$\left(\frac{D}{V}\right)_N = 1 - \left(\frac{L}{V}\right)_N \tag{27a}$$

$$\left(\frac{B}{V}\right)_M = \left(\frac{L}{V}\right)_M - 1 \tag{27b}$$

At the feed stage one may set $y_n = y_m$ and $x_{n+1} = x_{m+1} = x_F$ and so the foregoing equations may be combined to give

$$(y_D - x_B) - (y_D - x_F)\left(\frac{L}{V}\right)_N = (x_F - x_B)\left(\frac{L}{V}\right)_M \tag{28}$$

Using (25) to substitute for (L/V) in terms of the cuts yields the following after solution for θ_M:

$$\theta_M = \frac{(x_F - x_B)\,\theta_N}{2\,(y_D - x_B)\,\theta_N - (y_D - x_F)} \tag{29}$$

The cut for the stripping section of the example cascade is then readily calculated as 0.3471.

EQUILIBRIUM CURVES FOR THE EXAMPLE CASCADE

Substituting the cuts into (24) gives the equations of the equilibrium curves for the two sections of the cascade:

Rectifying Section

$$y = 0.7143\, x^{-1/\epsilon}\left\{(1-x)^{\sigma}\left[\frac{0.5833\, y + 0.4167\, x}{1-(0.5833\, y + 0.4167\, x)}\right]^{\sigma} - x^{\sigma}\right\} \tag{30a}$$

Stripping Section

$$y = 1.8810\, x^{-1/\epsilon}\left\{(1-x)^{\sigma}\left[\frac{0.3471\, y + 0.6529\, x}{1-(0.3471\, y + 0.6529\, x)}\right]^{\sigma} - x^{\sigma}\right\} \tag{30b}$$

Solution of these equations by trial for various values of x by use of corresponding values of α from Equation (16) defines the equilibrium curves for the cascade of the example.†

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† Equilibrium x-y values, calculated from (30), are presented in Table 1.

ENRICHMENT DIAGRAM FOR H_2-N_2 CASCADE

Equations (26a) and (26b) represent the material balances respectively for the enriching and stripping sections of a square cascade. For the cascade of H_2-N_2 example these equations become

$$y_n = 0.7143\ x_{n+1} + 0.2829 \quad (31a)$$

$$y_m = 1.8810\ x_{m+1} - 0.0088 \quad (31b)$$

If Equation (30) is used for the equilibrium lines and (31) for the operating lines, a diagram like that of McCabe and Thiele for distillation may be constructed and the number of stages determined in the usual manner. Figure 5 is such a diagram for the H_2-N_2 cascade of the example; it shows that a cascade of fifteen theoretical stages is needed to effect the separation under the conditions used for this example.

LIMITATIONS OF THE METHOD

Utilization of this method for gaseous-diffusion enrichment calculations is subject to certain inaccuracies and limitations. The use of Knudsen's law of molecular effusion implies a barrier capable of producing effusive flow to the exclusion of ordinary mass flow, which is nonseparative. It is probable that some mass flow would take place through an actual barrier unless the fore pressure were very low.

Good stage design requires high turbulence of the undiffused gas to minimize depletion of light component from the film immediately adjacent to the barrier. This effect is neglected in the derivation of Equation (24) by the assumption of constant composition in the differential element of Figure 4 around which (17) is written.

In the integration of Equation (21) the separation factor is assumed constant across any one stage. Figure 3 shows the actual variation for the cascade of the example; however, since α is calculated from (16) based on the composition x leaving the stage, the value used is actually the lowest separation factor encountered within the stage. This should tend to compensate, at least in part, for losses in enrichment from the friction pressure drop in the undiffused-gas stream and from the other factors discussed above.

The nature of the method, however, makes very simple the use of an individual or over-all stage efficiency to account for the effects discussed here. Relatively small-scale experiments with the barrier material and stage design of choice should yield this information. Scale-up to production scale should then be possible with a minimum of intermediate development.

SUMMARY

The successful separation of uranium isotopes by gaseous diffusion has demonstrated the large-scale workability of the process for cases where product worth or other special considerations justify the high energy expenditure. In spite of inherent low thermodynamic efficiencies gaseous diffusion might compete economically with processes utilizing very low temperatures to separate gases of widely differing molecular weights.

A general method of calculating gaseous-diffusion-stage requirements for separating gases of widely differing molecular weights has been devised. For the separation of such gases by gaseous diffusion the actual separation factor is shown to depend on the ideal-separation factor (square root of the molecular weight ratio), the ratio of absolute pressures on each side of the barrier, and the undiffused-gas composition. The relationship is derived from Knudsen's law of molecular effusion, and its similarities to that for isotope separation are pointed out. By use of the Rayleigh concept, the equilibrium relationship between the compositions of the diffused- and undiffused-gas streams leaving any stage is also derived. Application of these equations is illustrated by determination of the required number of theoretical stages to separate a particular H_2-N_2 mixture. A diagram similar to that of McCabe and Thiele for distillation is used. Certain limitations of the method are pointed out, and the use of a stage efficiency is suggested to account for them.

NOTATION

B = cascade bottoms withdrawal rate, moles/min.
D = cascade overhead withdrawal rate, moles/min.
d = average diameter of barrier pores, in.
g = acceleration from gravity, ft./min^2.
L = interstage downflow rate, moles/min.
m = molecular weight
N = molar velocity through the barrier, moles/(sq.ft.)(min.)
$P = P''/P'$ = ratio of back pressure to fore pressure across barrier
P' = fore pressure (undiffused gas), lb./sq.ft.
P'' = back pressure (diffused gas), lb./sq. ft.
Q = gas rate entering a stage, moles/min.
q = undiffused-gas rate along the barrier at any cross section, moles/min.
R = universal gas constant, ft.-lb./(mole)(°R.)
S_{min} = minimum number of theoretical stages
T = cascade operating temperature, °R
V = interstage upflow rate, moles/min.
W = thickness of barrier, in.
x = mole fraction of light component in undiffused gas
y = mole fraction light component in diffused gas

Greek

α = separation factor
α^* = ideal separation factor = $\sqrt{m_H/m_L}$
$\epsilon = (\alpha - 1)$
θ = cut, the fraction of gas entering a stage which diffuses through the barrier
λ = fraction of barrier area open to flow
$\sigma = \alpha/\epsilon = \alpha/(\alpha - 1)$
ϕ = barrier permeability, defined by Equation (4)

Subscripts

B = bottoms
D = overhead
F = feed
H = heavy component
1 = entering a stage
L = light component
M = stripping section
m = any stage of stripping section
N = enriching section
n = any stage of enriching section
o = leaving a stage

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