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Kinetic Model for Oxidation of Carbon Fiber/Glass Matrix Composites

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A kinetic model predicting the oxidation of carbon fiber reinforced glass matrix composites has been described. The weight loss of composites during oxidation implied that a gasification of carbon fiber takes place and the transport of reactants (O_2) or product (CO or CO_2) in the glass matrix was partially the rate controlling step. The kinetic model in this study was based on the work of Sohn and Szekely which may be regarded as a generalization of numerous models in the gas-solid reaction system. A comparison of this model with experimental data is also presented.

Key words : C/Glass Composites, Oxidation, Effective Diffusivity

I. Introduction

Carbon fiber reinforced glass matrix composites are of interest because it has high temperature oxidation resistance provided by glass matrices compared with polymer based composites. Ideally the glass matrix protects the carbon fibers from oxidizing environments. However, microcracks formed during composite fabrication process provide a path for an oxygen transport in oxidizing environments, thereby, causing a severe oxidation problem.[1-6] These microcracks can result from at least three mechanisms: slurry drying shrinkage, external mechanical stresses and densification shrinkage. It is believed that these cracks serve as short circuit or pipeline diffusion paths by which oxygen can gain access to the fiber surfaces.

Since not much work has been done to characterize the oxidation of these composites, a kinetic model to predict the oxidation behavior is very useful for the understanding of the oxidation mechanism.

II. Experiments

Fortafil™ carbon fibers were received on spools containing four tows, with each tow containing 50,000 individual fibers. The average diameter of the fibers is 8.6 μm. Small specimens approximately 6.35 cm and 0.3 g in weight were cut from the large spools. The chemical compositions of a Corning borosilicate glass (CGW7740)used as matrix are given in Table 1.

Table 1. Nominal Composition of CGW 7740 (in wt %)

SiO_2	B_2O_3	Na_2O	Al_2O_3
81	13	4	2

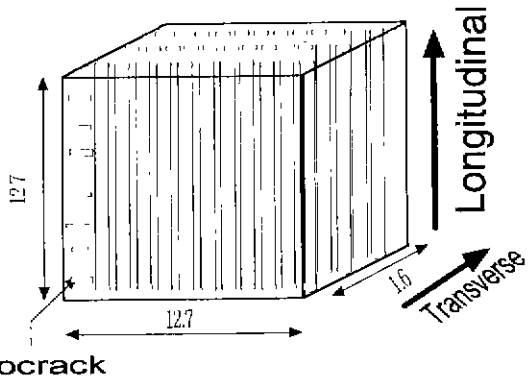

Fig. 1. Schematic diagram of carbon fiber/glass composites for experiment.

Carbon fiber/glass matrix composites has been made by a laboratory technique for the batch production of composites plies infiltrated with Corning boro-silicate glass. Twenty five of the plies have been hot pressed into $7.62\times7.62\times0.16$ cm samples. These hot pressed composites are machined into samples having approximate dimensions of $1.27\times1.27\times0.16$ cm, which would be used for modeling work(Fig. 1).

In order to understand the oxidation of C/Glass composite, the oxidation of carbon fiber has been studied. Fig. 2 shows a plot of data collected from the oxidation of unprotected, as received carbon fibers at 500°C, 550°C and 600°C.[9] By using the data the reaction rate at temperature T (R_T) was estimated.

The experimental data for the oxidation behaviors of carbon/glass composites at 600°C was presented in Fig. 3 and these values are compared with theoretical data from the modelling work. Prior to each oxidation test, the furnace tube, silica specimen holder, and alumina

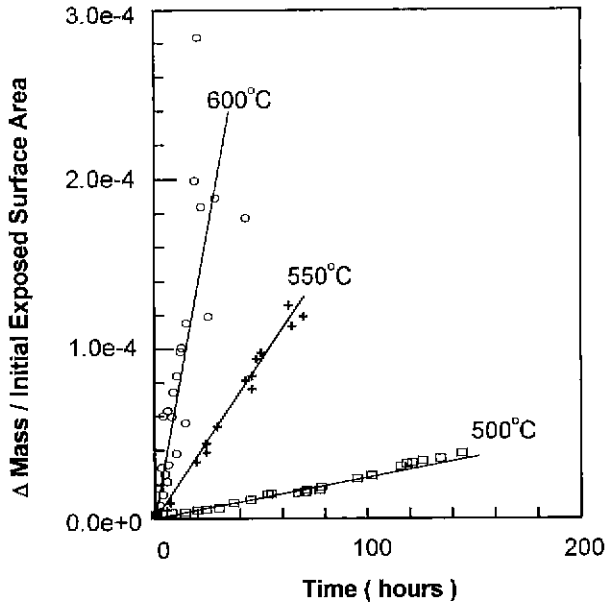

Fig. 2. Plot of oxidation data for carbon fibers at 500°C, 550°C and 600°C (reference 5).

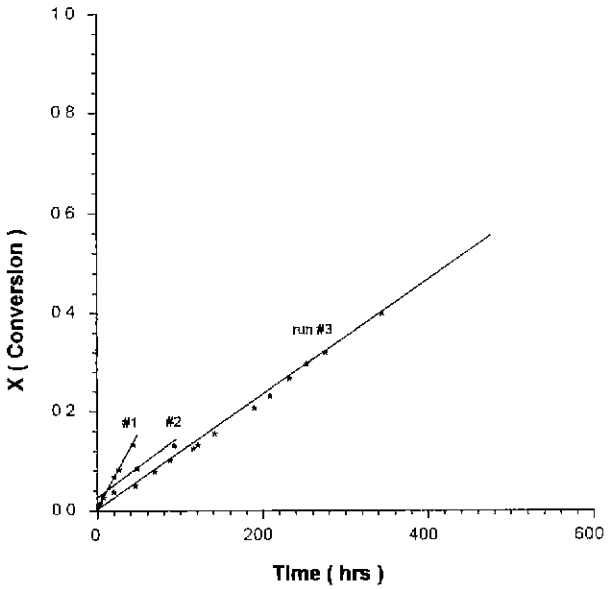

Fig. 3. Experimental data for the oxidation of C/Glass composites at 600°C.

boat are baked out at 800°C for approximately 3 hours to drive off water vapor. The furnace temperature are then lowered to the desired test temperature and the sample is loaded in the furnace. At designated times, the samples are removed from the furnace, placed in a desiccator to cool for 5 minutes, and subsequently weighed. The experimental procedure for oxidation experiments are elsewhere.[3-6] The dependant variable, X, is the fractional conversion of solid carbon to carbon oxide for the reaction:

$$2C(s)+O_2(g) \rightarrow 2CO(g)$$

and is mathematically defined as:

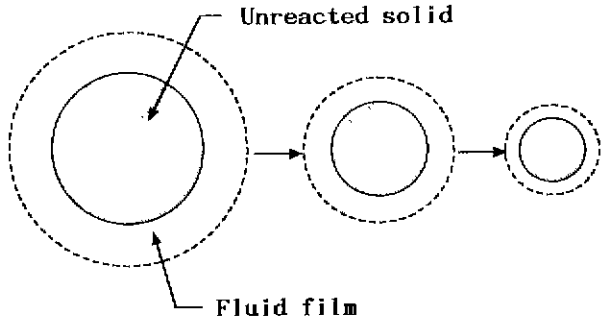

Fig. 4. A nonporous solid participating in a gas-solid reaction (gasification) in which no solid product is formed(reference 7).

$$X = \text{conversion} = \frac{m^i - m^t}{m^i - m^f}$$

m^i=initial mass
m^t=mass at t ime t
m^f=final mass

III. Kinetic Modeling

As mentioned previously, the data in this investigation will now be compared with a theoretical oxidation model developed by Sohn and Szekely which describes a gas-solid reaction system where the reactant shrinks with time and produces no solid product layer(Fig. 4).

Such a system can be described by the following generalized chemical reaction:

$$A(g)+bB(s)=cC(g) \quad (1)$$

Examples of this type often occur in chemical and metallurgical processes such as combustion and gasification of carbon and coal, the decomposition of solids into gases, the dissolution of solids in liquids, fluorination and chlorination of metals and ceramics and some electrochemical processes. The oxidation of carbon/glass composites also belongs in this category. Although the glass matrix should prevent the fibers from undergoing oxidation by oxygen contained in the ambient environment, the glass does not prohibit a progressive deterioration of the fibers propagating inward from exterior surfaces.

Therefore, the oxidation of carbon fibers is a significant life-limiting mechanism. However, little work has been done to develop models which predict the corrosion rate of carbon fiber/glass matrix composites in oxidizing environments. The oxidation of carbon fibers in glass matrices can occur by the following mechanisms:

a. Oxidation of the fibers from exposed ends.
b. General oxidation of the fibers due to diffusion of oxygen through the glass matrix.
c. Localized oxidation of the carbon fibers where a matrix microcrack intersects the fibers.

In this paper the discussion will primarily address (a) and (b) and the goal of this work is to mathematically

describe the oxidation behavior of C/glass composites with equations which consider both the diffusion of oxygen/carbon oxide through the glass matrix and the chemical reaction of carbon and oxygen, both of which contribute to the oxidation process of the materials.

The original model developed by Sohn and Szekely was used to describe the oxidation of a polycrystalline pellet. Thus, in the equations which follow, the subscripts "g" and "p" refer to grain and pellet respectively. Each can have one of three permissible shapes: a cylinder, a sphere, or a flat plate - 9 possible combinations. This model may be regarded as a generalization of numerous models that have been proposed to represent the diffuse reaction zone of a reacting porous solid. In this study the carbon fibers and composites are regarded as grain and pellets respectively. As the details of this model are presented elsewhere,[7-10] a slightly abbreviated presentation will be given here.

Mathematically, the oxidation process shown in equation (1) can be described by a mass balance of the gas reactant(oxygen) with the reactive solid(carbon) as:

$$D_e \nabla^2 C_A - V_A = 0 \tag{2}$$

where D_e is the effective diffusion coefficient for a porous medium. C_A is the concentration of reactant A and VA is the rate of consumption of component A and can be defined as:

$$V_A = (1-\varepsilon)\, kC_A \frac{A_g}{V_g}\left[\frac{A_g r}{V_g F_g}\right]^{F_g - 1} \tag{3}$$

where ε is the volume fraction of initial porosity of the "pellet" (composite)

k is the linear reaction rate constant

A is the external surface area

V is volume and

F is the shape factor. For a flat plate Fg=1, a cylinder Fg=2 and a sphere Fg=3

The local rate of reaction at a solid surface may be expressed as:

$$\rho_B \frac{dr_c}{dt} = bkC_A^n \tag{4}$$

where ρ_B is the molar density of the solid,

r_c is the distance coordinate perpendicular to the moving reaction from the individual grain,

b is a stoichiometric factor,

k is the linear reaction rate constant and n is the reaction order with respect to the gaseous reactant concentration.

The boundary conditions for equations (2) and (4) are: (a)initially, all the fibers are unreacted, (b) the reactant concentration is maintained at C_{Ao} at the outer surface of the composite sample, (c) the gaseous reactant concentration profile is symmertrical about the center of the sample and (d) the reaction is first order with respect to the gaseous reactant.

Substituting for V_A from equation (3) to equation (2) and introducing dimensionless variables into equation (2), the following approximate solution for the conversion of the solid as a function of reaction time is given as:

$$t_g^* = G_{F_g}(X) + \sigma^2 [P_{F_p}(X)] \tag{5}$$

where

$$t_g^* = \frac{bkC_{Ab}}{\rho_B}\left(\frac{A_g}{F_g V_g}\right) t$$

$$\sigma = \frac{V_p}{A_p}\left[\frac{\alpha_B F_p k}{2D_e}\left(\frac{A_g}{F_g V_g}\right)\right]^{1/2} \tag{6}$$

$$G_{F_g}(x) = 1-(1-X)^{1/F_g}$$

$$P_{F_p}(x) = \begin{cases} X^2 & \text{for } F_p = 1 \\ X + (1-X)\ln(1-X) & \text{for } F_p = 2 \\ 1 - 3(1-X)^{2/3} + (1-X) & \text{for } F_p = 3 \end{cases}$$

t_g^* is a dimensionless time constant which describes the time necessary for a given conversion of the solid reactant, which is carbon fibers, to the gaseous product (CO, CO_2).

ρ_B is the molar density of species B in equation (1).

$G_{F_g}(X)$ is a term which represents the chemical reaction, while $P_{F_p}(X)$ is a diffusional term.

σ is the gas-solid reaction modulus. As σ approaches zero, pore diffusion has little effect on the rate of oxidation and the chemical reaction dominates the process. The opposite is true when becomes large.

α_B is equivalent to 1-ε.

Although the mathematics of this model may seem cumbersome, the equations describe the oxidation of a porous material in terms of a mass transport term and a chemical reaction term. This can be put into symbolic form with the following equation.

$$t_g^*(X) = t_{g\sigma\to 0}^*(X) + t_{g\sigma\to\infty}^*(X) \tag{7}$$

If all parameters can be measured or reasonably estimated, this equation can be solved to predict the oxidation rate of composites. Except for k and De, all other parameters can be easily calculated. Knowing that the reaction is first order and that the rate of oxidation has been shown to follow an Arrhenius relationship, the reaction rate can be expressed as:

$$R_T = kC_{Ab} = k\frac{P}{RT} = C' e^{-(Q/RT)} \tag{8}$$

where P is pressure, k is linear rate constant, C_{Ab} is the concentration of A in the bulk gas, C′ is a pre-exponential constant, Q is the effective activation energy for oxidation. T is absolute temperature.

Using the data shown in Fig. 2, the linear reaction rate constant, k can be calculated from equation (8). It is also essential that the diffusivity of oxygen in the composite be known. This diffusivity, however, can be

affected by many factors such as the degree of matrix microcracking caused by thermal mismatch between the fibers and glass. If the diffusion of oxygen through the bulk glass is known (uncracked), then a new effective diffusivity can be defined as:

$$D_e = D_b(1-\varepsilon) + D_{eff(crack)}\frac{\varepsilon}{\tau} \quad (9)$$

where D_e is the effective interdiffusion coefficient, D_b is the bulk diffusivity, D_{eff} (cracked) is the effective pore diffusivity, ε is the volume fraction of porosity, τ is the tortuosity.

No information has been published on the bulk diffusion of oxygen in CGW 7740 borosilicate glass. Thus D_b was estimated using values for the diffusivity for oxygen in vitreous silica. To use these values, it has to be assumed that no chemical reaction occured between the fibers and the matrix. At 600°C, the bulk diffusivity of oxygen in silica is 7×10^{-11} cm^2/sec.[11]

There must be a reasonable understanding of the extent of matrix microcracking to calculate D_{eff}(cracked). Prewo and his coworkers at United Technologies Research Center used a dye penetrant method to examine the microcracking and its content to be 0.1-0.8 vol % for a composite containing 40 vol % fibers. In this investigation, it was assumed that 1 % of these cracks are interconnected and serve as effective channels for oxygen transport.[12] The oxygen diffusivity through these cracks is given as:

$$D_{eff(crack)} = D_{AB}\frac{\varepsilon}{\tau} \quad (10)$$

Estimating ε to be 4×10^{-5} and τ to be 1, then D_{eff}(cracked) is approximately 3.2×10^{-5} cm/sec at 600°C. Note that D_{eff} (cracked) is larger than D_b by as much as 6 orders of magnitude. If the radius of these cracks is very small, then the molecules of diffusing oxygen will collide with the walls of the pore more than they will collide with each other. Knudsen diffusivity must be considered in this instance rather than D_{AB}. D_{eff}(cracked) will then be expressed as:

$$D_{eff(crack)} = D_{kn}\frac{\varepsilon}{\tau} \quad (11)$$

$$D_{kn} = 9700\,r\sqrt{\frac{T}{MW}} \quad (12)$$

The variable, r is the crack radius and T is an absolute temperature and MW is a molecular weight.

Assuming the pore radius to be 50 Å (or half the width of the crack depending upon the geometry), and the porosity and tortuosity to be 0.004% and 1, respectively, D_{eff}(cracked) is approximately 10^{-6} cm^2/sec at 600 C, therefore D_{eff}(cracked) is also larger than D_b by 4 orders of magnitude. Since the Knudsen diffusivity (2.5×10^{-2} cm^2/sec) is smaller than D_{AB} (0.8 cm^2/sec), then it can be presumed that Knudsen diffusivity is the controlling mass transport mechanism.

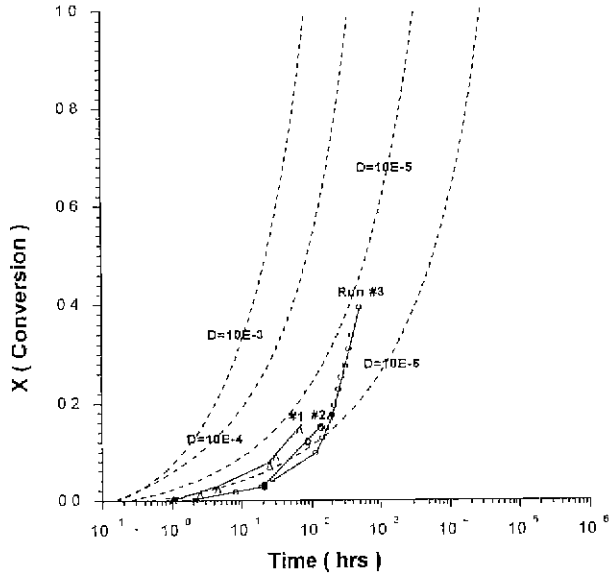

Fig. 5. Comparison of experimental data with theoretical data based on constant D_e for oxidation of C/Glass composites at 600°C in air.

Fig. 5 shows the theoretical data bases on constant D_e for oxidation of C/Glass composites at 600°C in air environment and the experimental data from Fig. 3. In the early stage of experiment, the experimental data seem to fit one of the theoretical data. However, as time goes on the curve does not follow the theoretical line. The reason is probably that changes in fiber diameter and length can have an effect on the composite porosity and oxidation behavior in addition to porosity caused by matrix microcracking. Because the fibers shrink as a function of time at a given temperature both in a transverse and in a longitudinal direction, D_e is strongly time dependent.

Fig. 6 shows a standard oxidation plot of weight

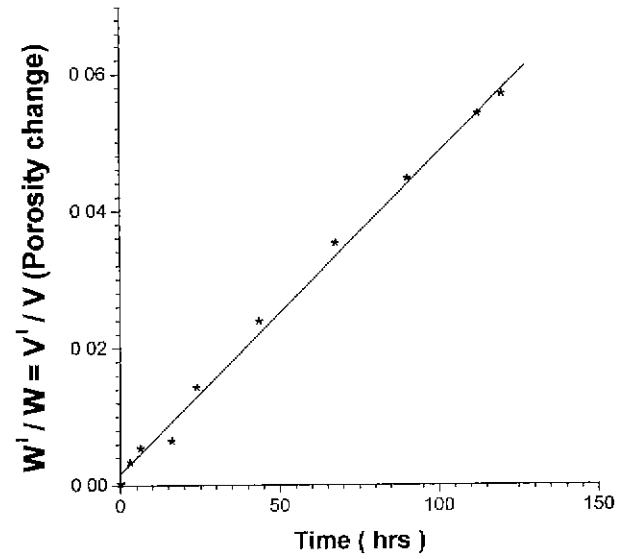

Fig. 6. Volume change due to shrinkage by oxidation of carbon fiber in C/Glass composites at 600°C in air.

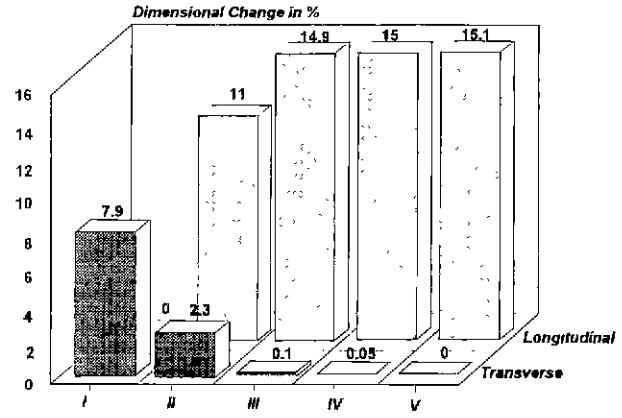

Fig. 7. Comparison of shrinkage rates of carbon fiber in each direction.

change/initial surface area for composite samples oxidized at 600°C. Assuming the bulk dimensions of the sample remained constant, then it is reasonable to assert that any increase in porosity is caused by a reduction in the dimensions of the fibers. Since the density of the glass and fibers are approximately the same (2 g/cm^3), the weight change divided by the initial weight (W'/W) is equal to the volume change per initial volume (V'/V). Porosity as a function of time is now known.

There are infinite number of combinations of changes in diameter and length that will account for porosity at a given time. At 122 hours, the sample has a total porosity of 0.0593 (w'/w=0.04529/0.762 g) by an oxidation of carbon fibers. Fig. 7 shows five possible combinations of Δradius/initial radius and length/initial length that would account for this porosity. These values were substituted back into the equations to calculate values of X. Here only the fiber shrinkages in a transverse (radial) direction can also provide a path for pipeline diffusion and can increase the porosity of the composites with increasing time while the fiber shrinkage in a longitudinal direction has little effect on porosity.

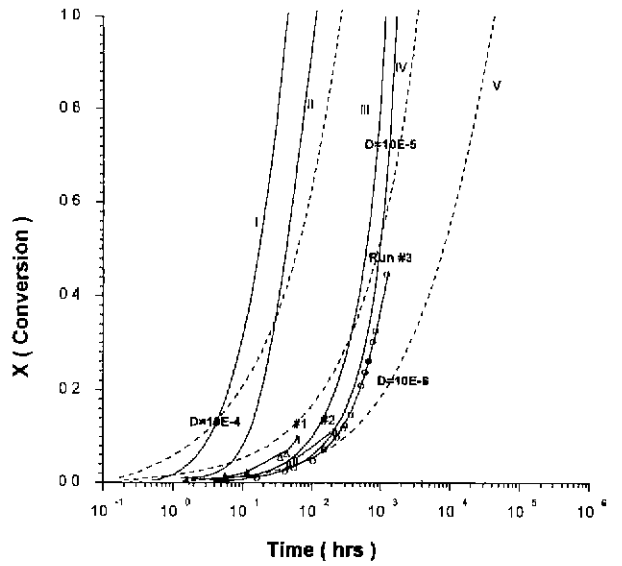

Fig. 8. Comparison of experimental data with theoretical data based on varying D_e for oxidation of C/Glass composites at 600°C in air.

Each curve in Fig. 8 represents a different Al/Ar ratio to account for the porosity as a function of time. Note that curves 3 and 4 are reasonably close to the experimental data. It should be mentioned, however, that the oxidation experiments were performed above the annealing point of CGW 7740 (565°C). Because of this, there is a possibility that some of the microcracks could partially heal over times. If this occured, then the actual porosity caused by matrix microcracking and fiber shrinkage would be less than the estimated values presented. Crack healing process of this material at 600°C is also evident.[13]

The sigma value is the gas-solid reaction modulus term defined by equation (6). This equation expresses the relative importance of diffusion as a resistance for the oxidation of the composite and is inversely proportional to the effective diffusivity. When D_e is larger than 100 cm^2/sec, the overall oxidation is controlled by the chemical reaction rate due to the small sigma value. If the D_e is smaller than 10^{-6} cm^2/sec, the overall oxidation is controlled by the diffusion rate due to the large sigma value and for intermediate values, both mechanism play a role. This seems to be the case with the oxidation of these composite materials. Therefore, the transport of oxygen (reactant) and/or CO (product) is partially the rate controlling step and it was initially assumed that D_e of gaseous reactants and product are equal in the kinetic equations. This argument may be true because CO and O_2 are linear molecules with similar interatomic distances (C-O:0.1128 nm, O-O:0.1208 nm). Therefore, it is expected that CO produced at C/glass interface is able to diffuse out through glass matrix of microcracks as well as O_2 molecules.

IV. Conclusions

1. The localized attack from fiber ends was mainly responsible for the oxidation of the composite and fiber shrinkage in a transverse direction was not significant.
2. The effective diffusivity of oxygen in a composite was a function of time due to changes in size of the micropores created by the vaporization of the carbon fibers.
3. The overall oxidation rate was controlled by both the chemical reaction rate at C/glass interface and diffusion rate of oxygen through glass matrix.
4. In general, the experimental data from the oxidation tests are in good agreement with theoretical data based on kinetic modelling.

Appendix

D_{AB} is the Chapman-Enskog interdiffusion coefficient[14]

which can be determined from the following equation:

$$D_{AB} = 1.8583 \times 10^{-3} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} \frac{T^{3/2}}{P\sigma_{AB}\Omega_{D,AB}}$$

where M_A is the molecular weight of A, M_B is the molecular weight of B, σ is the collision diameter and Ω is the collision integral.

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