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Gas Diffusion in Glassy Polymers by a Chain Relaxation Approach

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ABSTRACT: Plasticization of glassy polymers by small molecules was approached by the "concentration−temperature superposition" principle. The major effect of the plasticization by small molecules is on the reduction of the glass transition temperature. The present study suggests that the dependence of diffusion coefficients of small molecules on the penetrant concentration can be affected by the reduction of the glass transition of the penetrant/polymer system caused by a plasticization effect of the penetrant. With a WLF type shift factor, the concentration-dependent diffusion coefficient can be predicted. It is found that the calculated diffusion coefficient correlates very well to the experimental data. This study also proposes a prediction of time-lag values from the solubility and permeability measurements. Moreover, the diffusion coefficients for gases in glassy polymers can also be predicted using the time-lag values alone. The proposed diffusion model represents satisfactorily experimental data reported in the literature for CO_2 in poly(ethylene terephthalate), in polycarbonate, and in polyacrylate. The prediction of diffusion coefficient in glassy polymers is seen to agree well with the experimental data, whereas the prediction of time-lag values is less accurate due to the error propagation in solubility measurement, permeability measurement, and time-lag measurement, respectively.

I. Introduction

The solubility and transport of light gases in glassy polymers are very important in both application and theoretical considerations.[1−10] A new representation of gas solubility in glassy polymers was proposed based on a "concentration−temperature superposition" principle.[11] This representation describes the solution behavior of gases in glassy polymers by an approach of plasticization of penetrant gases. The effect of plasticization on the gas solubility is accounted for by means of a modified William−Landel−Ferry (WLF) equation.[12−14] The formulation of the gas solubility as a function of pressure (or concentration) derived from this principle is validated by experimental data for a variety of gas/polymer systems reported in the literature.[11] The objective of the present study is to use a similar methodology to describe the concentration dependence of diffusion coefficients for gases in glassy polymers.

II. Theoretical Background

A. Effect of Polymer Plasticization on Gas Solubility. In a previous publication, it was shown that the solubility of a plasticizing gas in a glassy polymer can be represented by the following isothermal relation over a wide range of pressures[11]

$$c = S(0)\alpha_T(c)p \tag{1}$$

where c is the penetrant concentration (the solubility) in the polymer at pressure p at solution equilibrium; S(0) is a solubility coefficient in the Henry's law limit, ($c \rightarrow 0$); and $\alpha_T(c)$ is the "concentration−temperature shift factor", which is given by the following expression:[11]

$$\log \alpha_T(c) = A\left[\frac{T_g(c)[T_g(c) - T_g(0)]}{[T_g(0)]^2}\right][T_g(0) - T] \tag{2}$$

where A is a parameter that depends only on temperature and the nature of the penetrant/polymer system; A is defined by the relation

$$A = \frac{B^s \alpha_f T_g(0)}{2.303 v_{f_{c0}}(T)K(T)} \tag{3}$$

where B^s is a characteristic constant. T is the absolute temperature, $T_g(0)$ is the glass-transition temperature of the pure polymer ($c = 0$), $T_g(c)$ is the glass-transition temperature of the polymer containing a dissolved penetrant at concentration c, α_f is the difference in the coefficients of thermal expansion of the rubbery and glassy states of the polymer, $v_{f_{c0}}$(T) is the fractional free volume of the pure polymer, and $K(T)$ is a function of temperature.

Equation 2 is based on the following premises. At very low concentrations, the solubility of a gas in a glassy polymer obeys Henry's law [$c \rightarrow 0$, $T_g(c) \rightarrow T_g(0)$, $\alpha_T(c) \rightarrow 1$].

$$c = S(0)p \tag{4}$$

If the concentration of the gas in the polymer is increased (by increasing the gas pressure) and the polymer is sufficiently plasticized by the penetrant gas, the glass-transition temperature of the polymer will be depressed from $T_g(0)$, the value for the pure polymer, to a lower value of $T_g(c)$ which will depend on the penetrant concentration, c.

The solubility of most gases and vapors in glassy polymers decreases as the temperature difference ($T_g - T$) decreases, where T_g is the glass-transition

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temperature of the penetrant/polymer system and T is the temperature at which the solubility is measured. The value of ($T_g - T$) can decrease in two ways: (1) either due to an increase in T, when T_g is constant, or (2) due to a decrease in T_g, when T is maintained constant. The latter case occurs when, as mentioned above, the polymer is plasticized by the penetrant gas [$T_g = T_g(c)$]. The solubility of the gas in the polymer is then described as a function of pressure by eq 1. The depression of the glass-transition temperature reflects a higher chain mobility of the polymer, and its effect on the solubility is represented by the shift factor $a_T(c)$, cf. eq 2. This relation is based on a modified Doolittle equation,[12,13] which has been widely used to describe the dependence of viscoelastic properties of polymers on their free volume.

It should be noted that eq 1 is nonlinear, a plot of c vs p being concave to the pressure axis. However, when the polymer is plasticized to such an extend that its glass-transition temperature is depressed to the experimental temperature [$T_g(c) \rightarrow T$], eq 2 becomes linear; the solubility isotherm (i.e., a plot of c vs p) will then exhibit an inflection point.[11]

B. Temperature Dependence of Diffusion Coefficients. It is suggested hereby that the concentration dependence of the mutual (binary) diffusion coefficient, $D(c)$, for a plasticizing penetrant gas in a glassy polymer can also be quantified by means of the shift factor $a_T(c)$, since diffusion coefficients strongly depend on the chain mobility of polymers. It is first necessary to examine the temperature dependence of diffusion coefficients.

It has been shown by Chen and Ferry[14] that the temperature dependence of the mutual diffusion coefficient for a gas in a given polymer can be expressed by the relation

$$\log\left[\frac{D(T)}{D(T_0)}\right] = \frac{c_1(T - T_0)}{c_2 + T - T_0} \qquad (5)$$

where $D(T)$ and $D(T_0)$ are the diffusion coefficients of the penetrant at temperature T and at a reference temperature T_0, respectively. c_1 and c_2 are characteristic constants in the William–Landel–Ferry (WLF) equation.[12–14] By comparing eq 5 with the original WLF equation,[12] one obtains

$$\log\left[\frac{D(T_0)}{D(T)}\right] = \log \alpha_T(T) = -\frac{c_1(T - T_0)}{c_2 + T - T_0} \qquad (6)$$

where $\alpha_T(T)$ is the temperature "shift factor" for relaxation times. The temperature-dependent diffusion coefficient for a penetrant in a polymer can then be written in the following form:

$$D(T) = \frac{D(T_0)}{\alpha_T(T)} \qquad (7)$$

C. Concentration Dependence of Diffusion Coefficients. Fujita has expressed the concentration dependence of the mutual diffusion coefficient for a penetrant/polymer system by the general expression:[15]

$$D(c) = D(0)F(c) \qquad (8)$$

where $D(c)$ is the diffusion coefficient for a penetrant gas or vapor at concentration c in the polymer, $D(0)$ is the diffusion coefficient at the limiting concentration $c \rightarrow 0$, and $F(c)$ is a factor which represents the variation of D with the penetrant concentration. Equation 8 is applicable under isothermal conditions. It is suggested that $F(c)$ can be related to $\alpha_T(c)$, the concentration–temperature shift factor mentioned above.

$$F^{-1} = \alpha_T(c) \qquad (9)$$

Equation 8 then becomes

$$D(c) = D(0)\alpha_T(c) \qquad (10)$$

This relation is similar in form to eq 7. The shift factor $\alpha_T(c)$ can be expressed by a relation analogous to eq 2. Equations 10 and 2 yield the expression

$$D(c) = D(0) \exp\left\{-A_D\left[\frac{T_g(c)[T_g(c) - T_g(0)]}{[T_g(0)]^2}\right][T_g(0) - T]\right\} \qquad (11)$$

where A_D is a parameter that depends on the nature of the penetrant/polymer system, and the other symbols are as defined earlier. To a given temperature T, eq 11 contains two adjustable parameters, $D(0)$ and A_D. These parameters can be determined by fitting eq 11 to experimental diffusion data for a range of penetrant concentrations in a polymer; $T_g(0)$ can be measured by differential scanning calorimetry or thermal mechanical analysis, and $T_g(c)$ can be estimated from Chow's equation.[13]

D. Time-Lag and Time-Lag Diffusivity Coefficients. Consider the permeation of a gas from a reservoir at a constant pressure p_h through a nonporous, homogeneous, and planar polymer membrane into another (finite) reservoir at a pressure p_l ($\ll p_h$). At time $t = 0$, the penetrant gas is allowed to contact one side of the membrane, while the pressure on the opposite side of the membrane and in the receiving reservoir is maintained near zero, $p_l \approx 0$. The increase of pressure p_l due to the permeating gas at $t > 0$ is then monitored as a function of time. The "time-lag" L is a measure of the period of time from the instant the gas contacts the membrane until the permeation process reaches steady-state condition. Time-lags are related to diffusion coefficients, and the measurement of time-lags is a common method of determining diffusion coefficients. The diffusion coefficients, D, can be determined from a solution of Fick's second law with the following initial and boundary conditions, which characterize the permeation process described above

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left\{D(c)\frac{\partial c}{\partial x}\right\} \quad \text{at } 0 < x < \delta,\ t > 0 \qquad (12)$$

with

$$c(x,0) = 0, \quad \text{for } x > 0$$
$$c(0,t) = c_h, \quad \text{for } t > 0$$
$$c(\delta,t) = 0, \quad \text{for } t > 0$$

where c is the local penetrant gas concentration at a position coordinate x in the membrane, c_h is the concentration at the "upstream" (high-pressure) interface of the membrane in contact with the gas at pressure p_h, and δ is the membrane thickness. When the diffusion coefficient is independent of concentration, i.e., $D(c) = D_0$, a constant, the asymptotic solution of eq 12 ($t \rightarrow \infty$) is[21]

$$L = \delta^2/6\,D_0 \tag{13}$$

Hence, D_0 can be calculated if L is known. However, the diffusion coefficients of gases in glassy polymers can be strongly concentration-dependent. The relation between L and $D(c)$ has been formulated for such cases by Frisch:[16]

$$L = \frac{\int_0^{\delta} x c_s(x)\,\mathrm{d}x}{\int_0^{c_h} D(u)\,\mathrm{d}u} \tag{14}$$

$$\int_{c_s}^{c_h} D(u)\,\mathrm{d}u = \frac{x}{\delta}\int_0^{c_h} D(u)\,\mathrm{d}u \tag{15}$$

where the steady-state concentration $c_s(x)$ in eq 14 can be found as a solution of eq 15 either analytically or numerically. For simpler cases, as diffusion of light gases in rubbery polymers, analytical solution of eq 15 may be obtained. For more complicated diffusion phenomena, when D is an implicit function of concentration as presented by eq 11, eq 15 is solved numerically. u in eq 15 is a dummy variable, and $D(u)$ is the concentration-dependent diffusion coefficient of a penetrant in a polymer.

To solve eq 14 for the time-lag L, it is necessary to know the functional dependence of D on the penetrant concentration c. Accordingly, eqs 14 and 15 were solved using the expression for $D(c)$ of eq 11. Examples of the results obtained are presented in the following section.

Conversely, if the concentration-dependent time-lags are known for a certain range of concentrations, one can determine the parameters A_D and $D(0)$ in eq 11 by a computer- optimized fitting of eqs 14 and 15 to the time-lag data. Once the values of A_D and $D(0)$ are known, the diffusion coefficient $D(c)$ can be calculated as a function of c from eq 11. This procedure provides an independent means of determining $D(c)$ from time-lag measurements alone. This method was first proposed by Frisch,[16] but it was applied only to specific cases because no general expression of the concentration dependence of diffusion coefficients for gases in glassy polymers was available.

III. Results and Discussion

Figures 1 and 2 illustrate the concentration dependence of the diffusion coefficients for CO_2 in poly(ethylene terephthalate), PET. The permeability and solubility data are from the literature.[17,18] The solid curves in Figures 1 and 2 were calculated from eq 11, whereas the experimental values of $D(c)$ were calculated from the following eq 21:

$$D(c_h) = \left(\bar{P}(p_h) + p_h\frac{\mathrm{d}\bar{P}}{\mathrm{d}p_h}\right)\left(\frac{\mathrm{d}p}{\mathrm{d}c}\right)_{|p_h} \tag{16}$$

where $\bar{P}$ is a mean permeability coefficient, and p_h is the pressure at the high-pressure interface of the membrane. The differential term of $\mathrm{d}\bar{P}/\mathrm{d}p_h$ was obtained from the dependence of $\bar{P}$ on p_h, while the $\mathrm{d}c/\mathrm{d}p$ was determined from solubility isotherms.

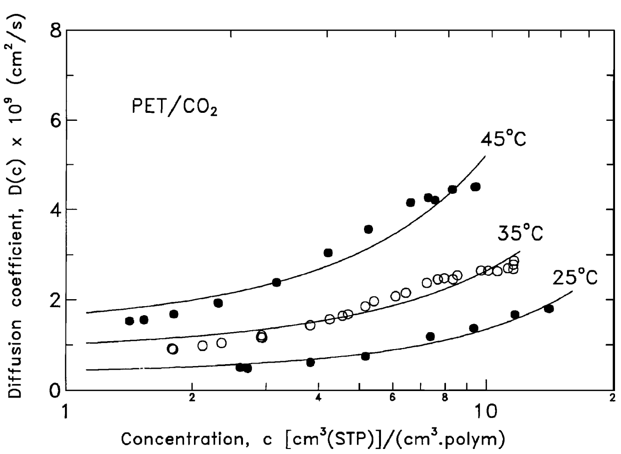

Figure 1. $D(c)$ vs c for PET/CO_2 at 25, 35, and 45 °C. The solid curves drawn through the data points were calculated from eq 11 in conjunction with the parameters listed in Table 1, whereas the data points were calculated from eq 16 using the literature permeability and solubility data.[17,18]

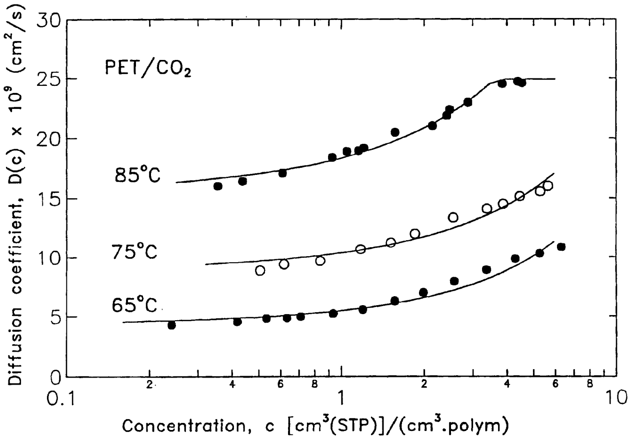

Figure 2. $D(c)$ vs c for PET/CO_2 at 65, 75, and 85 °C. The solid curves drawn through the data points were calculated from eq 11 in conjunction with the parameters listed in Table 1, whereas the data points were calculated from eq 16 using the literature permeability and solubility data.[17,18]

Table 1. Values of Parameters in Eq 11 for CO_2 in Poly(ethylene terephthalate)

temp, *t*	*D*(0)	A_D
25	0.3474	0.7379
35	0.8437	0.7372
45	1.3261	1.0824
55	2.4929	1.4327
65	4.3272	1.9864
75	8.8245	2.2695
85	15.883	6.9773

[a] Units: $D(0)$ [cm^2/s $\times 10^9$], A_D (K^{-1}); t (°C).

Referring to Figures 1 and 2, it is seen that the values of $D(c)$ calculated from eq 11 for the CO_2/PET system are entirely consistent with the values obtained from permeability and solubility measurements via eq 16, particularly when considering the combined experimental errors in these measurements. The parameters $D(0)$ and A_D used in eq 11 for the CO_2/PET system are listed in Table 1. The values of $D(0)$ and A_D were obtained from a direct fit of eq 11 to the $D(c)$ data in Figures 1 and 2. It is interesting to note that eq 11 predicts an inflection in the $D(c)$ vs c plot for this system at 85°C

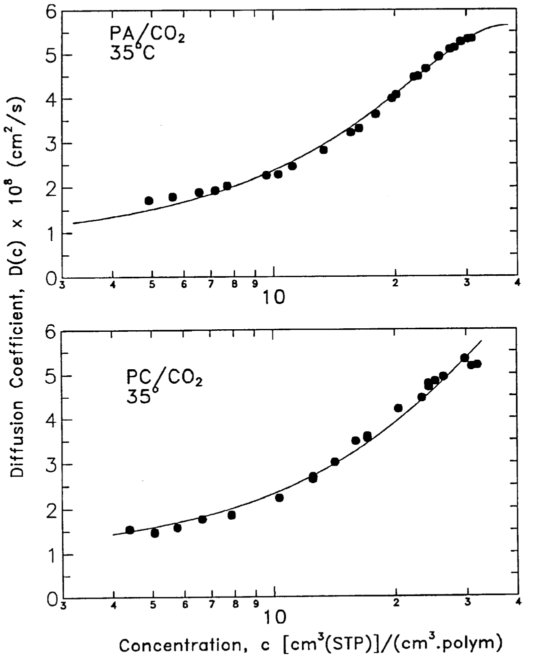

Figure 3. $D(c)$ vs c for PA/CO_2 and PC/CO_2 at 35 °C. The solid curves drawn through the data points were calculated from eq 11 in conjunction with the parameters listed in Table 2, whereas the data points were calculated from eq 16 using the literature permeability and solubility data.[19,20]

Table 2. Values of Parameters in Eq 11 for CO_2 in Two Glassy Polymers at 35 °C

polymer	$D(0)$	A_D
PA	7.0125	0.2869
PC	13.7125[a]	0.1897[a]
	14.3325[b]	0.1813[b]

[a] Calculated from eq 11 using the diffusivity data.[19,20] [b] Calculated from eqs 14 and 15 using the time-lag data.[19,20] Units: $D(0)$ [cm^2/s × 10^9], A_D (K^{-1}). PA = polyacrylate; PC = polycarbonate.

and at $c \approx 4$ cm^3 (STP)/cm^3 polymer, as shown in Figure 2.

Figure 3 shows a similar comparison for CO_2 in polyacrylate (PA) and polycarbonate (PC) at 35 °C. The permeability and solubility data are those reported in the literature.[19,20] Again, the values of $D(c)$ derived from eq 16 are in good agreement with the values obtained from eq 11 in conjunction with the parameters listed in Table 2. The values of $D(0)$ and A_D were obtained from a direct fit of eq 11 to the $D(c)$ data in Figure 3.

Referring to eq 14, one can predict the time-lag values of the penetrant in glassy polymers when the function of the concentration dependent diffusion is known. Figure 4 presents the prediction of the time-lag values of CO_2 in PC and PA. The solid curves were calculated from eq 14 using the $D(0)$ and A_D values listed in Table 2, whereas the experimental time-lags are from the literature.[20] It is seen, in Figure 4, that the time-lag values of the prediction do not agree with the experimental values as accurate as the diffusivity predictions in Figures 1–3. The readers should be reminded that, unlike Figures 1–3, Figure 4 is a totally independent prediction. The solid curves in Figures 1–3 were obtained by curve fitting, in which the two parameters $D(0)$ and A_D were obtained from a direct fit of eq 11 to the $D(c)$ data in Figures. However, we should note that, in Figure 4, the solid curves and the experimental data points are independent. The solid curves in Figure 4 are not curve fitting type, but are the prediction. This prediction was made only by using the pressure dependent permeability data and solubility data via eqs 11 and 14–16. Therefore, the contribution to the error in the prediction of the time-lag values has three factors, namely, the time-lag measurements, the permeability measurements, and the solubility measurements. The experimental error for the time-lag measurement is about 20%,[20] that for the permeability measurement is about 12%,[22] and that for the solubility measurement is about 8%.[23] In particular for time-lag measurement,

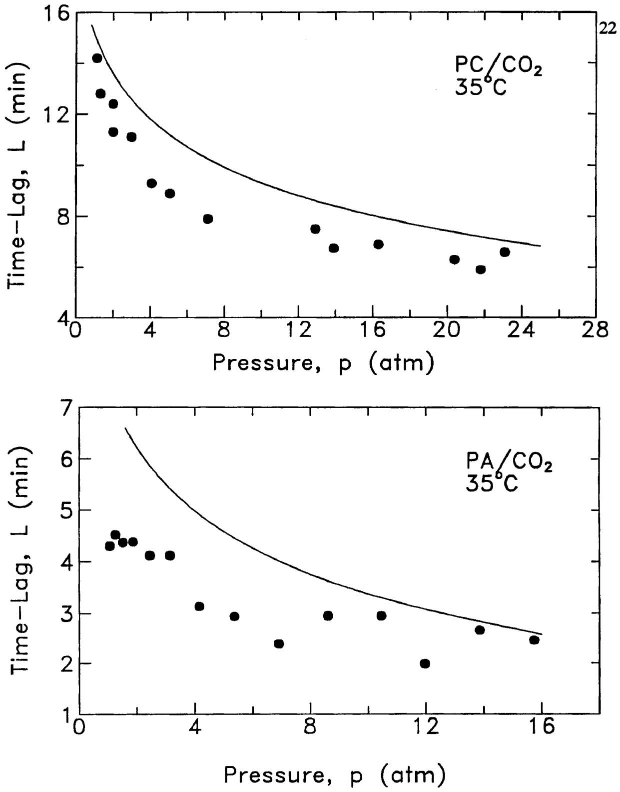

Figure 4. Prediction of the time-lag of CO_2 in polymers at 35 °C. The solid curves were calculated from eqs 14 and 15, whereas the data points are the literature time-lag data.[19,20]

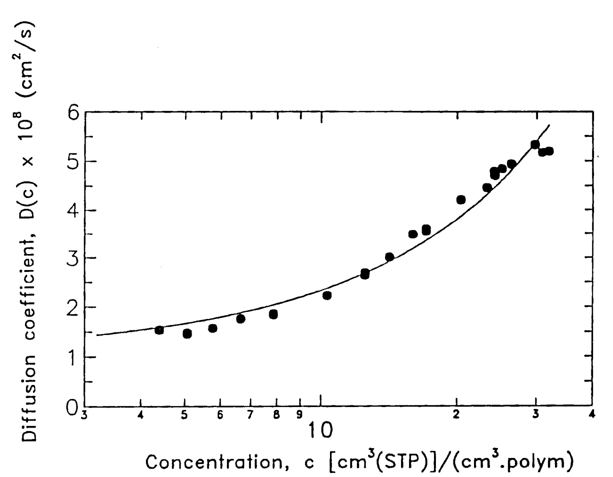

Figure 5. Prediction of diffusion coefficients, for CO_2 in PC at 35 °C, from the time-lag values only. The solid curve was calculated from eq 11 using parameters A_D and $D(0)$ determined from eq 14 [$A_D = 0.1813$, $D(0) = 1.433 \times 10^{-8}$ (cm^2/s)]. The experimental values of $D(c)$ (full circles) were calculated from eq 16 using the literature data.[19,20]

we found that the experimental error could be higher than 50% in the low- pressure region. Giving all those considerations, we feel that the prediction of the time-lag values as presented in Figure 4 is satisfactory.

Equations 14 and 15 can also be solved simultaneously to yield the values of the parameters $D(0)$ and A_D when the time-lags are known. $D(c)$ can then be **predicted** from eq 11 using time-lag data only. The solid curve in Figure 5 was calculated from eq 11 using the parameters $D(0)$ and A_D obtained from eqs 14 and 15 in conjunction with the time-lag data.[20] The full circles in Figure 5 were calculated from eq 16 using the permeability and solubility data for CO_2 in PC at 35 °C.[20] It is seen that the diffusion coefficients predicted from independent time-lag measurements alone are in good agreement with the value of $D(c)$ calculated from permeability and solubility measurements.

VI. Conclusions

Equation 11 represents satisfactorily the diffusion coefficients for gases in glassy polymers as a function of the penetrant concentration. This equation can also be used to calculate the time-lag values of gases in glassy polymers. It should be noted that a variety of membrane separation processes involve gas mixtures containing components which plasticize the polymer membranes, such as the removal of CO_2 and H_2S from crude natural gas, in the separation of CO_2 from mixtures with hydrocarbons in enhanced oil recovery, in the dehydration of natural gas, etc. The new concepts developed in this study should be useful for the design of membrane processes in such applications. Also, it should be noted that the present study assumes that the free volume of the penetrant/polymer system is additive. Therefore, the present results will not apply to systems where this condition is not held, e.g., in cases where the penetrant forms molecular clusters.

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