equation with four ternary constants. The results derived by the Wilson equation show that only nine data points out of total 60 experimental points for the carbon tetrachloride-cyclohexane-isopropanol system are consistent (they are runs 2, 4, 9, 11, 17, 18, 48, 50, and 51), and that for the n-hexane-ethanol-benzene system only 6 data points (runs 1, 2, 4, 11, 16, and 20) are considered consistent while the remaining 37 experimental points are considered less consistent or inconsistent. Larson and Tassios\(^{11}\) observed that the Wilson equation describes nonideal systems better than does the Margules equation, which is equivalent to the Redlich-Kister equation. The experimental data of these two systems are not considered of good quality, as shown in Table 4.

In conclusion, the Li-Lu and Mc Dermott-Ellis tests and the Redlich-Kister equation do not always detect random errors present in ternary vapor-liquid equilibrium data, but the Wilson equation does it well if vapor-liquid equilibrium data for three binary systems constituting a ternary system are represented accurately by the Wilson equation.

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Nomenclature

\(B_{ij}\) = second virial coefficient [cal/mol]  
\(D\) = value as defined by Eq.(2)  
\(E\) = value as defined by Eq.(14)  
\(F\) = objective function  
\(f\) = fugacity [atm]  
\(g_E\) = excess Gibbs free energy [cal/mol]  
\(P^*_i\) = saturated vapor pressure of pure component \(i\) [atm]  
\(P\) = total pressure [atm]  
\(Q\) = value as defined by \(g_E/RT\)  
\(R\) = gas constant \([1.987\text{cal/mol} \cdot \text{K}]\)  
\(T\) = absolute temperature [°K]  
\(v\) = molar volume of vapor mixture [ml/mol]  
\(v_i^L\) = molar liquid volume of pure component \(i\) [ml/mol]  
\(x_i\) = mole fraction of component \(i\) in the liquid phase  
\(y_i\) = mole fraction of component \(i\) in the vapor phase  
\(z\) = compressibility  
\(\gamma_i\) = liquid-phase activity coefficient of component \(i\)  
\(A_{ij}\) = constant as defined by Eq.(7)

\(\lambda_x\) = energies of interaction between an \(i\)-\(j\) pair of molecules [cal/mol]  
\(\phi_i\) = vapor-phase fugacity coefficient of component \(i\)  
\(\phi^*_i\) = vapor-phase fugacity coefficient of pure saturated component \(i\) at \(P^*_i\) and system temperature  
\(\Sigma^+\) = summation of positive terms in Eq.(1)  
\(\Sigma^-\) = summation of negative terms in Eq.(1)

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ON THE APPROXIMATE EXPRESSION OF THE EFFECTIVENESS FACTOR FOR THE ENZYME FILM REACTOR*

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As for the enzyme film reactor where the enzyme is naturally or artificially fixed in a film supporter of thickness \(L_0\), one side of which is attached to the inner wall and the other side exposed to the outer solution, Atkinson and Daoud\(^{1,2}\) reported that its effectiveness factor could be correlated by introducing the term \(m_A\) defined by Eq.(1) when the reaction rate is expressed

\[\eta = \frac{1}{1 + m_A} \frac{dN}{dt}\]

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Fig. 1 Representation of the effectiveness factor in terms of $m_A$.

Fig. 2 Dependency of the ratio of $m_G$ to $m_A$ on $B$ by the Michaelis-Menten type of rate equation.

$\frac{m_A}{m_G} = \frac{M}{(1+B)^{0.576}}$  \hspace{1cm} (1)

where

$M = \frac{V_{max} L}{K_m}$  \hspace{1cm} (2)

Here we will tentatively call $m_A$ Atkinson's modulus. Using this modulus they gave the following equation for the effectiveness factor of a film reactor.

$E_A = \tanh(m_A)$  \hspace{1cm} (3)

They plotted $E_A$ against $m_A$ for the various values of $B$ to show an agreement of $E_A$ in the region of $B$ greater than about 3 with a corresponding exact value, $E$, which can only be given by solving numerically the differential equation of one-dimensional steady-state diffusion with the Michaelis-Menten type of reaction under the given conditions of $B$ and $M$. But through a closer examination of their plots, which are partly shown in Fig. 1, it can be found that there are systematic departures of $E$ from $E_A$, for example, on one side of the line for $B$ of 5 and on the opposite side for such a large value of $B$ as 500, as shown in Fig. 1.

Comparison of Atkinson's Modulus with the General Modulus

We compared $m_A$ with the general modulus $m_G$, $m_G = \frac{M}{\sqrt{2}} \cdot \frac{B}{1+B} \cdot \frac{1}{\sqrt{B-\ln(1+B)}}$  \hspace{1cm} (4)

which was derived by Bischoff for the Michaelis-Menten type of rate equation. Figure 2 shows that the ratio of $m_G$ to $m_A$ becomes minimum, 0.923, at $B$ of 5.523, reaches unity as $B$ decreases and increases monotonously beyond unity as $B$ increases. Figure 2 reveals that the Atkinson's modulus can be considered as an approximate but not always an adequate expression of the general modulus.

Approximate Expression of the Effectiveness Factor in Terms of the General Modulus

Introducing the general modulus, we can rewrite Eq.(1) into the following form to obtain a probably more successful approximate equation.

$E_A = \frac{\tanh(m_A)}{m_A}$  \hspace{1cm} (5)

According to Bischoff's theory, the exact value of the effectiveness factor for large $m_G$ becomes very close to the reciprocal of $m_G$, which coincides with $E_G$ under the condition of large $m_G$.

Figure 3 shows that the exact values of the effectiveness factor are well correlated by Eq.(5) in the region of $m_G$ greater than about 4, even for such values of $B$ as 5 and 500 for which Eq.(3) fails to approximate the exact values. Figure 4 shows that in the region of $m_G$ between 0.1 and 4, the ratio of $E_G$ to $E$ decreases to less than unity as $B$ increases, reaching its minimum at $m_G$ of unity. Some corrections are needed for the effect
The best value of $a$ depends on $m_G$, for example, as shown in Fig. 5, as well as on $B$. Through the comparative examination of $E_E/E$ changing the value of $a$ of a positive integer from 1 to 10 and also the value of $B$ from 0.5 to 500, a of 5 was found to give better correction on average over the range of $B$ tested. With $a$ as 5, Eq. (7) gives an estimation of $E$ within 4% error at most when $B$ is 5, and maximum error becomes less than 4% as $B$ increases or decreases from 5, i.e., 2% maximum error for $B$ of 0.5 and 1% for 500. The value of $m_G$ where the maximum error occurs decreases from about 1.4 to 1.0 as $B$ increases from 0.5 to 500.

Figure 6 shows the ratio of $E_A/E$ to $E$ against $m_A$ where rather complicated relations are observed between $E_A/E$ and $B$. It seems quite difficult to find an appropriate correction equation for $E_A$, although Atkinson and Daoud proposed a rough correction equation for the effect of $B$ larger than unity.

**Conclusion**

Making it clear that the term $m_A$ defined by Atkinson and Daoud is an approximate but not always an adequate expression of the general modulus, we propose Eq. (5) instead of Eq. (3). The former gives better and theoretically founded approximate expression of the effectiveness factor of the enzymic film reactor for $m_G$ greater than 4 or less than 0.1. We also examined Eq. (7) as a correction equation for the range of $m_G$ between 0.1 and 4.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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| $a$    | constant appearing in Eq. (5) [
| $B$    | ratio of the substrate concentration of outer liquid to $K_m$ [-] |
| $D$    | diffusion constant of the substrate in the film supporter [cm$^2$/sec] |
| $E$    | exact value of the effectiveness factor [-] |
| $E_A$  | effectiveness factor given by Eq. (3) [-] |
| $E_C$  | effectiveness factor given by Eq. (6) [-] |
| $E_G$  | effectiveness factor given by Eq. (5) [-] |
| $K_m$  | Michaelis constant [mol/cm$^3$] |
| $L$    | thickness of the film reactor [cm] |
| $M$    | Thiele modulus defined by Eq. (2) [-] |
| $m_A$  | modulus defined by Eq. (1) [-] |
| $m_G$  | general modulus defined by Eq. (4) [-] |
| $V_{max}$ | maximum velocity of the Michaelis-Menten equation [mol/cm$^3$.sec] |

**Literature Cited**