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ANALYTICAL REVIEW OF PASSIVE MASS TRANSFER OF WATER VAPOR IN A SPACE SUIT

BY
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ARNOLD P. SHLOSINGER AND KAY F. STERRETT

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3401 WEST BROADWAY
HAWTHORNE, CALIFORNIA

for the

AMES RESEARCH CENTER

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ANALYTICAL REVIEW OF PASSIVE MASS TRANSFER
OF WATER VAPOR IN A SPACE SUIT

By Joseph A. Peterson, Constantino Cafaro,
Arnold P. Shlosinger and Kay F. Sterrett

SUMMARY

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This report presents the results of an engineering study and analysis to determine the feasibility of transporting water vapor from the skin of an astronaut through an oxygen-water vapor mixture filled gap and on to a surface capable of adsorbing or condensing and removing the moisture in a space suit. A desiccant bed or a wick cooled below the required dew point were the devices considered for adsorbing or condensing and retaining or removing the moisture.

The theoretical analysis of binary diffusion coefficients indicates that the rate of diffusion across a gap is adequate for application in a space suit. The thermal diffusion coefficient has been found to have no significant effect upon the diffusion rate in the space suit.

Application of the derived design criteria for desiccant beds indicates their feasibility in removing water vapor for limited time periods. The concept of condensing on a cooled wick appears feasible for application to extended periods of time.

The analysis of condensing on cooled wicks requires experimental input parameters and a digital computer solution in order to provide numerical performance data. Direct empirical determination of these performance data appears more practical than experimental input parameter determination and computer analysis.

Author

INTRODUCTION

Presently used or planned space suit humidity control relies on circulation of the pressurization gas for control of the humidity level in the proximity of the human skin. In gas ventilated suits, the function of moisture removal is inherently satisfied by a relatively high rate of gas circulation, required by reliance on evaporation of sweat for removal of metabolic heat.

Advanced space suit thermal control concepts consider means other than gas circulation, such as circulating liquids, for metabolic heat control. As a result of better sensible heat removal, the amount of perspiration moisture may be drastically reduced, yet a means of removal of moisture is still required and circulation of suit pressurization gas, at a rate smaller than required in gas ventilated suits, is used.

The desire for reduced system complexity leads to moisture control concepts relying on molecular diffusion of perspiration water vapor in a stagnant pressurization gas for vapor transfer to locations of vapor removal. Surface adsorption on a desiccant or surface condensation on surfaces cooled below the required dew point are concepts considered for vapor removal. Physical arrangements where the water vapor removal surface is not in contact but at a distance of a few millimeters from the skin appear probable for reasons of astronaut comfort and non interference with liquid cooled thermal under-garments. Such arrangements require exploration of molecular diffusion rates of water vapor across a gap filled with the pressurization gas and of surface adsorption and surface condensation processes in absence of forced or gravity induced convective gas flow.

This report presents the results of an analytical study of molecular diffusion, mass transfer within an adsorption bed, and condensation on a cooled wick as they apply to space suit concepts.

SYMBOLS

Symbol	Description	Dimensions
C	Total molar concentration of a gas mixture, $C = C_o + C_w$	moles/cm ³
C _o	Molar concentration of oxygen in a gas mixture	moles/cm ³
C _w	Molar concentration of water vapor in a gas mixture	moles/cm ³
C*	Molar concentration of water vapor at any point on the desiccant bed	moles/cm ³ of bed
\bar{C}^*	Average concentration of water vapor in the entire desiccant bed	moles/cm ³ of bed
D _T	Thermal diffusion coefficient	cm ² /sec
D ₁₂	Binary diffusion coefficient	cm ² /sec
E	Desiccant bed equilibrium constant, C_w/C^*	
F	Flux parameter, $J_w L (1 - x)/\alpha_D C_w$	
J _w	Molar flux of water vapor relative to space suit coordinates	$\frac{\text{moles}}{\text{cm}^2 \text{ sec}}$
J _w *	Molar flux of water vapor relative to the average gas velocity	$\frac{\text{moles}}{\text{cm}^2 \text{ sec}}$
K _T	Ratio of thermal diffusion coefficient to the binary coefficient, D_T/D_{12}	
L	Total depth or thickness of desiccant bed	cm
Q	Adsorption Efficiency, $\bar{C}^* E / [C_w (1 + E)]$	
R. H.	Relative Humidity	percent
T	Average temperature of gas mixture	°K
t	Time	seconds
\bar{U}	Average gas velocity	cm/sec
U _o	Average velocity of oxygen molecules	cm/sec
U _w	Average velocity of water vapor	cm/sec

w	Weight of water vapor that can be adsorbed in 100 gms of dry desiccant	gms
x	Mol fraction of water vapor in the gas, C_w/C	
α_D	Bed diffusivity, $D_{12} \phi \left[1 - (1/3) (1 - \phi) \right] E / (1 + E)$	
θ	Time parameter, $\alpha_{Dt} / 4L^2$	
ρ_E	Bulk density of desiccant	gms/cm ³
ϕ	Pore volume fraction in a desiccant bed	
∇C_w	Concentration gradient of water vapor across gas layer, $\frac{dC_w}{d \text{ length}}$	$\frac{\text{moles/cm}^3}{\text{cm}}$
∇T	Temperature gradient across gas layer, $\frac{dT}{d \text{ length}}$	$\frac{^\circ\text{K}}{\text{cm}}$
∇x	Mole fraction gradient across gas layer, $\frac{dx}{d \text{ length}}$	$\frac{1}{\text{cm}}$
(1 - x)	Mol fraction of oxygen in the gas mixture, $\frac{C_o}{C}$	

MOLECULAR DIFFUSION IN BINARY MIXTURES

The transfer of water vapor resulting from binary diffusion through the space suit pressurization gas, assumed to be pure oxygen, may be described by Fick's First Law of Diffusion. The differential equations describing the diffusion process are discussed by Jost in his book "Diffusion in Solids, Liquids and Gases" (Ref. 1). Other sources, including the recent volume by Bird, Stewart and Lightfoot (Ref. 2), describe and illustrate the equivalence of the different forms of Fick's law.

Bird, Stewart and Lightfoot express Fick's first law as:

$$J_w^* = -D_{12} \nabla C_w = -CD_{12} \nabla x \quad (1)$$

Thermal diffusion is only significant where temperature gradients are of the order of magnitude of the absolute gas temperatures. The lighter smaller molecules of H_2O are in a greater state of agitation than the heavier large molecules of O_2 and will arrange themselves in a manner which will minimize the entropy increase of the system. This means that O_2 will concentrate in the cooler regions and the H_2O will concentrate in the warmer regions (Ref. 5). Including the thermal diffusion effect, the flux J_w^* becomes, for water vapor generated in the warmer region (i. e., at the human skin):^w

$$J_w^* = -D_{12} \left[\nabla C_w - \frac{K_T (C_o + C_w)}{T} \nabla T \right] \quad (2)$$

This expression results from including only the mole fraction gradient and thermal gradient in the more general expression in Reference 3, (Hirschfelder, Curtis & Bird equations 8.1-1 and 8.1-2 p. 516). It can be shown that no significant effect results from thermal diffusion at the small temperature gradients existing in a space suit.

Other forces which would tend to cause mutual diffusion of one gas mixture component through the other are not considered significant for a space suit. For example, large pressure gradients will accelerate the lighter molecules relative to the heavier molecules. This phenomenon causes the separation in a rocket exhausting to a vacuum, (Ref. 4), but has obviously no effect in a space suit. Generalized diffusion equations which include all of the effects are discussed in Chapter 14 of Reference 5.

The flux term J_w^* does not exactly describe the movement of water vapor away from the human skin and toward a locale of vapor removal as it exists in a space suit, because of its relationship to the "molar average gas velocity" term rather than to the man-suit coordinates. However, it provides a reasonable approximation. The "molar average gas velocity" as defined in Reference 2 (Bird, Stewart & Lightfoot pg. 498) is:

$$\bar{U} = x U_w + (1 - x) U_o \quad (3)$$

If the oxygen molecules are assumed to be stationary relative to the container of the gases, i. e., the space suit coordinates,

then

$$\begin{aligned} U_o &= 0 \\ \bar{U} &= x U_w \end{aligned}$$

The molar flux relative to the stationary suit coordinates includes the flux due to the "molar average gas velocity" with respect to the coordinate system of the space suit.

Neglecting the thermal diffusion effect is equivalent to the assumption that total molar concentration C , and temperature T as well as total pressure are constant along the path length.

Then

$$\begin{aligned} J_w &= C_w U_w \\ &= -D_{12} \nabla C_w + \frac{C_w}{C_w + C_o} (C_w U_w + C_o U_o) \end{aligned} \quad (4)$$

Since

$$\begin{aligned} C_o U_o &= 0 \\ x &= C_w / (C_o + C_w) \\ C &= C_o + C_w \end{aligned} \quad (5)$$

We conclude that

$$J_w = -C D_{12} \nabla x + x J_w \quad (6)$$

from which,

$$J_w = \frac{C D_{12} \nabla x}{1 - x} \quad (7)$$

The binary diffusion coefficient of water vapor in oxygen is discussed in Appendix A. Based upon the evaluation of different published data it was concluded that the low temperature data of Schwertz and Brow (Ref. 6) was most applicable to conditions of the space suit. The classical diffusion relation using a Lennard Jones (12-6-3) interaction potential with collision integrals by Monchick and Mason was fitted to the experimental data of Schwertz and Brow. A least mean square fit technique was used.

An analysis of the thermal diffusion coefficient is presented in Appendix B. Equation (7) will be utilized in the following example in analyzing diffusion in a typical space suit application. The water vapor flow between two parallel plates one square meter in area and one half centimeter apart will be determined. It is assumed that the first plate (skin side) is at 32.2°C (90°F) and has a vapor pressure corresponding to 50% relative humidity and 32.2°C. The water vapor condenses at the second plate at a temperature of 10°C (50°F) and saturation. The space between the two plates contains water vapor and pure oxygen at a total pressure of 0.238 atmospheres (3.5 psia). From Figure A-3 in Appendix A, the coefficient of diffusion for 0.238 atmospheres at 32.2°C is 1.17 cm²/sec. The total molar concentration of the gas mixture is:

$$C = \frac{0.238 \text{ atmospheres}}{82.057 \times 305.2^\circ\text{K}} = .950 \times 10^{-5} \frac{\text{gm moles}}{\text{cm}^3}$$

The mole fraction water vapor at the skin side plate is

$$x_s = \frac{P_w}{P_T} = \frac{50\% (P_w) \text{ sat. for } T = 32.2^\circ\text{C}}{P_T} = \frac{.5 (0.04749) \text{ atmos.}}{0.238 \text{ atmos.}}$$

$$x_s = 0.0998$$

The mole fraction of water vapor at the condensing plate side is

$$x_c = \frac{100\% (P_w) \text{ sat. for } T = 10^\circ\text{C}}{P_T} = \frac{0.01216 \text{ atmos.}}{0.238 \text{ atmos.}} = 0.0509$$

The average mole fraction of water vapor (x) in the mixture is

$$\frac{0.0998 + 0.0509}{2} = 0.0754.$$

The concentration gradient (∇x) across the gaseous mixture gap is:

$$\nabla x = \frac{0.0998 - 0.0509}{0.5 \text{ cm}} = \frac{0.0978}{\text{cm}}$$

then the water vapor flux is

$$J_w = \frac{C D_{12} \nabla x}{(1-x)} = \frac{0.950 \times 10^{-5} \frac{\text{moles}}{\text{cm}^3} \times 1.17 \frac{\text{cm}^2}{\text{sec}} \times 0.0978/\text{cm}}{(1 - .0754)}$$

$$J_w = 0.1176 \times 10^{-5} \frac{\text{moles}}{\text{cm}^2 \text{ sec}} \times \frac{10000 \text{ cm}^2}{\text{meter}^2} \times \frac{18 \text{ gms}}{\text{mole}} \times \frac{3600 \text{ sec}}{\text{hr}}$$

$$J_w = 762.0 \frac{\text{gm}}{\text{hr-meter}^2} \quad (0.156 \text{ lbs/ (ft}^2 \text{ - hr)})$$

The skin area of an average man is 1.81 meter² (19.5 ft²). The total water vapor that can be diffused from the skin is

$$762.0 \frac{\text{gms}}{\text{meter}^2 \text{-hr}} \times 1.81 \text{ meter}^2 = 1379.2 \frac{\text{gms}}{\text{hr}} \quad (3.04 \text{ lbs/hr}).$$

This rate of water emission from the man would be approximately equivalent to a latent heat emission of 766.1 $\frac{\text{kilocalories}}{\text{hr}}$ (3040 BTU/hr). In a space suit using a liquid coolant to provide adequate sensible heat removal, the metabolic latent heat emission is not expected to

exceed 201.6 $\frac{\text{kilocalories}}{\text{hr}}$ (800 BTU/hr). This indicates the feasibility of diffusing water vapor across the gaseous gap in a space suit using only a fraction of the full suit area for condensation of the water vapor.

In order to show that in the application to a space suit the thermal diffusion effect is negligible, the example is calculated with inclusion of the thermal diffusion effect. Using the expression including diffusion effects and using a form of the expression that includes the velocity across the gap with respect to the space suit coordinates, the flux J_w has been derived in a manner similar to equation (7).

$$J_w = - \frac{C D_{12}}{1-x} \left(\nabla x - \frac{K_T}{T} \nabla T \right) \quad (8)$$

The method of computation of the thermal diffusion coefficients K_T is described in Appendix B. The results are given in Figure B-1.

From Figure B-1, with the average $x = .0754$ and $.011 < K_T < .016$, using the higher value of K_T , the term $\frac{K_T}{T} \nabla T$,

$$\frac{K_T}{T} \nabla T = \frac{0.016}{294.1^\circ\text{K}} \left(\frac{32.2^\circ - 10^\circ\text{C}}{.5 \text{ cm}} \right) = 0.00242$$

is $\frac{0.00242}{0.0978} = 0.0248$ or 2.48% of the concentration gradient. The flux considering the thermal gradient effects therefore is actually reduced to 743.1 gms/(hr-meter²). This 2.48% error is negligible considering the errors which are unavoidable as a result of the assumptions required in deriving the diffusion coefficient.

MASS TRANSFER PHENOMENA FOR ADSORPTION AND CONDENSATION

Two water vapor removal techniques are presently being considered for the space suit application. The water vapor may be condensed on and within wick surfaces maintained below the dew point. Or, the water vapor may be adsorbed and condensed on desiccant surfaces. In either case, flow of an oxygen water vapor mixture through a porous bed will occur. It is expected that the rate of this flow will be controlled by the coefficient of diffusion of the gas mixture into the porous bed.

The effect of porosity and bed porosity geometry upon the coefficient of diffusion are discussed in Appendix C. Because of the randomness of the wick fibers and the adsorbent particles, equation (9) is recommended for modification of the binary diffusion coefficients as given in Figure A-3.

$$D_{\text{eff}} \leq D_{12} \phi \left[1 - (1/3)(1 - \phi) \right] \quad (9)$$

It is furthermore emphasized that this is a maximum value for the effective binary diffusion coefficient which may actually be less than this.

MASS TRANSFER WITHIN AN ADSORPTION BED

The conditions of mass transfer within an adsorber differ significantly from conditions within a wick. The wick continues to condense water vapor provided that the temperature is maintained below the dew point of the surrounding gas. On the other hand the adsorber ceases to adsorb vapor as soon as the active surface of the adsorber is covered with one or a few molecular layers of adsorbate. The wick can retain more water than the adsorber in its pores, or can transport the water to an evaporator and provide continuous operation. However, the temperature of the wick must be held below the dew point corresponding to the desired moisture content of the surrounding gas. The adsorber on the other hand will adsorb water at adsorption bed temperatures above the dew point until the water vapor and the adsorbed phase are in equilibrium.

The analytical evaluation of mass transfer in an adsorption bed is derived in Appendix D. The results of the analysis, namely Figures D-1, D-2 and D-3 in the Appendix, will be used in the following example applicable to space suit conditions.

It is assumed that the moisture removal system in a space suit shall be designed to remove the water vapor from the suit gas at 0.238 atmospheres (3.5 psia) pressure, 32.2°C (90°F) and 50% relative humidity, for a suit operational period of 4 hours. Starting with a dry 0.6 cm thick bed having a surface area of 1.81 square meters (the skin surface area of an average man), the bed efficiency and water vapor removal rate is sought at the end of the 4 hours of operation. Using silica gel as the adsorbent, the example calculation includes determining the total water adsorbed in this time period.

The properties of silica gel as obtained from Reference 15 are,

$$\rho_E = .70 \text{ gms/cc}$$

$$\phi = 50\%$$

$$w = 20\%$$

The mole fraction of water vapor in the gaseous mixture,

$$x = \frac{(\text{R. H.}) P_{\text{sat at } T = 32.2^\circ\text{C}}}{P_{\text{total}}} = \frac{(0.50) 0.0475 \text{ atmos}}{0.238 \text{ atmos}} = 0.0998$$

The water vapor concentration at the face of the bed is,

$$C_w = (\text{R. H.}) (C_w)_{\text{sat at } T = 32.2^\circ\text{C}}$$

$$(C_w)_{\text{sat at } T = 32.2} = \frac{0.0475 \text{ atmos}}{82.057 \frac{\text{cm}^3 \text{ atmos}}{\text{moles } ^\circ\text{K}} \times 305^\circ\text{K}} = 0.1897 \times 10^{-5} \frac{\text{moles}}{\text{cm}^3}$$

$$C_w = .5 (1897 \times 10^{-5})$$

The equilibrium constant E is calculated as follows

$$E = \frac{C_w}{C^*} = \frac{\text{R. H. } (C_w)_{\text{sat}} \times 18}{(w/100) \rho_E} = \frac{0.5 (C_w)_{\text{sat}}}{0.20 \times .70}$$

$$E = 64.3 (C_w)_{\text{sat}} = 12.198 \times 10^{-5}$$

The next step will involve calculating the time parameter (θ).

$$\theta = \frac{D_{12} \phi \left[1 - \frac{1}{3} (1-.5) \right] E t}{4 L^2 (1 + E)}$$

$$\theta = \frac{1.17 \times .5 \left[1 - \frac{1}{3} (1-.5) \right] 12.198 \times 10^{-5} \times 4 \text{ hrs} \times 3600 \frac{\text{sec}}{\text{hr}}}{4 \times (0.6)^2 (1 + 12.198 \times 10^{-5})}$$

$$\theta = 0.595$$

From Figure D-1 of Appendix D, the Flux Parameter $F = 0.0056$ at $\theta = 0.595$. The flux at the end of four hours is,

$$J_w = \frac{F D_{12} \phi \left[1 - \frac{1}{3} (1-\theta) \right] C_w}{L (1 - x)} = \frac{0.0056 \times 1.17 \times .5 \left[1 - \frac{1}{3} (1-.5) \right] C_w}{0.6 \text{ cm} (1 - x)}$$

$$J_w = 0.0479 \times 10^7 \frac{\text{moles}}{\text{cm}^2 \text{ sec}} \times 18 \frac{\text{gms}}{\text{mole}} \times 1.81 \text{ meter}^2 \times 10^4 \frac{\text{cm}^2}{\text{meter}^2} \times \frac{3600 \text{ sec}}{\text{hr}}$$

$$J_w = 5.62 \frac{\text{gms}}{\text{hr}} \text{ or } 3.105 \frac{\text{gms}}{\text{hr-meter}^2}$$

From Figure D-2 of Appendix D, the adsorption efficiency $Q = .999$ at $\theta = 0.595$.

The weight of water adsorbed in the four hours can be calculated as follows:

$$\bar{C}^* = \frac{C_w Q (1 + E)}{E} = \frac{.5 (.1897 \times 10^{-5}) \times .999 (1 + .000122)}{12.198 \times 10^{-5}}$$

$$\begin{aligned}
\bar{C}^* &= 0.007768 \text{ moles/cm}^2 \\
&= 0.007768 \text{ moles/cm}^2 \times 18 \text{ gms/mole} \times 0.6 \text{ cm} \times 1.81 \text{ meter}^2 \times \frac{10^4 \text{ cm}^2}{\text{meter}^2} \\
&= 1518 \text{ gms} \\
&= 838.7 \text{ gms/meter}^2 \text{ in four hours}
\end{aligned}$$

Values of water removal rate and weight of water accumulated in the 0.6 inch thick silica gel adsorber, calculated by use of the techniques presented above, have been plotted in Figure 1 and Figure 2 respectively for various relative humidities at the bed face as a function of time. The information as presented in Figure 2 can be used to indicate the suit performance using the 0.6 cm thick silica gel desiccant bed. If lines of constant sweat rate are plotted across this Figure 2, then a family of curves as shown in Figure 3 can be obtained indicating the actual relative humidity build-up in the suit as a function of time.

For example, in a space suit using a 0.6 cm thick bed throughout the total skin area of the man (1.81 meter²), and for an assumed sweat rate of 210 gms/hr-meter² (116.6 kcal/m²-hr latent heat), the relative humidity level in the suit increases from zero (assuming an initially dry desiccant) to 50% at the end of the four hour period (Fig. 3). Hence a constant metabolic latent heat output of approximately 1.81 x 116.6 = 211 kilocalories/hr (838 BTU/hr) from the man would result in a relative humidity of 50% at the end of the four hours. Higher sweat rates result in a more rapid built-up of relative humidity in the suit as shown in Figure 3.

Actually the sweat rate in a suit will not be constant but will vary as a function of the activity level, as well as the mental and physical stresses on the astronaut. In a space suit using a liquid coolant to provide adequate sensible heat removal, the sweat rate is not expected to exceed

$$\frac{200 \text{ gms}}{\text{hr-meter}^2} .$$

Since application of the desiccant over an area equal to the full skin area may not be practical, a trade off between the desiccant face area and an increased bed depth will be required. However, it can be concluded that a wide range of sweat rates can be accommodated by the use of a desiccant in a suit for limited periods of time.

CONDENSATION ON A COOLED WICK

The water vapor diffusing from the skin of the astronaut toward a wick surface, which is cooled below the required dew point will begin to condense as it comes into contact with the wick. The assumption is made that the wick is continuously cooled and that temperature gradients within the wick are negligibly small because of selection of wick materials of high thermal conductivity or because of short heat path length of thin wick layers.

An analytical evaluation of condensation and mass transfer phenomena in a cooled wick is presented in Appendix E of this document. The analytical approach to this particular problem, as shown in the Appendix, leads to a complex mathematical model requiring digital computer solutions.

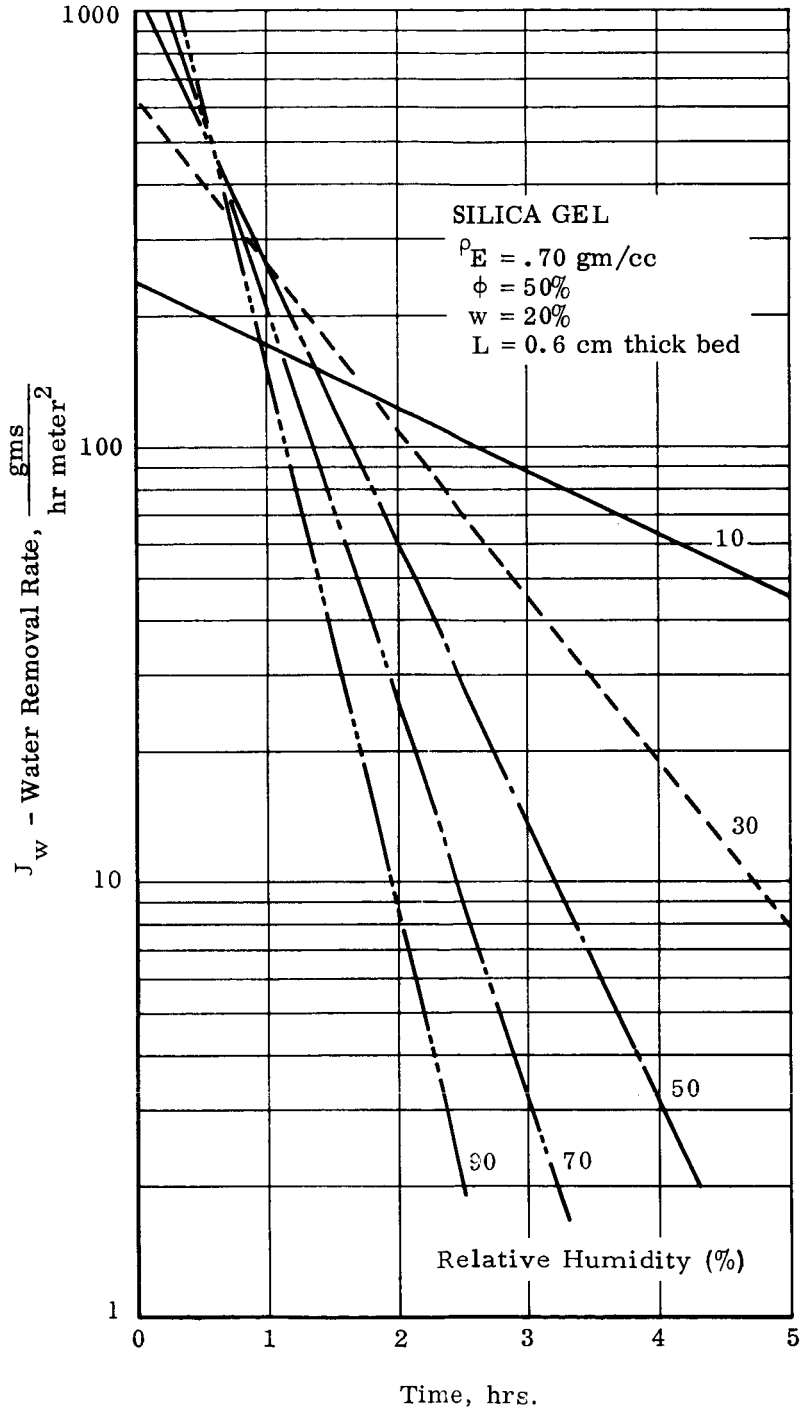


FIGURE 1 ADSORPTION BED PERFORMANCE (Rate of Flow vs Time)

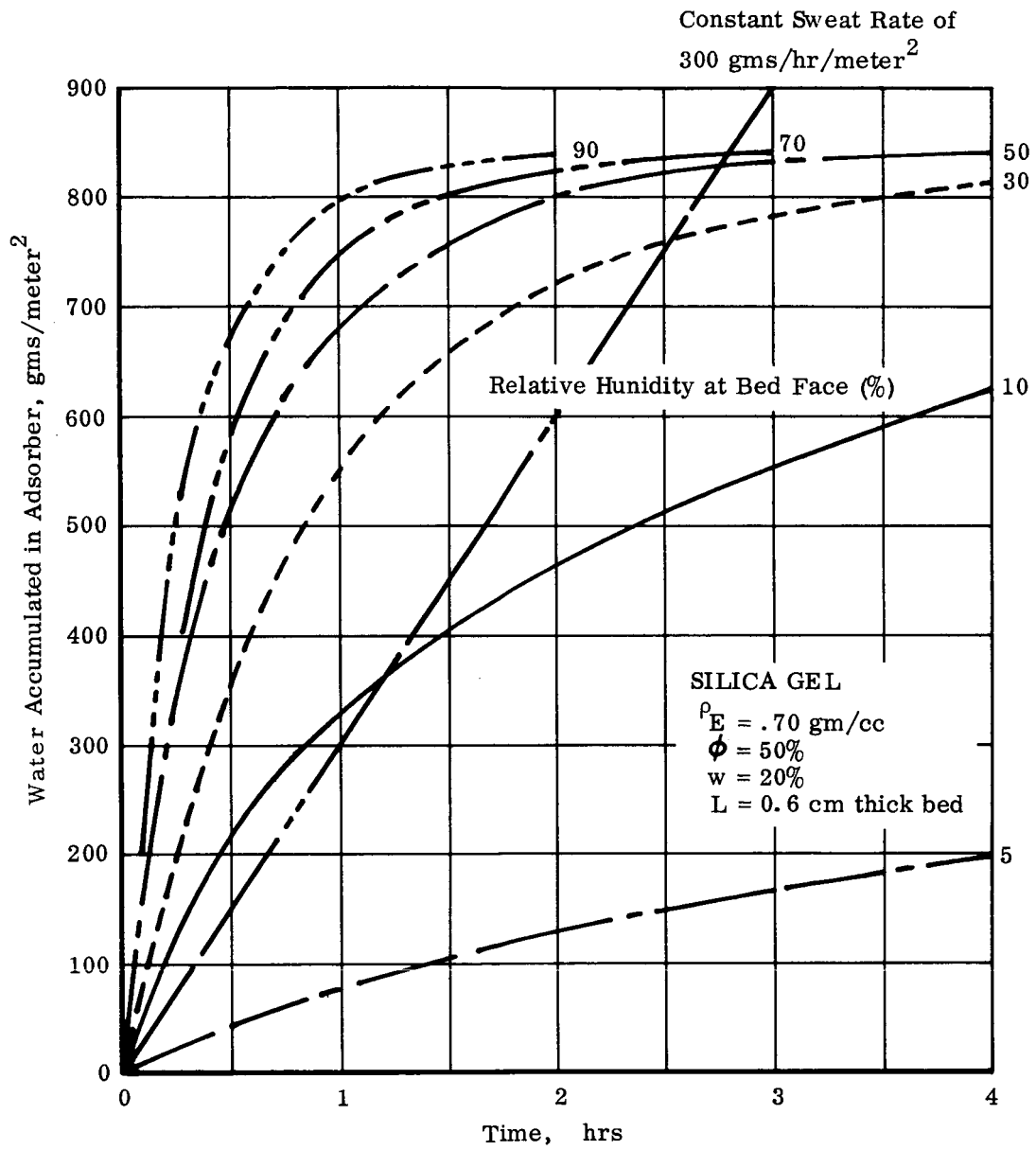


FIGURE 2 ADSORPTION BED PERFORMANCE (Weight of Water Accumulated vs Time)

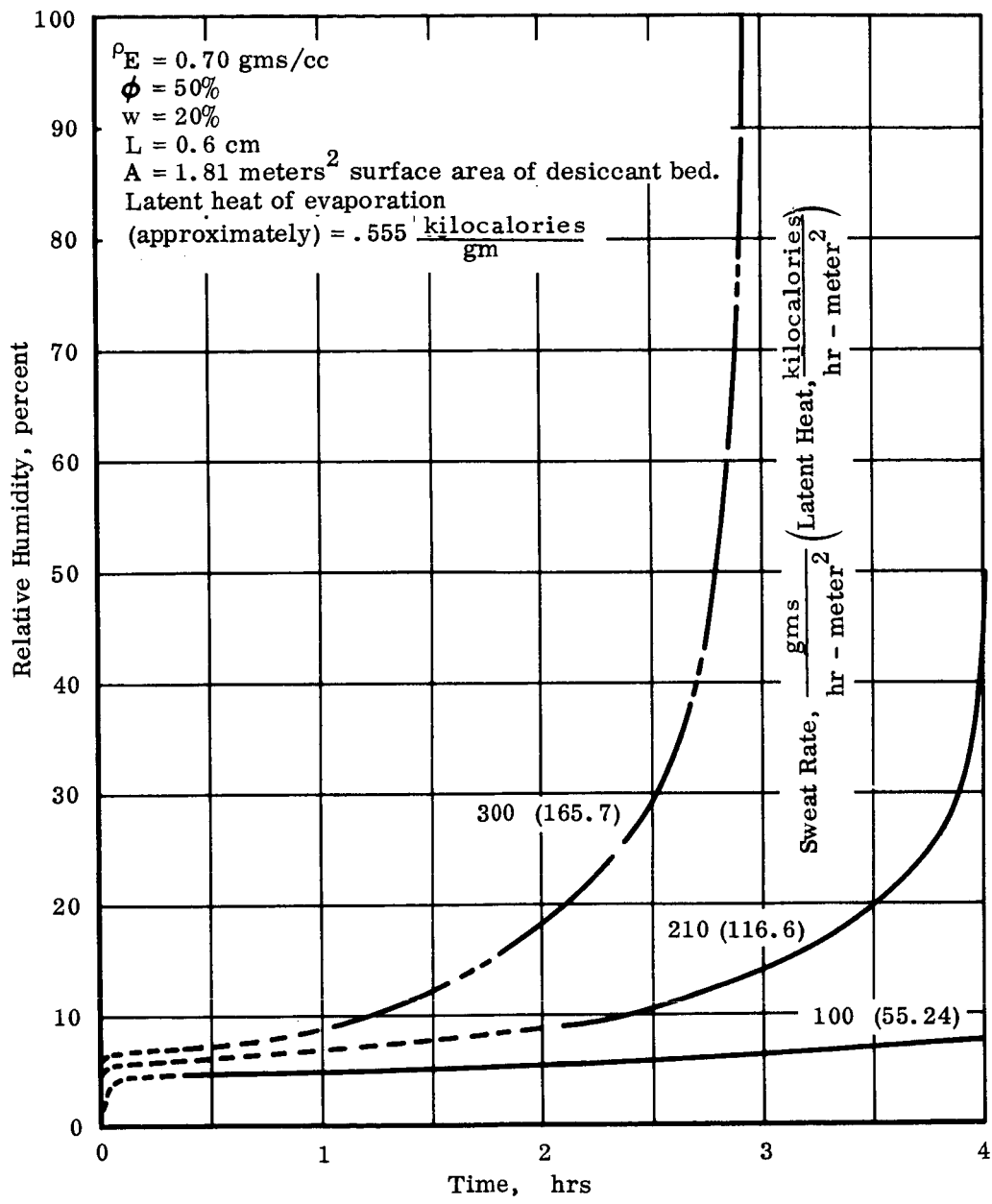


FIGURE 3 SPACE SUIT PERFORMANCE WITH A SILICA GEL DESICCANT

As shown in Appendix E extensive experimentation would be required to provide input parameters to such a computer analysis. Furthermore, as the mathematical model must be based on certain simplifying assumptions, it is felt that a direct experimental investigation simulating a physical model will provide a more direct approach for obtaining the performance data at condensation on a cooled wick.

CONCLUSIONS

The analytic effort presented in this report and its appendices indicates the feasibility of transferring water vapor from the skin of an astronaut through an oxygen-water vapor mixture filled gap and on to a surface capable of condensing or adsorbing and removing the moisture. The binary diffusion coefficients as presented in Figure 3-A of Appendix A were derived from expressions that have been fitted to experimental data. These experimental data were derived under conditions reasonably close to those of a space suit and deviations between the values computed and actual diffusion coefficients are expected to be small. Thermal diffusion effects in a space suit are negligible.

An equation expressing the upper limit of diffusion of water vapor within either an adsorber or a condensing wick as a function of bed porosity is discussed in Appendix C. This expression was used in deriving the mass transfer in both an adsorber bed and a condensing wick. Experimental determination of the actual porosity of an adsorber bed or wick will be required.

Derivation of the design parameters for use in designing a space suit desiccant bed relies upon a knowledge of the adsorption isotherm and the physical characteristics of the adsorber bed. Experimental data from the literature have been used in a sample problem to demonstrate the use of the curves derived from the analysis in Appendix D. The results of the analysis have been used as a first approximation to demonstrate the feasibility of using a desiccant for humidity control in a space suit for limited durations. A simplifying assumption of constant humidity at the bed face was made in the analysis in Appendix D. However, the results are useful in predicting suit performance. Given knowledge of actual evaporation rates in a space suit as a function of time, curves such as those presented in Figures 1, 2 and 3 can be used to design a space suit adsorbent bed. However experimentation to verify the analysis is recommended.

The condensing wick concept is expected to have applicability for more extended periods of time or continuous operation. The results of the analysis presented in Appendix E are based upon interaction energies for condensation which require determination by experiment. It is recommended to perform experimentation with a system arrangement simulating a space suit and obtain performance data directly from the experiment. More reliable results are expected from this approach than from experimentation providing data to the analysis.

APPENDIX A

Analysis of Diffusion Coefficients

A literature review of the methods employed and results obtained in estimating the diffusion coefficient was performed. The diffusion coefficient of water vapor in oxygen was found to be absent from compilations of early data, including the International Critical Tables (Ref. 8) and texts on diffusional processes such as Sherwood (Ref. 9) and Perry's Chemical Engineers Handbook (Ref. 10). Until recently the only experimental data available for oxygen was Schwartz and Brow's (Ref. 6) results, and these were determined only at three temperatures. In 1960 Westenberg and Walker (Ref. 11) published data on the mutual diffusion coefficient of water vapor and oxygen for 300°K to 1200°K. The determination of these data was part of an effort directed toward combustion processes (Ref. 11, 12, 13).

Up until the present decade, the methods appearing in "The Molecular Theory of Gases and Liquids" (Ref. 3) were considered the best. Several reports were reviewed which discussed and summarized these methods (Ref. 14, 15). Figure A-1 illustrates the results of computations on three water vapor-gas mixtures using these methods and, as may be seen, the results compare favorably with experimental data, except for the case of oxygen.

Additional bibliographic material which were reviewed and are listed in References 16 through 63 deal with the general problem area of diffusion data and does not specifically relate to water vapor-oxygen diffusion.

A large number of gases appear to have diffusion coefficients that follow the semi-empirical diffusion coefficient law of Gilliland (Ref. 10). The Gilliland Law has been derived from the kinetic theory of gases for hard, spherical molecules with no interactions. The coefficient .0043 has been determined from experiment. The Gilliland expression from Reference 10 is:

$$D_{12} = \frac{0.0043 T^{3/2}}{(V_o^{1/3} + V_w^{1/3})} \frac{1}{P} \sqrt{\frac{M_o + M_w}{M_o M_w}} \quad (A1)$$

- where: T = Temperature of gas mixture (°K)
 P = Total pressure of mixture (atmosphere)
 M_w = Molecular weight water vapor ($\frac{\text{gms}}{\text{mol}}$)
 M_o = Molecular weight of oxygen ($\frac{\text{gms}}{\text{mol}}$)
 V_w = Molar volume of water vapor (cm^3/mol)
 V_o = Molar volume of oxygen (cm^3/mol)

The molar volumes V_w and V_o are determined from the density of the saturated liquid at the normal boiling point. Figure A-2 depicts the diffusion coefficients calculated by Gilliland's empirical expression at one atmosphere pressure, for various temperatures.

More accurate binary diffusion coefficients can be obtained from the kinetic theory of gases by using a more realistic model. This model will account for the interaction forces between the molecules. The trajectories of the molecules are computed for initial velocity distributions, estimated from statistical laws. The greatest uncertainty lies in the assumption which must be made for the correct interaction potential. The collision integrals of Monchick and Mason used a (12-6-3) Lennard Jones potential interaction for this analysis in order to account for attractive and repulsive forces (Ref. 2). In the case of water vapor and oxygen, an additional effect must be considered, namely, the polar nature of the water molecules. This required that the statistical distribution of translational energy at a given temperature must include those energy levels associated with the dipole moment of the water molecule and polarization of the non-polar oxygen molecule.

Theoretically, the binary diffusion coefficient could be estimated as accurately as desired if the interaction forces were known. By a series of successive iterations, the entire spectrum of collision possibilities could be considered and added to the result. For the purposes of this study, only a first iteration will be used, since including further iterations become unwieldy. The diffusion coefficient is determined from the following equation:

$$D_{12} = D_{21} = \frac{0.001858 T^{3/2} \sqrt{\frac{M_o + M_w}{M_o M_w}}}{P \sigma_{wo}^2 \Omega_{wo} (1, 1)^*} f_D \quad \begin{matrix} \text{(A2)} \\ \text{(Reference 3)} \end{matrix}$$

where: T = Temperature ($^{\circ}$ K)

M_w, M_o = Molecular weight of water vapor and oxygen respectively (gms/mol)

P = Absolute pressure (atmospheres)

σ_{wo} = Molecular collision diameter (average for collision) (Angstroms)

$\Omega_{wo} (1, 1)^*$ = Collision integral for diffusion determined as a function of a reduced temperature and dipole moment parameter and tabulation in Reference 7.

f_D = Correction term for higher order approximations (Assume $f_D = 1.0$)

$T_{wo} = \frac{TK}{\epsilon_{wo}}$ = Reduced temperature for collisions indicated by subscripts (dimensionless)

ϵ_{wo} = Interaction potential for collisions between molecules indicated by subscripts (ergs)

K = Boltzmann constant 1.38×10^{-16} (erg/ $^{\circ}$ K)

μ = Dipole moment (Debyes)

δ_{wo} = Reduced sidole moment for collisions between molecules indicated by subscripts (dimensionless)

Subscripts:

o = Refers to oxygen (non-polar)

w = Water (polar)

For polar-polar collisions (only polar gases present)

$$\epsilon_{wo} = (\epsilon_{ww} \epsilon_{oo})^{1/2} \quad (A3)$$

$$\sigma_{wo} = \frac{1}{2} (\sigma_{ww} + \sigma_{oo}) \quad (A4)$$

$$\delta_{wo} = \frac{1}{2} \left(\frac{\mu_{ww} \mu_{oo}}{\epsilon_{wo} \sigma_{wo}^3} \right) \quad (A5)$$

For polar-nonpolar interactions such as water vapor and oxygen, Monchick and Mason (Reference 16) have shown the dipole interaction term, δ_{ow} to be negligible.

Hence for polar-nonpolar collisions

$$\delta_{wo} = 0 \quad (A6)$$

$$\epsilon_{wo} = (\epsilon_{oo} \epsilon_{ww})^{1/2} \quad (A7)$$

$$\delta_{wo} = \frac{1}{2} (\sigma_{oo} + \sigma_{ww})^4 \quad (A8)$$

In the above expressions, the resulting binary diffusion is a function of the force constants used to describe the gaseous mixture. Tabulated force constants from a nomograph by Monchick and Mason were used to calculate the diffusion coefficient. These force constants are for pure water vapor and oxygen determined from experimental gas viscosities and second virial coefficients and are shown in Table I. The resulting binary diffusion values are shown on the middle curve of Figure A-2.

Finally, the force constants determined from experimental diffusivity data of Schwertz and Brow (Ref. 6) ($\sigma_{wo} = 3.907\text{\AA}$, $\epsilon/K = 19.6^\circ\text{K}$) were used in the diffusion expressions using a method by Monchick and Mason (Ref. 7, 16, 17, 18, 19, 20). The upper curve of Figure A-2 and Table II indicate the binary diffusion coefficients obtained from this data.

Data calculated from diffusion data by Schwertz and Brow (Reference 6), and experimental data reported by Westenberg and Walker (Reference 11) and Schwertz and Brow are compared in Figure A-2. All of the experimental data are within 7% of the values calculated from Schwertz and Brow data. However, use of the collision parameters tabulated by Monchick and Mason from viscosity data result in the middle curve on Figure A-2 which indicates a diffusion coefficient approximately 25% below the data computed from diffusion collision parameters. The Gilliland (Ref. 10) correlation, long accepted as good approximation for most gases, is about 30% low.

Figures A-1 and A-2 demonstrate the dependence of the calculated diffusion coefficients upon experimental methods to provide data from which the parameters appearing in the assumed potential function can be determined. The figures show some good agreement between calculated and experimental diffusion coefficients. This is to be expected when the experimental data used for the comparison and the data used for the evaluation of parameters in the potential function have both been determined by means of the same experiment. This comparison cannot demonstrate consistency of experimental and calculated results. It does demonstrate the consistency of the assumed potential function in representing the data and does thereby provide a reasonable degree of confidence in applying published experimental data to the space suit application.

In both the collision integral form of the equation for diffusion coefficient and the Gilliland expression, the diffusion coefficient is inversely proportional to the total pressure. This has been illustrated for the collision integral method using Schwertz and Brow in Figure A-3. The data of Figure A-3 represent the best analytical results of this study, and will be used henceforth in this report.

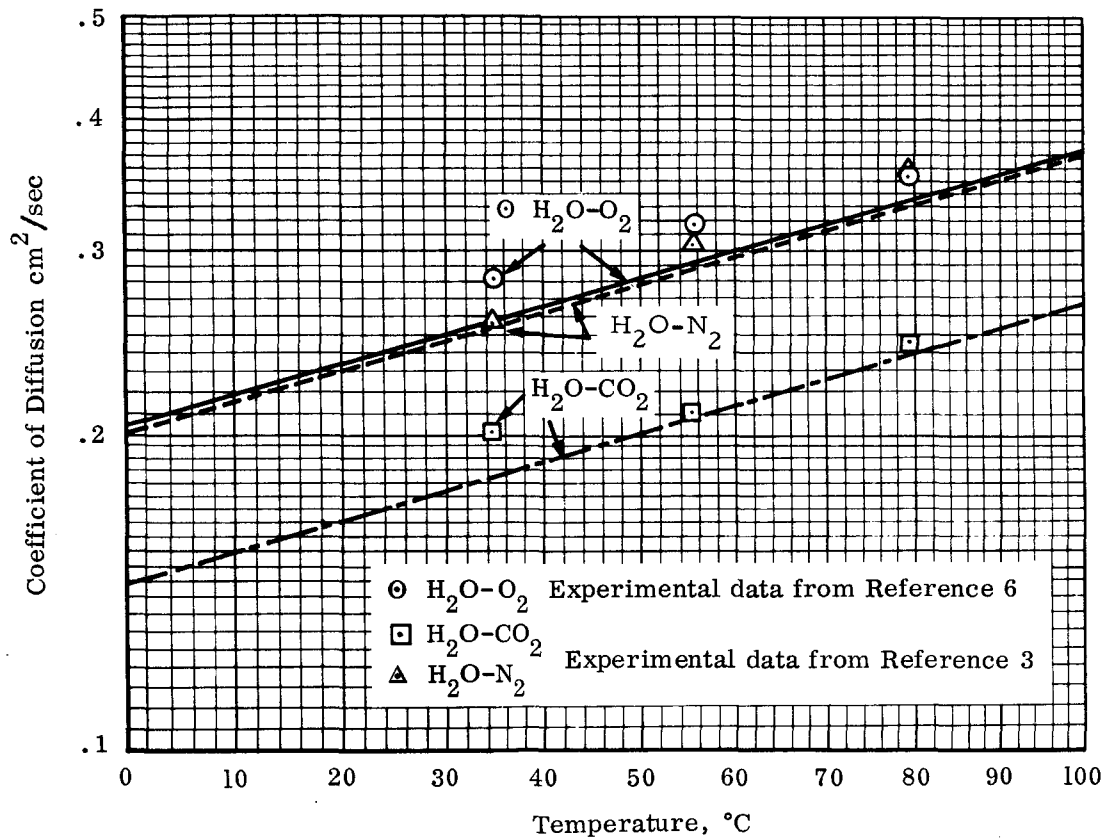


FIGURE A-1 BINARY DIFFUSION COEFFICIENTS AT 1.0 ATMOSPHERE ^a

^aCurves are computed from Collision Parameters (Reference 3)

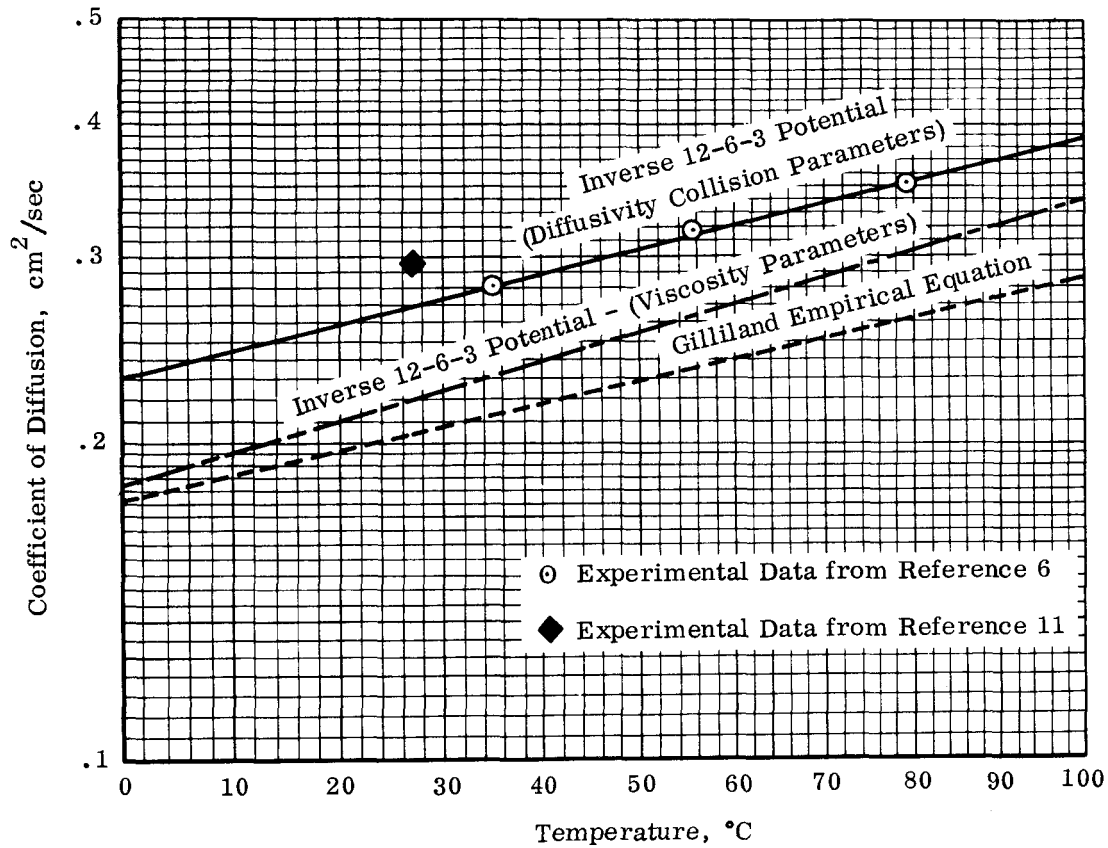


FIGURE A-2 MUTUAL DIFFUSION COEFFICIENT WATER VAPOR IN OXYGEN
ATMOSPHERIC PRESSURE

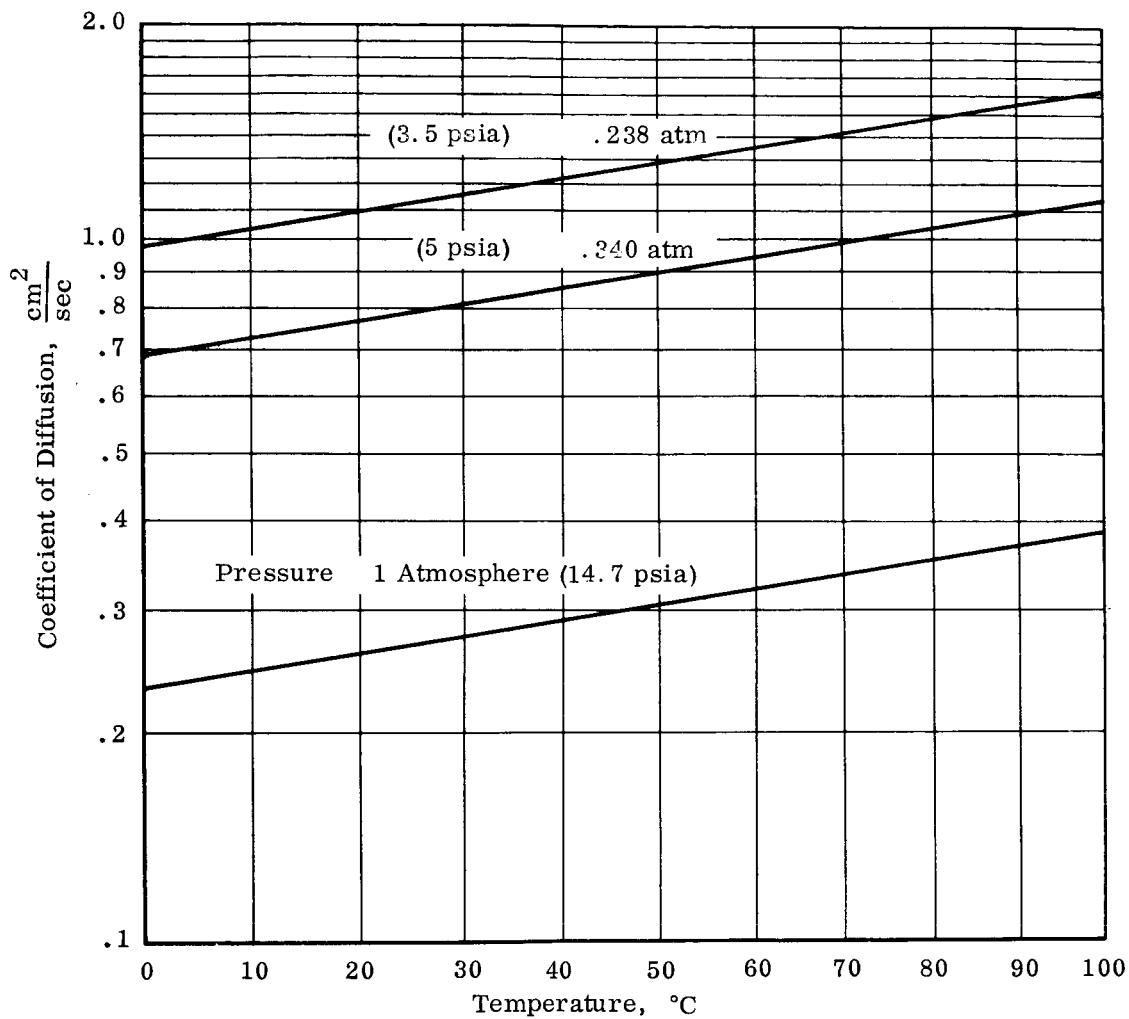


FIGURE A-3 EFFECT OF PRESSURE ON THE DIFFUSION COEFFICIENT FOR WATER IN OXYGEN^a

^aTheoretical calculation using Schwertz and Brow (Ref 6) and experimental data using the methods of Monchick and Mason (Ref 7, 16, 17, 18, 19, 20)

TABLE I

FORCE CONSTANT DATA USED IN THE CALCULATION OF DIFFUSION COEFFICIENTS^a

Constituent	H ₂ O	O ₂
Assumed Potential Function	Stockmayer	L. J. 12-6 Potential
Source of Experimental Data	2nd Virial Coefficients	Viscosity Measurements
Reference Temperature, $\frac{\epsilon}{K}$ (°K)	380°K	113.0°K
Molecular Diameter σ (Å)	2.65	3.433
Dipole Moment, μ (Debyes)	1.83	----
Polarizability	1.210	16.0

^aReference 3, Page 214, 1111.

TABLE II

WATER VAPOR-OXYGEN DIFFUSION COEFFICIENT

Temperature		Pressure		
°C	°F	1 Atm. (14.7 psia)	.340 Atm. (5 psia)	.238 Atm. (3.5 psia)
Diffusion Coefficient, cm ² /sec, D ₁₂				
0	32	.2321	.6824	0.9748
10	50	.2464	.7244	1.0349
20	68	.2610	.7673	1.0962
30	86	.2759	.8111	1.1588
40	104	.2912	.8561	1.2230
50	122	.3068	.9020	1.2886
60	140	.3227	.9487	1.3553

APPENDIX B

Analysis of Thermal Diffusion

The thermal diffusion coefficient was estimated using a hard elastic sphere model for the interaction potential of the water-oxygen molecules. The effects of composition were considered, assuming that the molecular diameter of water and oxygen corresponded to the density of the saturated liquid at the normal boiling point. The results of the computations using the collision terms of Chapman and Cowling are illustrated in Figure B-1, from the relation of Chapman and Cowling, given in Taylor and Glasstone Treatise on Physical Chemistry (Ref. 21), page 169.

$$K_T = \frac{D_T}{D_{12}} = x_o (1 - x_o)^5 (C' - 1) \left[\frac{S_o x_o - S_w (1 - x_o)}{q_o x_o^2 + q_w (1 - x_o)^2 + q_{ow} (1 - x_o) x_o} \right] \quad (B1)$$

where: K_T = Ratio of thermal diffusion coefficient to the binary diffusion coefficient

D_T = Thermal diffusion coefficient (cm²/sec)

D_{12} = Binary diffusion coefficient (cm²/sec)

x_o = Mole fraction O₂ = $\frac{C_o}{C_o + C_w}$

d_o = Molar diameter of O₂ = 4.41 Å

d_w = Molar diameter H₂O = 3.91 Å

d_{ow} = (1/2) (d_o + d_w)

m = Reduced mass = $\frac{M_o + M_w}{M_o M_w}$

Δ = $\frac{M_o - M_w}{M_o M_w}$

C' = Parameter which is 6/5 for hard sphere molecule

C_w = Molar concentration of water vapor

C_o = Molar concentration of oxygen gas

M_o, M_w = Molecular weights of O₂ and H₂O

$$S_o = \frac{4}{5} \frac{m}{\sqrt{2} (1-m)} \left(\frac{d_o}{d_{ow}} \right)^2 - (m - 1) \left(\frac{8}{5} m - 3\Delta \right) \quad (B2)$$

$$S_w = \frac{4}{5} \frac{1-m}{\sqrt{2m}} \left(\frac{d_w}{d_{ow}} \right)^2 - m \left(\frac{8}{5}m + 3\Delta \right) \quad (\text{B3})$$

$$q_o = \frac{24}{5} \frac{1}{\sqrt{2(1-m)}} \left(\frac{d_o}{d_{ow}} \right)^2 \left[1 - \frac{22}{15}m + \frac{9}{10}m^2 \right] \quad (\text{B4})$$

$$q_w = \frac{24}{5} \frac{1}{\sqrt{2m}} \left(\frac{d_w}{d_{ow}} \right)^2 \left[1 - \frac{22}{15}(1-m) + \frac{9}{10}(1-m)^2 \right] \quad (\text{B5})$$

$$q_{ow} = \frac{16}{25} \frac{1}{\sqrt{m(1-m)}} \frac{d_o^2 d_w^2}{d_{ow}^4} + \frac{344}{25} m(1-m) + \frac{39}{5} \Delta^2 \quad (\text{B6})$$

Figure B-1 also indicates the variation of K_T with mole fraction by a method using diffusivity collision parameters as presented in Reference 7. This figure can be used to determine the magnitude of thermal diffusion effects in the space suit.

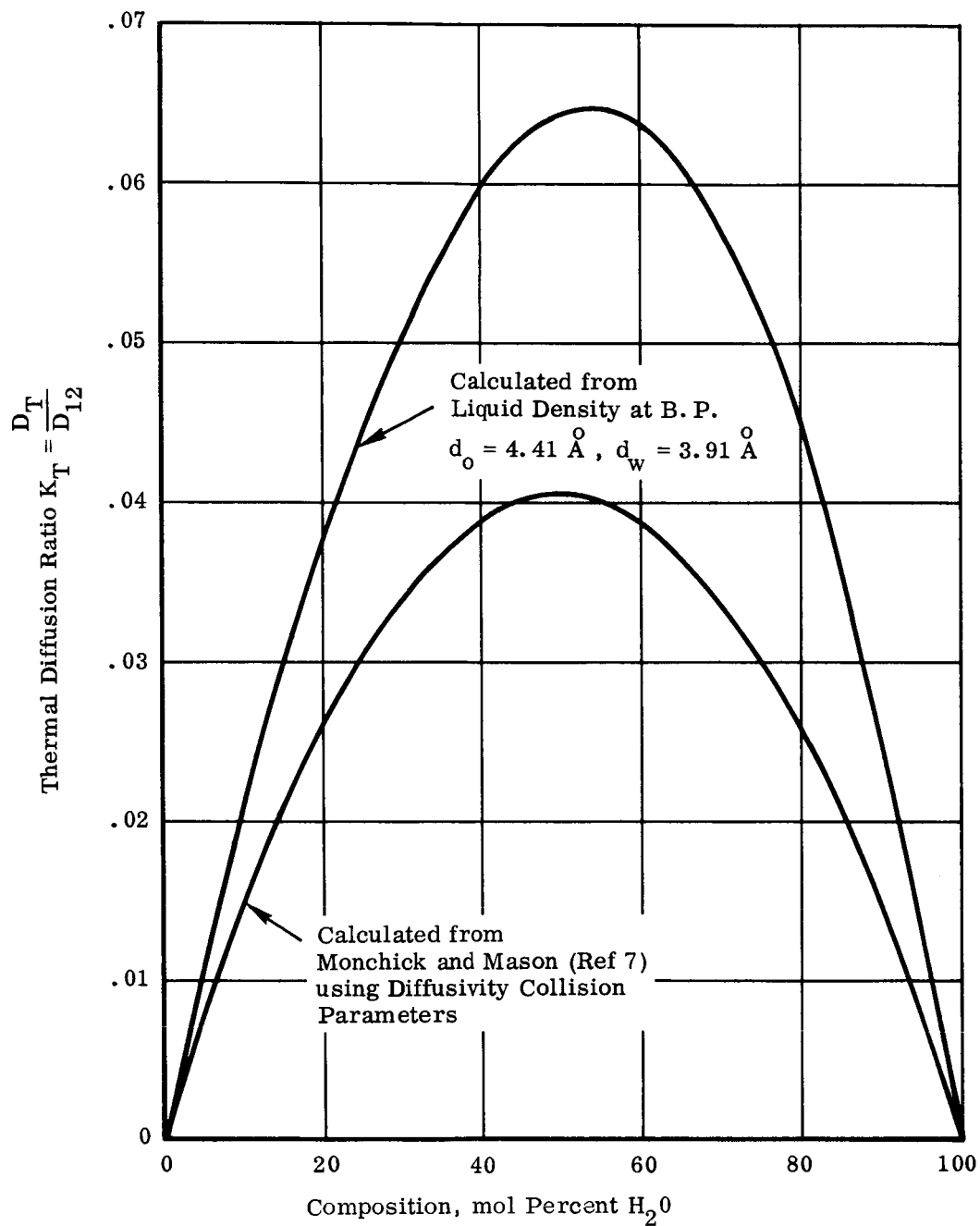


FIGURE B-1 THERMAL DIFFUSION RATIO FOR WATER VAPOR-OXYGEN MIXTURES

APPENDIX C

Mutual Diffusion in a Heterogeneous Media

A special condition exists where the diffusing gases encounter the adsorption bed or wick material of a water vapor removal device. The presence of the solid causes the molecules to collide with the pore walls of the solid and in effect reduces the counter diffusion of the two gaseous species. This effect is generally handled by substituting an effective diffusivity for the homogeneous diffusivity

$$D_{\text{eff}} = \phi D_{12}/g \quad (\text{C1})$$

where: ϕ = Pore volume fraction

g = A geometry factor

D_{eff} = Effective diffusivity (cm^2/sec)

D_{12} = Mutual coefficient of diffusion in a homogeneous phase (cm^2/sec)

The effective diffusivity in a porous media may be determined from statistical considerations. This technique was pioneered by A. Einstein in 1905 (Ref. 64) when he did his classical work on Brownian movement. As a direct result of this work, the effective diffusivity in porous media consisting of uniform spheres was estimated:

$$D_{\text{eff}} = D_{12} \phi \left[1 - \frac{1}{2} (1-\phi) \right] \quad (\text{C2})$$

Subsequent studies have extended this analysis to other shapes, particularly in the case of viscous flow through porous solids. These theories require the particles to be independent of each other. That is, the flow through the media is only affected by those particles in the immediate vicinity. The result is that the analyses are strictly valid only for very large mean free paths. Stephen Prager (Ref. 65) at the University of Minnesota has considered diffusion and viscous flow from the point of view of a single point, two point and three point correlation functions in conjunction with the principle of minimum entropy production. He concludes that the coefficient of diffusivity in a porous media is less than any upper bound established under the conditions where entropy production is minimized as expressed by

$$D_{\text{eff}} \leq D_{12} \phi \left[1 - \frac{1}{3} (1-\phi) \right] \quad (\text{C3})$$

The principle of minimum entropy production states that the steady state of a system in which an irreversible process is occurring is the state for which the rate of entropy production has a minimum value consistent with the constraints which prevent the state from reaching equilibrium. Martin Klein (Ref. 66) in a note to the International Symposium on Transport Processes in Statistical Mechanics has pointed out the validity of this principle even under conditions far removed from equilibrium. The validity of the principle of minimum entropy production along with the comparison with the equation for uniform spheres,

indicates that for a random pore size and shape the effective diffusivity of Prager will be approached. Where a desiccant or wick has a regular structure such as uniform spheres, the effective diffusivity is lowered slightly and should be estimated for the particular structure. A complete discussion of the principle of minimum entropy production is in Chapter 6 of the Prigogine's book on irreversible thermodynamics (Ref. 67).

APPENDIX D

Analysis of Mass Transfer Within an Adsorption Bed

A review of techniques which describe the equilibrium characteristics of desiccants has been made. An article by J. W. Carter (Reference 67) describes the more recent advances in analysis of adsorption processes. Other short articles describe the basic mass transfer considerations required for the design of adsorption beds (Reference 68, 69). This Appendix derives expressions in parametric form that may be used to design a desiccant bed of the type used for the passive moisture control in a space suit.

The water vapor adsorption rate will depend upon the resistance encountered by the water vapor as it passes through the gas in the pores of the adsorbent bed and on the kinetics of the adsorption process. A quasi equilibrium condition exists between water vapor and water adsorbed by the desiccant, which is represented by the equation,

$$C_w = E C^*{}^\eta \quad \text{(Reference 68)} \quad (D1)$$

where: C_w = Molar concentration of water vapor in gas mixture $\left(\frac{\text{mols}}{\text{cm}^3}\right)$

E = Equilibrium constant

C^* = Molar concentration of water adsorbed at any point on bed $\left(\frac{\text{mols}}{\text{cm}^3}\right)$

η = Empirical exponent

Since much of the data (Reference 10) on common desiccants such as silica gel relates the relative humidity $\frac{C_w}{(C_w)_{\text{sat}}}$ to the percent of water adsorbed on a dry basis, the foregoing relationship may be fitted to empirical data to yield

$$E = \left(\frac{C_w}{(C_w)_{\text{sat}}}\right) \left(\frac{18}{\rho_E \frac{w}{100}}\right) (C_w)_{\text{sat}} \quad (D2)$$

where: ρ_E = Bulk density of adsorber (gms/cm³)

w = Weight of water vapor that can be adsorbed in a 100 gms of dry adsorber

The desiccant bed in the space suit may be assumed to be a flat plate of desiccant with gases entering at one side and without forced flow. Adequate cooling to remove the heat of adsorption will be assumed and the bed is considered isothermal. As the first molecules of water vapor contact the surface of the bed they are adsorbed. Eventually the inlet positions of the bed become saturated and the water vapor must diffuse deeper into the bed. The rate of removal of water vapor becomes limited by the path length through which the water vapor must diffuse. This will limit the effective depth of the adsorbent bed. The rate of removal of water vapor is a function of the degree of saturation of the desiccant bed.

The water vapor balance on a molar basis equates the change in concentration with time and the change in flux through an infinitesimal element of path to the quantity adsorbed or condensed. The total concentration of the gas-vapor mixture (C), in moles per cubic cm is assumed constant. The equation of change of water vapor concentration in one direction is derived as in Reference 2.

$$\frac{\partial x}{\partial t} + \frac{\partial (x U_w)}{\partial \xi} = \frac{\dot{W}}{C M_w} \quad (D3)$$

where: C = Concentration of gas (mol/cm³)

x = Mole fraction water vapor in gas = $\frac{C_w}{C}$ (dimensionless)

U_w = Velocity of water vapor relative to bed

Ẇ = Weight rate of removal of water vapor by adsorption or condensation for each cm³ of bed

M_w = Molecular weight of water vapor (18 gms/mol)

ξ = Distance along flow line (cm)

Since the oxygen is assumed to be neither adsorbed nor condensed and since the molar concentration is constant, the oxygen balance may be determined in terms of mol fraction water vapor. The equation of change for oxygen concentration is:

$$\frac{\partial (1-x)}{\partial t} + \frac{\partial ((1-x) U_o)}{\partial \xi} = 0 \quad (D4)$$

where: U_o = Velocity of oxygen relative to bed

The relative velocity between the water vapor and the oxygen may be determined from Fick's first law

$$x (U_w - \bar{U}) = -D_{\text{eff}} \frac{\partial x}{\partial \xi} \quad (D5)$$

$$(1-x) (U_o - \bar{U}) = +D_{\text{eff}} \frac{\partial x}{\partial \xi} \quad (D6)$$

where: \bar{U} = Mean molar velocity = U_wx + U_o(1-x)

D_{eff} = Effective binary diffusion coefficient

We will express Fick's law in an alternate form, by substituting the definition of mean molar velocity

$$U_w - U_o = -\frac{D_{\text{eff}}}{(1-x)x} \frac{\partial x}{\partial \xi} \quad (\text{D7})$$

The adsorption isotherm describes the concentration in the vapor phase as a function of the amount of water adsorbed onto the surface. The adsorption isotherm determines the weight percentage of water vapor that can be adsorbed. The rate of adsorption of water vapor by the desiccant is dependent on the weight percentage of water adsorbed in the desiccant bed.

$$-\frac{\partial C^*}{\partial t} = -\frac{1}{\eta} \left(\frac{C}{E}\right)^{\frac{1}{\eta}} x^{\frac{1-\eta}{\eta}} \frac{\partial x}{\partial t} = \frac{\dot{W}}{M_w} \quad (\text{D8})$$

Substitution into the water balance relationship D3 yields,

$$x \frac{\partial U_w}{\partial \xi} + U_w \frac{\partial x}{\partial \xi} = - \left(1 + \frac{(Cx)}{\eta E} \frac{1-\eta}{\eta} \frac{\partial x}{\partial t} \right) \quad (\text{D9})$$

The equation describing the oxygen balance (D4) will relate concentration to the velocity and change in velocity

$$(1-x) \frac{\partial U_o}{\partial \xi} - U_o \frac{\partial x}{\partial \xi} = \frac{\partial x}{\partial t} \quad (\text{D10})$$

From the diffusion equation (D7) it is possible to express U_o and $\frac{\partial U_o}{\partial \xi}$ in terms of U_w and $\frac{\partial U_w}{\partial \xi}$. Substitution into the oxygen balance yields a second form for the oxygen balance

$$(1-x) \frac{\partial U_w}{\partial \xi} - U_w \frac{\partial x}{\partial \xi} = \frac{\partial x}{\partial t} + \frac{D_{\text{eff}}}{x^2} \left(\frac{\partial x}{\partial \xi}\right)^2 - \frac{D_{\text{eff}}}{x} \frac{\partial^2 x}{\partial \xi^2} \quad (\text{D11})$$

Equations (D9) and (D11) may be solved simultaneously to obtain U_w and $\frac{\partial U_w}{\partial \xi}$

$$\frac{\partial U_w}{\partial \xi} = \frac{D_{\text{eff}}}{x^2} \left(\frac{\partial x}{\partial \xi}\right)^2 - \frac{D_{\text{eff}}}{x} \frac{\partial^2 x}{\partial \xi^2} - \frac{(Cx)}{\eta E} \frac{1-\eta}{\eta} \frac{\partial x}{\partial t} \quad (\text{D12})$$

$$U_w = \frac{\frac{\partial^2 x}{\partial \xi^2} - \frac{D_{\text{eff}}}{x} \left(\frac{\partial x}{\partial \xi}\right)^2 - \left(1 + (1-x) \frac{(Cx)}{\eta E} \frac{1-\eta}{\eta}\right) \frac{\partial x}{\partial t}}{\frac{\partial x}{\partial \xi}} \quad (\text{D13})$$

In this form, the equations cannot be solved explicitly. However, they may be solved by numerical methods.

Two assumptions may be made to simplify the differential equation. The concentration of water vapor will always be much less than unity. The oxygen molecules are assumed to be stationary relative to the adsorption bed. Then from the diffusion law (equation D7 with $U_o = 0$ and $(1-x) \rightarrow 1$)

$$U_w = - \frac{D_{\text{eff}}}{x} \frac{\partial x}{\partial \xi} \quad (\text{D14})$$

Differentiating (C14) with respect to ξ ,

$$\frac{\partial U_w}{\partial \xi} = - \frac{D_{\text{eff}}}{x} \frac{\partial^2 x}{\partial \xi^2} + \frac{D_{\text{eff}}}{x^2} \left(\frac{\partial x}{\partial \xi} \right)^2 \quad (\text{D15})$$

Substitution of (D14) and (D15) into Equation (D-12) yields an expression which states that the product

$$\frac{(Cx)^{(1-\eta)}}{\eta E^{1/\eta}} \left(\frac{\partial x}{\partial t} \right) = 0 \quad .$$

Since the exponent η is very nearly unity for most common desiccants (Ref. 65), $\frac{\partial x}{\partial t}$ is zero and Equation (D-13) may be solved by the substitution of (D14) for U_w and conclude that:

$$D_{\text{eff}} \frac{\partial^2 x}{\partial \xi^2} = 0 \quad . \quad (\text{D-16})$$

This is Ficks second law of diffusion for the trivial case where adsorption has stopped. If we assume that $\frac{\partial x}{\partial t} \neq 0$, we may arrive at an approximate solution. As x approaches zero, the value U_o approaches zero. Substituting

$$U_w = - \frac{D_{\text{eff}}}{x} \frac{\partial x}{\partial \xi}$$

into Equation (D13), we get the following differential equation

$$\left[\frac{D_{\text{eff}}}{1 + \frac{(Cx)^{(1-\eta)}/\eta}{\eta E^{1/\eta}}} \right] \frac{\partial^2 x}{\partial \xi^2} = \frac{\partial x}{\partial t} = \alpha_D \frac{\partial^2 x}{\partial \xi^2} \quad (\text{D17})$$

$$\text{where for } \left. \begin{array}{l} \eta = 1 \\ \alpha_D = E x D_{\text{eff}} / (1 + E) \end{array} \right\} \quad (\text{D18})$$

It is assumed that the adsorber has a random pore distribution as discussed in Appendix C. Substituting for D_{eff} from equation (C3) in Appendix C, yields

$$\alpha_D = \left\{ D_{12} \phi \left[1 - (1/3)(1-\phi) \right] E \right\} / (1+E) \quad (\text{D19})$$

The solution to (D17) becomes relatively simple if we assume that the adsorbent bed is a flat plate of finite thickness L with the following boundary conditions. Initially the concentration of water vapor inside the bed is assumed at $x = 0$. The boundary concentration is assumed as x_1 , and the bed is assumed to have a concentration gradient of $\frac{\partial x}{\partial \xi} = 0$ on the back face. A convenient method of solution is to assume two beds, back to back, of total thickness $2L$. The vapor concentration is assumed equal and constant on both sides.

The boundary conditions become

$$\left. \begin{aligned} x(\xi, 0) &= 0 & x(0, t) &= x_1(t) \\ \frac{\partial x}{\partial \xi}(\xi, 0) &= 0 & x(2L, t) &= x_1(t) \end{aligned} \right\} \quad (\text{D20})$$

Transforming the dependent variable by letting

$$v = x - x_1 \quad (\text{D21})$$

equation (D17) then becomes

$$\frac{\partial v}{\partial t} = \alpha_D \frac{\partial^2 v}{\partial \xi^2} \quad (\text{D22})$$

with boundary conditions

$$\left. \begin{aligned} v(\xi, 0) &= -x_1 & v(0, t) &= 0 \\ \frac{\partial v}{\partial \xi}(\xi, 0) &= 0 & v(2L, t) &= 0 \end{aligned} \right\} \quad (\text{D23})$$

The solution to (D20) may be expressed as a sine series

$$v = \sum_{n=1}^{\infty} A_n e^{-\frac{n^2 \pi^2 \alpha_D t}{4L^2}} \sin \frac{n\pi\xi}{2L} \quad (\text{D24})$$

The coefficients A_n may be determined from the initial condition

$$v(\xi, 0) = -x_1 \quad (\text{D25})$$

$$v(\xi, 0) = \sum_{n=1}^{\infty} A_n \sin \frac{n\pi\xi}{2L}$$

Multiply both sides by $\sin \frac{n\pi\xi}{2L}$ and integrate from 0 to $2L$.

Then

$$\sum_{n=1}^{\infty} \left(- \sum \int_0^{2L} x_1 \sin \frac{n\pi\xi}{2L} d\xi \right) = \sum_{n=1}^{\infty} \int_0^{2L} A_n \sin^2 \frac{n\pi\xi}{2L} d\xi \quad (D26)$$

and

$$A_n = -x_1 \frac{4}{n\pi} \quad (n \text{ odd}) \quad A_n = 0 \quad (n \text{ even}) \quad (D27)$$

also

$$v = x - x_1 = -x_1 \sum_{n=1, 3, 5, \dots} \frac{4}{\pi} \left(\frac{e^{-n^2\pi^2\alpha_D t}}{4L^2} \sin \frac{n\pi\xi}{2L} \right) \quad (D28)$$

Expanding the sum

$$\frac{x_1 - x}{x_1} = \frac{4}{\pi} \left(e^{-\Theta\pi^2} \sin \frac{\pi\xi}{2L} + e^{-9\pi^2\Theta} \sin \frac{3\pi\xi}{2L} + \dots + e^{-n^2\pi^2\Theta} \sin \frac{n\pi\xi}{2L} \right)_{n, \text{ odd}} \quad (D29)$$

where: x = Mol fraction of water vapor in gas phase (mol/cm^3) in the bed

x_1 = Mol fraction water vapor in gas phase at bed surface (mol/cm^3)

ξ = Distance into bed (depth) cm

L = Total depth of bed

t = Time

α_D = Bed diffusivity = $\left\{ D_{12} \phi \left[1 - \frac{1}{3} (1 - \phi) \right] E \right\} / (1 + E)$

Θ = Time parameter = $\frac{\alpha_D t}{4L^2}$

ϕ = Bed porosity

E = Equilibrium constant

n = Integer 1 to ∞

At the surface of the bed the water vapor adsorption rate is determined by differentiating equation (D29) with respect to ξ and substituting this gradient into the diffusion equation.

$$J_w = \frac{C_w D_{12} \theta \left[1 - \frac{1}{3} (1 - \phi) \right] \left(\frac{\partial x}{\partial \xi} \right)_{\xi=0}}{(1-x)_{\xi=0}}$$

$$= \frac{C_w D_{12} \phi \left[1 - \frac{1}{3} (1 - \phi) \right]}{(1-x)_{\xi=0}} \frac{2}{L} \left(e^{-\pi^2 \theta} + e^{-9\pi^2 \theta} + \dots + e^{-n^2 \pi^2 \theta} + \dots \right) \quad (D30)$$

In nondimensional form we may define

$$F = \frac{J_w (1-x)_{\xi=0} L}{C_w D_{12} \phi \left[1 - \frac{1}{3} (1 - \phi) \right]} = 2 \left[\sum_1^{\infty} e^{-n^2 \pi^2 \theta} \right], \quad (n = 1, 3, 5 \dots) \quad (D31)$$

where: J_w = Water removal rate per square cm of desiccant bed ($\text{mol}/\text{cm}^2 \text{sec}$)

F = Water removal rate parameter

C_w = Concentration of water vapor (mol/cm^3)

L = Bed length (cm)

In Figure D-1 and D-3, F is plotted as a function of θ . Thus we may determine the water removal rate at which the operation of the bed becomes marginal and thus determine when regeneration is required.

An adsorption efficiency parameter (Q) may be determined by integrating the flow rate into the desiccant bed. This may be expressed in terms of a bed efficiency since it is identical with the average number of moles per unit volume of bed divided by the maximum number of moles per unit volume that can be adsorbed under the conditions determined by the relative humidity of the surroundings.

$$\bar{C}^* L = \int_0^t J_w dt = \frac{C_w D_{12} \phi \left[1 - \frac{1}{3} (1 - \phi) \right] L}{\alpha_D} \left[1 - \frac{8}{\pi^2} \left(e^{-\pi^2 \theta} + \frac{e^{-9\pi^2 \theta}}{9} + \dots + \frac{e^{-n^2 \pi^2 \theta}}{n^2} \right) \right] \quad (D32)$$

$$Q = \frac{\bar{C}^* E}{C_w (1 + E)} = \frac{8}{\pi^2} \left[\frac{\pi^2}{8} - \left(e^{-\pi^2 \theta} + \frac{e^{-9\pi^2 \theta}}{9} + \dots + \frac{e^{-n^2 \pi^2 \theta}}{n^2} + \dots \right) \right] \quad (D33)$$

where: Q = Adsorption efficiency parameter (dimensionless)
 \bar{C}^* = Average concentration of water vapor on the entire desiccant bed
(mol/cm³ of bed)
 C_w = Water vapor concentration at surface bed (mols/cm³)

The adsorption efficiency parameter was computed as a function of the time parameter (θ) and plotted in Figure D2 and D3. Computed values of the flux parameter (F) are illustrated in Figure D1 and D3. Given performance requirements and the properties of the adsorber so that the flux parameter (F) and the equilibrium constant (E) can be calculated, the adsorption bed can be designed using Figures D1, D2 or D3.

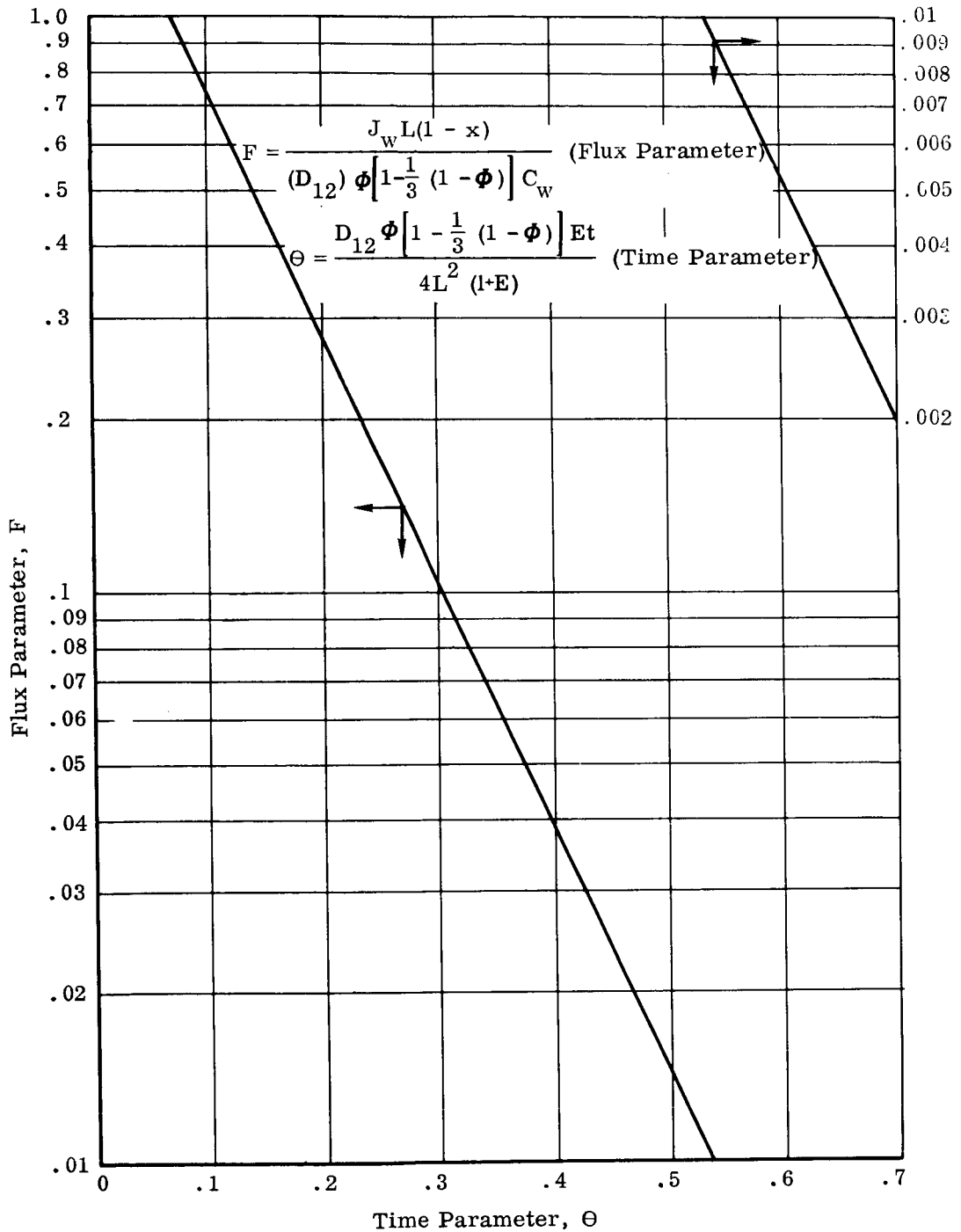


FIGURE D-1 ADSORPTION BED FLUX vs. TIME PARAMETER

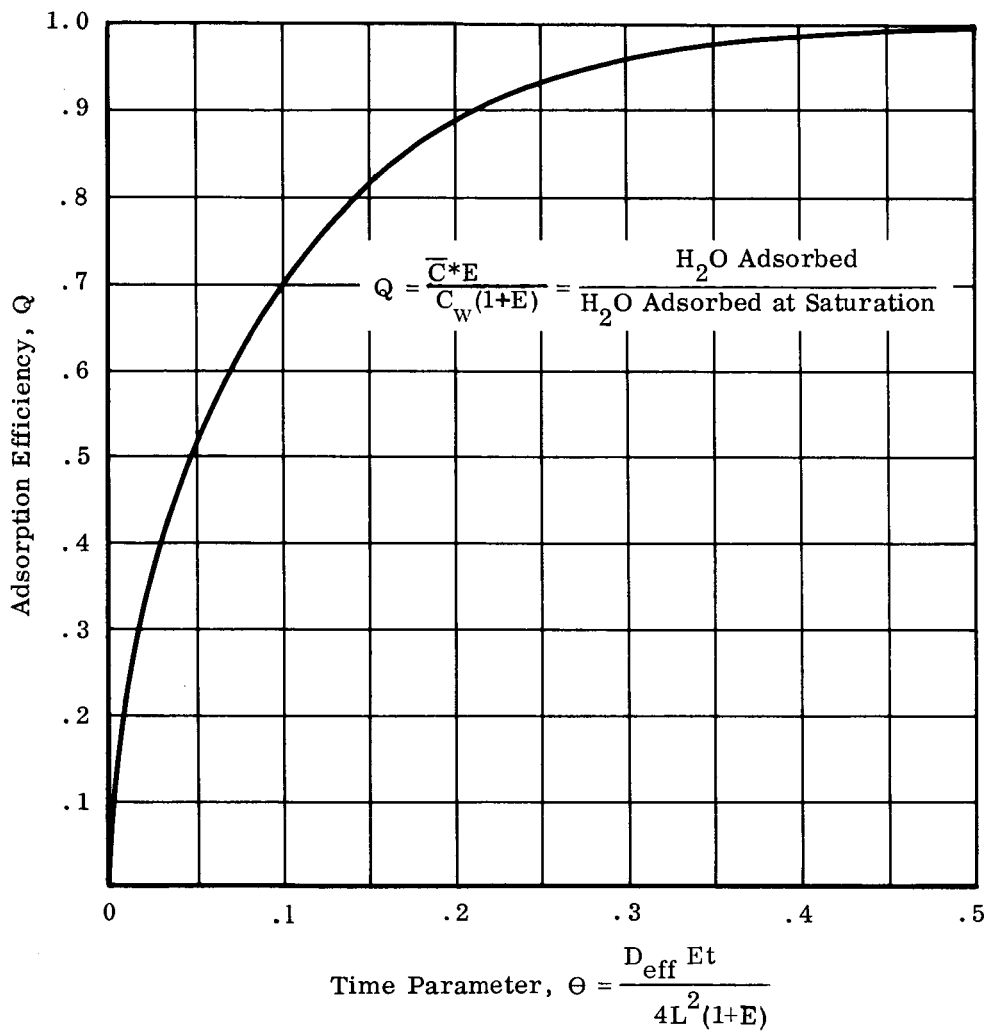


FIGURE D-2 ADSORPTION EFFICIENCY vs. TIME PARAMETER

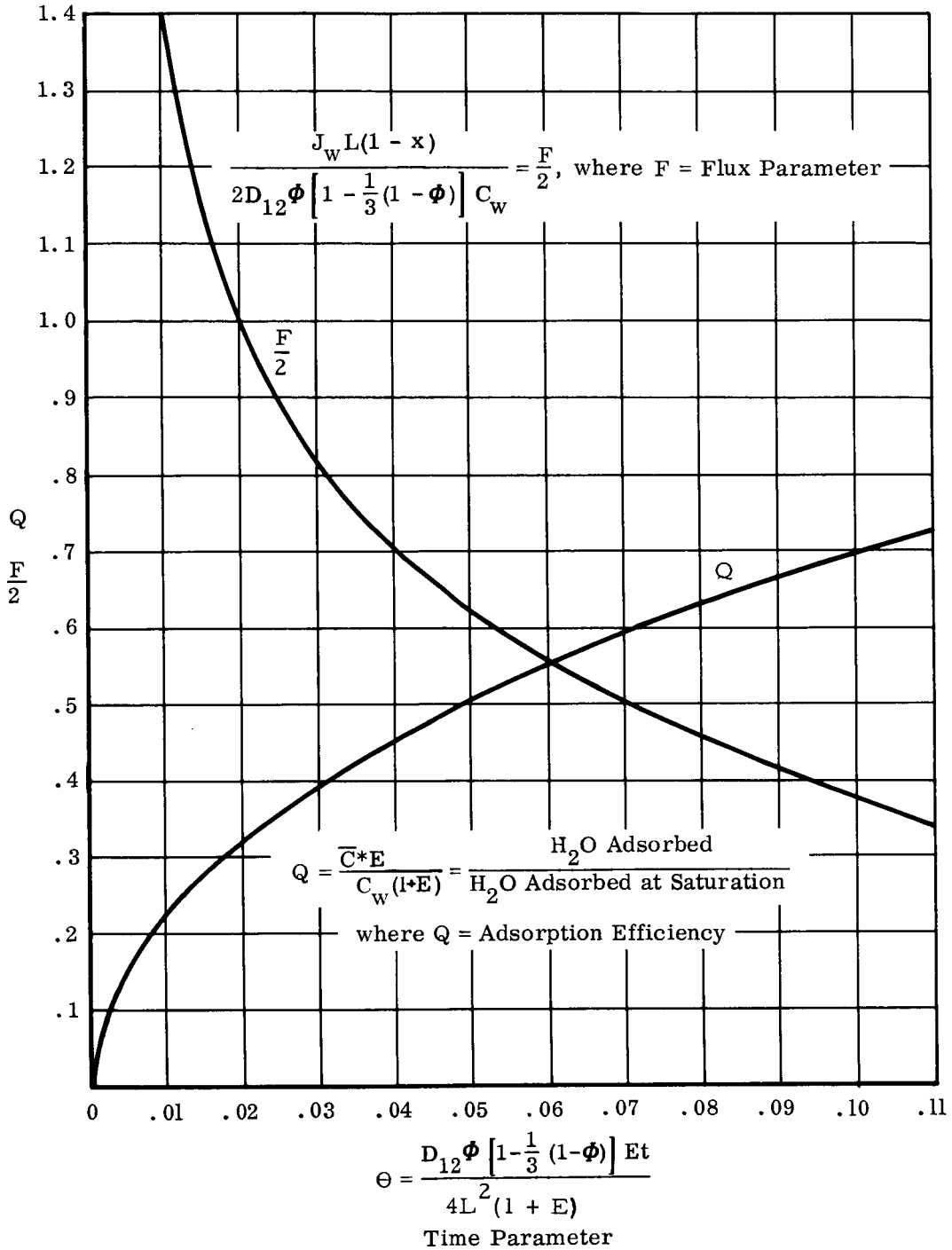


FIGURE D-3 ADSORPTION BED PERFORMANCE PARAMETERS

APPENDIX E

Analysis of Condensation and Mass Transfer Within a Porous Wick

The water vapor given off by the astronaut must diffuse through the space between the skin and the surface of a porous wick or desiccant. The water vapor must then diffuse through the passages in the porous wick to cool areas, where condensation may occur. The condensation rate is controlled by the gas kinetics at the surface. The liquid water must then be removed physically by flow through the porous passages to an area where it may be stored or dumped. This appendix describes the condensation on the wick surface and diffusion to areas where condensation may occur. It is assumed that the liquid phase water is removed immediately following condensation.

The condensation phenomenon depends upon the kinetics of water vapor molecules near the gas liquid surface. In the appendix of Lype's article on "Kinetic Theory of Evaporation of Liquids" (Ref. 71) the flux of molecules hitting the surface is derived. For cases where the mean free path is small compared to the product of $\alpha_v \tau$, he derived the following approximation:

$$Z = \frac{N_v \alpha_v}{2\sqrt{\pi}} \tau \sigma \quad (E1)$$

where Z = number of molecules hitting the surface σ in time τ

N_v = number of molecules of condensible in unit volume of gas phase

α_v = most probable molecular velocity

In order to account for the dilution effect of the oxygen gas in the wick, the equation (E1) is expressed in terms of P by substituting $N_v = \frac{P}{hT}$ for an ideal gas obeying Henry's law.

Then

$$J_i = \frac{Z}{\sigma \tau} = \frac{P}{\sqrt{2\pi M R T}} \quad (E2)$$

where P = Water vapor partial pressure just above the liquid vapor interface (dynes/cm²)

J_i = Flux at liquid-vapor interface (mols/cm²sec)

M = Molecular weight of water vapor (gms/mole)

\bar{R} = Universal gas constant (ergs/mole^oK)

T = Temperature of gas above the vapor interface (^oK)

If we assume local equilibrium at the gas liquid interface, the number of molecules entering the surface is exactly balanced by the number of molecules leaving. Under steady state conditions the number of molecules entering the vapor space is a function of the temperature of the interface and if it is assumed that the temperature of the gas and liquid at the interface are the same, the net condensation rate in moles of vapor per unit of surface area may be determined from the following equation

$$J_i = \frac{P_i - P_{sat}}{\sqrt{2\pi M \bar{R} T_i}} \quad (\text{ideal}) \quad (\text{E3})$$

where: P_{sat} = Saturated water vapor pressure at the interface temperature (dynes/cm²)

P_i = water vapor partial pressure at the liquid-vapor interface (dynes/cm²)

T_i = temperature of liquid at the vapor-liquid interface (°K)

Actual condensation rates are roughly one order of magnitude less than the predicted value. A proportionality constant, α , may be used to indicate true condensation rate.

$$J_i = \frac{\alpha(P_i - P_{sat})}{\sqrt{2\pi M \bar{R} T_i}} \quad (\text{actual}) \quad (\text{E4})$$

A possible phenomena which may account for small values of α such as in water has been discussed by Lype (Ref 71). The explanation is based upon the Polanyi-Wigner theory of sublimation. He hypothesized that water was a 'pseudo crystalline' liquid where condensation occurred only in holes left on the surface by evaporation. If considerable care is utilized in making measurements, it is possible to determine that for certain substances, (for example glycerol) the proportionality constant α may be correlated with the ratio of partition functions for rotation in the liquid and in the gas. Heidiger and Boudart (Ref. 72) describe a method of measuring α directly.

If condensation phenomena can be explained on the basis of a pseudo crystalline solid, α takes the form of a probability that condensation will occur for a molecule hitting the surface. According to Lype, α is the ratio of the area of holes at the surface divided by total surface area. In weight units, the rate of condensation may be estimated from the following equation of Lype from Reference 71:

$$G = \frac{\sqrt{\bar{R}}}{\sqrt{2\pi}} \left[\sqrt{\frac{T'}{v'}} - \sqrt{\frac{T''}{v''}} \right] e^{-\frac{\Delta U'}{2RT}} \quad (\text{E5})$$

where: G = Mass of condensation per unit area time (gms/cm²sec)

$R = \frac{\bar{R}}{M}$ = Gas constant per unit weight for condensate $\left(\frac{\text{ergs}}{\text{gm}^\circ\text{K}}\right)$

M = Molecular weight of liquid and vapor (gms/mol)

- T' = Temperature of vapor ($^{\circ}\text{K}$)
 v' = Volume of unit mass of saturated vapor at T' (cm^3/gm)
 T'' = Temperature of sub-cooled liquid ($^{\circ}\text{K}$)
 v'' = Volume of saturated vapor at temperature T'' (cm^3/gm)
 $\Delta U'$ = Internal energy of evaporation per unit mass $\left(\frac{\text{ergs}}{\text{gm}}\right)$

For the condensation of water vapor the relationship derived by Lype from pure kinetics is valid. Water may be shown to have an ordered structure as a result of its x-ray diffraction pattern. Furthermore, water is strongly polar and will associate itself in complex molecules. The experiments of Dergarabedian (Ref. 73) on the rate of bubble growth correlate with rates predicted by Lype's relation. As Lype points out, these factors indicate the validity of this equation.

In its application to a space suit, the relationship of Lype must be modified to account for the dilution effect of oxygen in the vapor phase. Furthermore, condensation occurs on the wick, under conditions where gas temperature is greater than the dew point and the partial pressure of water vapor in the gas phase is greater than the vapor pressure of water at the liquid interface. The partial pressure of water vapor in the gas phase, P_w , may be substituted for the term $\frac{RT'}{v'}$. Substituting in Equation (E5), Lype's relationship becomes

$$G = \frac{(P_w - P_{\text{sat}})}{\sqrt{2\pi RT}} e^{-\frac{\Delta U'}{2RT}} \quad (\text{E6})$$

If the effective surface area per unit volume of the wick material is S , then the condensation rate for a unit volume of wick becomes

$$r_c = \frac{SP \left(x - \frac{P_{\text{sat}}}{P}\right) e^{-\frac{\Delta U'}{2RT}}}{\sqrt{2\pi RT}} \quad (\text{E7})$$

where: S = Surface area per unit volume (cm^2/cm^3)

r_c = Rate of condensation $\left(\frac{\text{gms H}_2\text{O}}{\text{cm}^3 \text{ sec}}\right)$

P = Total pressure $\left(\frac{\text{dynes}}{\text{cm}^2}\right)$

P_{sat} = Pressure of saturated water vapor at T (dynes/cm^2)

T = Wick temperature ($^{\circ}\text{K}$)

The mass transfer rate within the porous wick may be determined from a knowledge of the driving forces and resistances encountered by the water vapor as it passes through the wick and is removed by condensation on the surface of the wick. In order to simplify our solution, it is assumed that the wick is made from a porous material of sufficient conductivity so that the temperature is constant. The condensation rate is proportional to the difference between partial pressure of the water vapor and the saturated vapor pressure at the wick temperature according to Equations (E1) through (E7). The binary diffusion coefficient is assumed to be corrected for the porosity (see Appendix D). The flow of water vapor through the stagnant oxygen atmosphere is assumed to be unidirectional.

If we consider a small increment for length $\Delta\xi$ along the diffusion path, and assume the oxygen is stagnant, a water vapor mass balance on a molar basis will yield the following partial differential equation, which is a form of Ficks second law (Ref 2):

$$r_c' (x) = \frac{C D_{\text{eff}}}{(1-x)^2} \left[\left(\frac{\partial x}{\partial \xi} \right)^2 + (1-x) \frac{\partial^2 x}{\partial \xi^2} \right] \quad (\text{E8})$$

where: D_{eff} = Binary diffusion coefficient corrected for bed porosity (cm^3/sec)

ξ = Length along flow line relative to the wick outer surface (cm)

C = Concentration of gas (mols per unit volume of wick)

$r_c' = \frac{r_c}{M}$ = Rate of condensation of water vapor (moles per second per cm^3)

For the steady state case where the rate of condensation is a function only of the partial pressure and position below the wick surface the differential equation becomes:

$$\left(\frac{dx}{d\xi} \right)^2 + (1-x) \frac{d^2 x}{d\xi^2} = r_c' (x) \frac{(1-x)^2}{C D_{\text{eff}}} \quad (\text{E9})$$

From equation (E7), the rate of condensation may be expressed in terms of partial pressures or for ideal solutions in terms of mole fractions in the vapor phase.

$$r_c' = \frac{r_c(x)}{M} = \frac{S P \left(x - \frac{P_{\text{sat}}}{P} \right) e^{-\frac{\Delta U'}{2RT}}}{M \sqrt{2\pi RT}} \quad (\text{E10})$$

$$r_c' = A (x - B) \quad (\text{E10a})$$

where:

$$A = \frac{S P e^{-\frac{\Delta U'}{2RT}}}{M\sqrt{2\pi RT}}$$

$$B = \frac{P_{sat}}{P}$$

Substituting into the differential equation,

$$\left(\frac{dx}{d\xi}\right)^2 + (1-x) \frac{d^2x}{d\xi^2} = C_0 + C_1x + C_2x^2 + C_3x^3 \quad (E11)$$

$$\text{where: } C_0 = -\frac{AB}{CD_{eff}} \quad (E12)$$

$$C_1 = \frac{A(2B+1)}{CD_{eff}} \quad (E13)$$

$$C_2 = \frac{A(2+B)}{CD_{eff}} \quad (E14)$$

$$C_3 = \frac{A}{CD_{eff}} \quad (E15)$$

The solution to the differential equation may be obtained by expansion in an infinite series in the region of the surface of the wick in the direction of diffusion of the water vapor since there are no singularities. The solution as a function of ξ has the form:

$$x = a_0 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \dots + a_n\xi^n \quad (E16)$$

After solving for a_0 and a_1 from the initial conditions at the surface of the wick the terms a_2, \dots, a_n may be determined by substituting into the differential equation and solving for successive coefficients in terms of the preceding ones.

The first coefficient a_0 is determined from the initial mole fraction of water vapor at the surface of the wick, x_0 . The second coefficient a_1 is determined from the water removal flux from the space suit by the wick, J_w .

$$a_1 = -\frac{(1-x_0)}{CD_{eff}} J_w \quad (E17)$$

The third coefficient is determined in terms of a_0 and a_1 by equating the coefficients of the zero order terms after substituting into the differential equation.

$$a_2 = \frac{C_0 + C_1 a_0 + C_2 a_0^2 + C_3 a_0^3 - a_1^2}{2(1-a_0)} \quad (E18)$$

Similarly for the first order terms in ξ

$$a_3 = \frac{C_1 a_1 + C_2 \cdot 2a_1 a_0 + C_3 (3a_0^2 a_1) - 2a_1 a_2}{2 \cdot 3 (1-a_0)} \quad (E19)$$

In general

$$a_{n+2} = \frac{C_1 a_n + C_2 \sum_{i=0}^n a_i a_{n-1} + C_3 \sum_{i=0}^n a_i \left(\sum_{k=0}^{n-i} a_k a_{n-2-k} \right)}{(n+1)(n+2)(1-a_0)} \quad (E20)$$

$$+ \frac{- \sum_{i=0}^n (1-i)a_{1+i} (n+1-i)a_{n+1-i} - \sum_{i=1}^n (n+1-i)(n+2-i)a_i a_{n+2-i}}{(n+1)(n+2)(1-a_0)}$$

These equations cannot be solved explicitly. They could be solved by numerical methods. The analytical approach assumes that the coefficients and parameters based upon Lype's extension of the Polanyi-Wigner theory must be substantiated by experiment.

The correction of binary diffusion coefficient for bed porosity does no more than specify a maximum value of D_{eff} . The effective binary diffusion coefficient must be determined experimentally on an actual wick before this analysis can be utilized.

The utilization of the numerical solutions of the equations of transfer derived in this Appendix must use experimental data to determine the parameters necessary for the analytical solution. It is preferable that the experimental data be obtained in a system which models the physical conditions in the space suit.

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