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Temperature—Separation Factor Relationships in Gaseous Diffusion

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A theoretical equation was developed to predict the enrichment produced by a single stage porous Vycor diffusion cell as a function of temperature. The separations of five binary gas mixtures were measured experimentally over a temperature range of 80 to 600°K. The agreement between theoretical predictions and experimental results was good over most of the temperature range. The largest deviations occurred when the operating temperature approached the critical temperatures of the gases. Mixtures of oxygen-carbon dioxide and helium-nitrogen were observed to become nonseparative at predicted temperatures. Overall, both separation and separative capacity were observed to increase with a decrease in temperature.

Enrichment calculations for gaseous diffusion systems have been developed for a number of barriers and gas mixtures (*2, 8, 10, 12, 23*); but no attempts were made by these investigators to establish a relationship between temperature and enrichment. Recent publications by Barrer (*1*) and Hwang (*11*) show, however, that pure gas diffusion is temperature dependent, particularly so in the region of the gas critical temperature. Surmising that the diffusion of gas mixtures might also be similarly affected, Hwang used his pure gas data to predict separation factors for binary mixtures. He did not attempt to verify these predictions experimentally. Therefore, based on Hwang's pure gas flow theory, this paper derives an expression relating temperature and enrichment for porous Vycor diffusion cells. Results from numerous experimental runs using five binary gas mixtures at temperatures from 80 to 600°K. are recorded and compared with the derived equation.

THEORETICAL DEVELOPMENT

Equations for calculating the enrichment achieved with single stage permeability cells were originally published for binary mixtures by Weller and Steiner (*24, 25*). Although these well known formulas were derived for semipermeable polymer barriers, they have been shown to be applicable to other barriers as well. Kammermeyer and Brubaker (*7*) adapted them to microporous media and extended the case I, perfect mixing model, to multicomponent systems. In a later publication Naylor and Backer (*17*) presented a much simpler development for the case II, laminar flow model, when large separation factors are encountered. Benedict and Pigford (*3*) accomplished the same goal for the close separations encountered in isotope recovery. A recent extensive study by Breuer (*6*) further suggests that self-mixing within the gas streams also affects the separation, giving an illusion of perfect mixing.

For this work, two basic assumptions were made; (a) that different membranes made of the same porous Vycor material behave similarly, and (b) that the Weller-Steiner equations for perfect mixing provide a justifiable starting point for the theoretical development and data correlation. Incorporating these assumptions, an equation representative of the W.-S. case I conditions can be generated which is consistent with the experimental design. That is, the molar ratio of the two components in the diffused stream will be:

$$\frac{y}{1-y} = \alpha^* \frac{(x-Py)}{(1-x)-P(1-y)} \tag{1}$$

For a single stage separation, the actual enrichment achieved is indicated by the stage separation factor α, traditionally defined as:

$$\alpha = \frac{y}{1-y} \cdot \frac{1-x}{x} \tag{2}$$

Combining Equations (1) and (2), it is possible to theoretically predict a stage separation factor, α_T:

$$\alpha_T = \frac{y}{1-y} \cdot \frac{1-x}{x} = \alpha^* \frac{(x-Py)}{(1-x)-P(1-p)} \cdot \frac{1-x}{x} \tag{3}$$

It is important to note that α_T of Equation (3) is only a measure of the performance of a single stage operation and not a property of the system. Thus α_T varies with the operating conditions of the cell. For example, when $P = 1.0$, no driving force exists to produce a separation and $\alpha_T = 1.0$. Correspondingly if P approaches zero, that is, diffusion into vacuum, then α_T becomes:

$$\alpha_T = \frac{y}{1-y} \cdot \frac{1-x}{x} = \alpha^* \tag{4}$$

which further illustrates that α_T approaches α^* as a maximum limit.

If Equation (3) is used to predict the magnitude of

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the stage separation factor, the values of P, x, y, and α^* must be known. Accurate determinations of the first three variables are obtained by using simple laboratory techniques. Reliable values of α^* are much more difficult to obtain, however. As defined, it is equal to the ratio of the pure component transfer coefficients. Thus it is definitely a function of the gas system being separated and more importantly, a function of temperature.

The problem of predicting a reasonable value for α^* evolves from the more basic problems associated with the prediction of transfer coefficients. Usually predictions based on empirical methods are used, which, while they may give reliable results are time consuming. One notable exception occurs with the rarified gas diffusion described by Knudsen flow principles. Under these conditions α^* becomes a constant, dependent only upon the molecular weights of the components of the mixture:

$$\alpha^* = \frac{Q_1}{Q_2} = \left(\frac{M_2}{M_1}\right)^{0.5} \tag{5}$$

Thus, the theoretical stage separation factor as represented by Equation (3) becomes:

$$\alpha_T = \left(\frac{M_2}{M_1}\right)^{0.5} \cdot \frac{(x - Py)}{(1-x) - P(1-y)} \cdot \frac{1-x}{x} \tag{6}$$

It is interesting to note that many investigators have shown Equation (6) to be reasonably valid for operating conditions considerably different from those of rarified gas flow. Spiegler (*22*) for example used an extension of the friction model to demonstrate mathematically why Equation (6) might be valid under operating conditions for which it is not defined. All too frequently the equation fails, however, to predict a reasonable separation factor and consequently an alternate solution is needed.

To accomplish this, α^* values were predicted from Hwang's pure gas theory. According to this model the individual transfer coefficient is expressed as:

$$Q_1 = \frac{A}{\sqrt{M_1 T}} + \frac{B_1 T}{\sqrt{M_1 T}} e^{\Delta_1/T} \tag{7}$$

In this case Hwang (*11*) shows that the transfer coefficients are a function of the microporous medium, the gas, and most importantly, temperature. Moreover, Hwang also demonstrated that the constant A is the same for all gases for a given porous medium. Thus it must be determined only once by experimental methods. Correspondingly, $(1/B)$ is proportional to Δ, and Δ is proportional to the molecular collision diameter (*27*). Since both constants are dependent upon the molecular species, B and Δ must be experimentally determined for at last two gases and preferably more. Once B and Δ values are known for several gases the appropriate plots are drawn. Thus based on these curves and knowledge of the collision diameter, B and Δ values may be predicted for any new gas, and the resulting permeability coefficient obtained from Equation (7). In this study values for A, B, and Δ had already been measured by Hwang (*11*) for all the gases except ethylene. For ethylene they were predicted by the procedure outlined above and developed elsewhere (*27*). The predicted values for ethylene which were used were: $A = 4.02 \times 10^{-4}$, $B = 0.40 \times 10^{-7}$, and $\Delta = 850$. These values were not confirmed by pure gas measurements, however. By incorporating Equation (7) into calculation of α^*, it too becomes a function of temperature:

$$\alpha^* = \frac{Q_1}{Q_2} = \left(\frac{M_2}{M_1}\right)^{0.5} \cdot \frac{A + B_1 T e^{\Delta_1/T}}{A + B_2 T e^{\Delta_2/T}} = \alpha_H^* \tag{8}$$

Inspection of this expression shows α^* to be consistent with Equation (5), or Knudsen separation, at high temperatures.

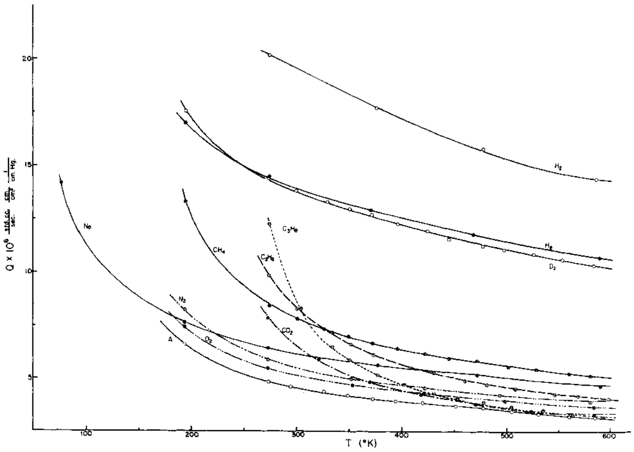

Fig. 1. Transfer coefficient chart; standardized permeabilities of gases and vapors vs. temperature.

The α_H^* of Equation (8) is next introduced into Equation (3) to obtain a general expression for the theoretical separation factor as a function of temperature.

$$\alpha_T = \alpha_H^* \cdot \frac{(x - Py)}{(1-x) - P(1-y)} \cdot \frac{1-x}{x} \tag{9}$$

These theoretically predicted values for α_T can now be compared with experimentally determined values of α as a test of the validity of the derivation and the inherent assumptions.

Although the expression for α_H^* in Equation (8) appears to be somewhat complex, the computer generated solutions which were used are quite routine. A less exact but more simplified solution for α_H^* is also possible through the use of the transfer coefficient chart shown in Figure 1. This chart represents a composite plot of the pure gas transfer coefficients as a function of the temperature. Values of α_H^* can, therefore, be obtained by determining the ratio of the ordinates for the desired pure gases at the required temperature. In addition to providing a covenient method for quickly estimating α_H^*, the transfer coefficient chart also shows an interesting phenomenon not discernible by simple inspection of Equation (8). This is, that the lines representing the pure gas transfer coefficients as a function of absolute temperature intersect one another at apparently random locations. Each intersection implies that at that temperature the transfer coefficients are equal. Therefore, $\alpha_H^* = 1.0 = \alpha_T$, or the mixture is nonseparable. Generally speaking these nonseparative mixtures are analogous to azeotropic mixtures observed with boiling liquids. Unlike azeotropes, however, they are not a function of composition, but are generated by the relative dependence of gas phase flow and surface flow on temperature. As the transfer coefficient chart shows, there are a significant number of mixtures which become nonseparative at some point along the temperature range.

DESIGN OF THE EXPERIMENT

The porous Vycor diffusion cell was assembled to produce cocurrent flow on both sides of the barrier. This type of assembly was used previously by Brubaker and Kammermeyer (*7*). The physical properties of the porous barriers have also been well establishel (*1, 7, 14* to *16, 18, 26*). Five binary gas mixtures were selected for investigation. They were helium-nitrogen, hydrogen-nitrogen, oxygen-carbon dioxide, carbon dioxide-propane, nitrogen-ethylene. The analysis of each mixture and that of the numerous samples was performed by gas chromatography.

DISCUSSION OF RESULTS

Validity of Assumptions

Two tacit assumptions were made throughout this investigation in order to limit the variables to be determined experimentally to a manageable number. First it was assumed that different barriers made of the same porous Vycor material would yield consistent pure gas and mixture data. Thus reliable data obtained from one barrier can be used to define the behavior of a different barrier. Such an assumption is common to all barrier studies. Its justification can usually be provided through the reproducibility of experimental results. In this particular instance a large amount of data was already available for diffusion through microporous Vycor glass (*15*). This evidence indicates that the assumption that Hwang's pure gas data could be used to predict flow data for another Vycor barrier was both reasonable and valid.

The second assumption dealt with the flow patterns within the test cell. Since the physical dimensions of the barrier made it impractical to create mixing by turbulent flow across its surface, another approach was required. Conditions of perfect mixing can be approached if the feed stream is itself thoroughly mixed before entering the cell, and only a small fraction of feed diffuses through the barrier. Thus, the composition of the flowing stream is essentially invariant, and to an undiscriminating porous barrier appears to be thoroughly mixed. For this investigation then, the feed was well mixed before introduction into the cell, and the cut or fraction permeated was always kept at less than 10% of the feed rate. Under these conditions the Weller-Steiner case I predictions are reasonably valid.

Experimental Results

Figure 2 shows the relationship between absolute temperature and the separation factors for the five mixtures which were studied. These data definitely follow the trends predicted by theory.

The most obvious discrepancies occurred over the lower portion of the temperature range. In this region the experimental values fell from 7 to 40% below the theoretically predicted values. Since the average experimental error was approximately 5%, these larger differences could not be attributed to systematic errors. The most logical conclusion is that the theoretical interpretation simply failed to give an adequate prediction at the lower temperatures. This failure was not unexpected. The pure gas theory derived by Hwang and used in this work was based on the assumption that adsorption would not exceed monolayer surface coverage. There was sufficient evidence in this study to suggest that not only was monolayer surface coverage exceeded, but that capillary condensation occurred in the smaller pores at the lower temperatures. This type of behavior is certainly inconsistent with the theoretical development. It is interesting to note, however, that if multilayer adsorption or capillary condensation does occur, the enrichment of the more condensable component will be favored. This results from the blocking of the gas phase flow of the volatile component in all but the largest pores. This interpretation is further supported by the experimental data which show that in every case the higher boiling component underwent the greater enrichment. Similar behavior was reported by Barrer (*1*) for other porous barriers. He suggested that perhaps a type of molecular sieve could be created by inducing total capillary condensation of one component throughout the porous barrier. In any event, the data make it obvious that some modification is necessary if the theory is to cover this low temperature region.

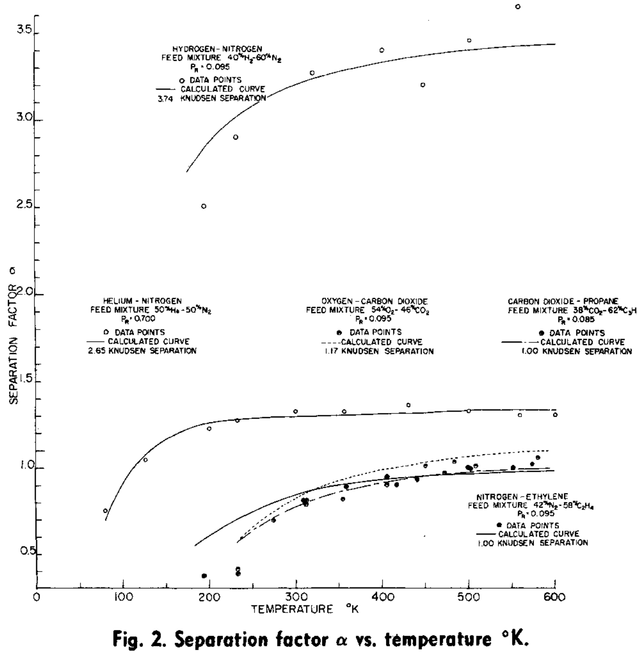

Fig. 2. Separation factor α vs. temperature °K.

Although it had been suggested (*11*) that the theoretical predictions might also fail at extremely high temperatures, no supporting evidence of such was found in this investigation. This was probably due to the fact that none of the experimental runs exeeded the 600°K. limit used in the pure gas measurements. In contrast, the lower temperature runs were frequently well below those reported for pure gas studies.

In looking at the gas mixtures individually several apparent characteristics are worth noting. First the oxygen-carbon dioxide mixture and the helium-nitrogen mixtures both experienced an inversion in their separation factors. The oxygen-carbon dioxide inversion point came at 400°K. while the helium-nitrogen occurred at a temperature of 115°K. Both of these temperature pinch points were predicted theoretically. The helium-nitrogen data also demonstrate the effect of pressure drop across the barrier (driving force) upon the separation factor. This effect is not new and has been reported by other investigators (Figure 3).

The carbon dioxide-propane mixture and the nitrogen-ethylene data were significant in that the components of each of these mixtures have essentially identical molecular weights. This means that gas phase separations by diffusion are impossible. Thus the separations which were achieved with these mixtures could only have been produced by a surface flow phenomenon. As shown, this type of phenomenon occurs most noticeably at the lower temperatures.

Finally it should be noted that for high temperatures and diffusion into vacuum all the separation factors approach their Knudsen flow predictions. This implies that the theory developed is consistent in this region. Also, as the temperature decreases, both the separation factor and the mass transfer increase for several mixtures. This suggests that both the separation and separative capacity of a single stage can be increased at lower operating temperatures for these mixtures.

SUMMARY

1. The separation factors for five binary mixtures were measured experimentally as a function of temperature with microporous Vycor as the selective barrier.

2. By using Hwang's working equation for pure gas flow in microporous media and Weller-Steiner case I as-

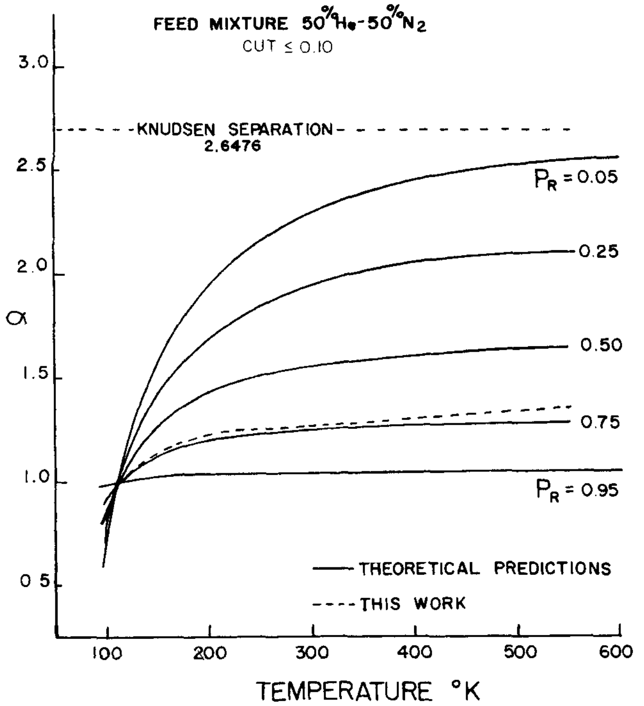

Fig. 3. Separation factor α as a function of temperature °K. and pressure ratio P_R.

sumptions for flow in a separation cell, a general equation was derived to predict theoretical separation factors as a function of temperature.

3. The agreement between theoretical predictions and experimental results was good for the overall temperature range of 80 to 600°K. The average error for 125 runs was approximately 5%. However, obvious inconsistencies were evidenced at the lower temperatures for all mixtures. These deviations were attributed to multilayer adsorption of the more condensible component, which restricts the gas phase flow of the more volatile component to only the larger capillaries.

4. Enrichment of the more condensible component was found to increase rapidly as the temperature decreased. Again this was attributed to an increased amount of surface flow at the expense of the gas phase flow of the less adsorbable component. This type of phenomenon was shown to be responsible for the inversion in separation factors for some mixtures. These inversion points can be predicted by finding the temperature at which the ratio of the pure gas transfer coefficients equals 1.0.

5. Lower temperature operation promises to produce even larger separation factors by creating molecular sieve action at near total capillary condensation conditions. However, the maximum separation factor observed experimentally was still less than 4.0.

6. As expected, the pressure ratio affected the separation. Large pressure drops or the permeation into a vacuum gave the best separations.

ACKNOWLEDGMENT

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NOTATION

A = constant in Hwang's theoretical equation which is primarily dependent upon the porous barrier. Its derivation can be found in *(11)*
B = constant in Hwang's theoretical equation *(11)*
M = molecular weight
P = ratio of the down stream pressure to upstream pressure
Q = pure gas transfer coefficient (cc./sec.) (cm./sq. cm.) (1/cm. Hg.)
T = absolute temperature °K.
x = mole fraction of the most permeable component at room temperature on the high pressure side of the barrier
y = mole fraction of the most permeable component at room temperature in the diffused stream (low pressure side of the barrier)
α^* = isothermal separation factor, defined as the ratio of the pure gas permeability coefficients
α = single stage separation factor as defined in distillation
α_T = theoretically calculated single stage separation factor
α_H^* = temperature dependent separation factor defined as the ratio of the pure gas permeability coefficients when predicted by Hwang's theory
Δ = constant in Hwang's theoretical equation *(11)*

Subscripts

1 = components of a binary mixture, mole fractions y and x
2 = components of a binary mixture, mole fraction $(1 - y)$ and $(1 - x)$

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