LETTERS TO THE EDITOR

To the Editor:

In a recent paper by R. K. Sharma and R. D. Srivastava [*AIChE J.* 27 41 (1981)] a statistical interpretation of rate data relative to certain rate equations for toluene and methanol oxidation on vanadium catalysts is presented. While the statistical methods may be sound per se, it appears that some of the conclusions are rather meaningless due to lack of appropriate data. For example, table A1 reveals that the oxygen partial pressure, p_B, is nearly constant at 0.2 atm in all experiments with toluene oxidation. The corresponding statement holds for methanol oxidation also with $p_B \simeq 0.18$ atm. Yet the erratic temperature dependence of the regressed value of K_B (multiplier to p_B), as well as the insignificance of the determined values, leads the authors to a rejection of model SSAOD-4. Examination of the model expression and of the values of $K_B \cdot p_B$ shows that $K_B \cdot p_B \gg 1$ and that $K_B \cdot p_B$ is nearly constant for all runs, in which case model SSAOD-4 reduces to $r = k \cdot p_A$. Since the determined variation of k with temperature is reasonable, there appears to be no justification for rejection of model SSAOD-4.

Similarly, model DAOD-4 for methanol oxidation is rejected due to the peculiar temperature dependence of the two determined constants. If the values of K_B at 320°C and at 345°C are assumed to be representative of the size of K_B, then $(K_B p_B)^{1/2} \gg 1$ and model DAOD-4 reduces to $r = (k \cdot K_B^{-1/2}) p_B^{-1/2} \cdot p_A$. The low values of k and K_B simultaneously at 370°C may then be ascribed to the correlation between k and K_B. Indeed, if $k \cdot K_B^{-1/2}$ calculated from the results in table 4 is plotted as function of 1/T a straight line with slope corresponding to an apparent activation energy of 184 kJ/mol·K is obtained.

Thus, it seems as if further data covering larger ranges of the partial pressures are needed to give sufficient support to the statistical analysis presented by Sharma and Srivastava.

Finally, it appears that the rate data given in the last column of table A2 are in error. If the rates at 320°C from that table is multiplied by $(k_B p_B + 0.5\ k \cdot P_A) \cdot P_A^{-1} p_B^{-1}$ (The reciprocal of the pressure dependent part of the authors' accepted rate equation) the constant value $k \cdot k_B = 0.0159 \cdot 0.0091 = 1.447 \cdot 10^{-4}$ $\text{gmol}^2\text{h}^{-2}\text{g}^{-2}\text{atm}^{-2}$ should obtain. However, the products are not constant but show questionable trends with the run number.

TABLE I

Run	Product 10^{-4} gmol²/h²g² atm²	Run	Product 10^{-4} gmol²/h²g² atm²	Run	Product 10^{-4} gmol²/h²g² atm²
1	2.812	6	2.946	11	2.925
2	0.998	7	1.945	12	2.016
3	0.969	8	1.044	13	1.940
4	0.938	9	0.628	14	1.938
5	0.922	10	0.586	15	1.867

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To the Editor:

We appreciate having Stig Wedel's comments on our paper "Kinetics of Selective Oxidation of Toluene and Methanol Over Supported V_2-O_5-Alkali Metal Sulphates" [*AIChE J*, 27, 41 (1981)], brought to our attention. As mentioned in our paper, model SSAOD-4 for toluene and models SSAOD-4 and DAOD-4 for methanol were rejected based on the requirement of the proper trend of the constants with the temperature. The models were also eliminated because they contained at least one parameter that was not significantly different from zero or was negative at the 95% confidence level.

As regards the ranges of the partial pressures of oxygen in the tables A1 and A2, it is seen that the variations are of the same order as those for other reaction components. Figures 3 and 4, however, show the results when the partial pressures are varied over a sufficient range.

Table 5 gives the nonlinear estimates of the parameters for methanol oxidation along with the 95% confidence intervals in which the true values lie. The closeness of fit of the derived kinetic equation to the data was examined by performing different statistical tests on the regression coefficients. The parameters predicted the average rates quite accurately.

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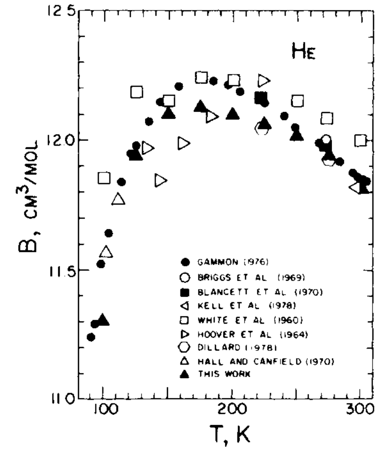
To the Editor:

Holste, *et al* (1980) have presented pure-component and interaction second virial coefficients for the system He-CO_2. Their results (see their Figure 5) for He show a lower B_{He}-T relationship (in the region of maximum B_{He}) than most previous investigations. Exceptions are the works of Hoover, *et al* (1964) and Dillard (1975), whose data lie below those of Holste, *et al.*

I wish to point out that the values of Dillard (1975) are incorrect. A more precise analysis of Dillard's experimental data appears in Dillard, *et al* (1978); these values are in excellent agreement with the results of Holste, *et al.* Table I and a revision of Figure 5 of Holste, *et al* appear above. These two data sets agree to within 0.02 cc/mol at (nominal) temperatures of 0 and −50°C. This substantiation of the results of Holste, *et al* indicates that the maximum in B_{He} is, in fact, lower than that reported by previous investigators.

TABLE I COMPARISON OF HELIUM SECOND VIRIAL COEFFICIENTS

Temperature, T (K)	Second Virial Coefficient B_{He} (cc/mol) Holste (1980)	Second Virial Coefficient B_{He} (cc/mol) Dillard (1978)
223.15	—	12.04
225.00	12.06	—
273.15	—	11.93
273.16	11.95	—



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