Reply to Paper on "Kinetics of Dehydration of *tert*-Butyl Alcohol"

Yamanis, Vilenchich and Adelman (*1*) present an interesting analysis of the data, but the conclusions are questionable.

Estimation of liquid phase activities from equilibrium vapor compositions, as done by Frilette, Mower and Rubin (*2*) is a classical approximation technique and implicitly recognizes the nonideality of the liquid *t*-butanol water system. The results with this technique reflect the increased activity of water due to the presence of small amounts of hydrocarbon (isobutene) in the liquid. The calculated liquid phase activities of Yamanis, Vilenchich and Adelman (*1*) are based on *pure* liquids, giving rise to serious doubt that their estimates are superior to those of Frilette, Mower and Rubin (*2*). In spite of their questionable validity, we shall use the proposed calculated values for the balance of this criticism.

If one assumes about 50% occupation of free sites by alcohol, i.e., assigns a value $K_A = 1$, Eq. (7) [Frilette, Mower and Rubin (*2*)] reduces to:

$$\frac{R}{\alpha_A}(\alpha_A + 1) = k_3 - K_W R \frac{\alpha_W}{\alpha_A}.$$

in which equation α_A and α_W are the activities of alcohol and water calculated by Yamanis, Vilenchich and Adelman (*1*).

Least squares fit of the data in Table 1 [Frilette, Mower and Rubin (*2*)] give positive values for k_3 and K_W. These values are acceptable and reasonable, highly significant in the *t* test, and provide a fit to the theoretical curve which is judged about within the error of experiment (see Fig. 1). The variation in the values of k_3 and K_W with larger quantity of catalyst and larger particles probably reflect increased experimental error in the high rates (due to fast accumulation of water) and a residual diffusion effect, respectively.

If one assumes low coverage, i.e., K_A is small compared to 1, then Eq. (7) reduces to:

$$\frac{R}{\alpha_A} = k_3 K_A - K_W R \frac{\alpha_W}{\alpha_A}.$$

Least squares fit for this case gives positive values for k_3K_A and K_W which also are reasonable and fit the data well.

We agree with the Houghen and Watson criterion that for a model to be acceptable the least squares estimate of the parameters must be nonnegative, *provided the least squares analysis is valid.* The *almost* linear interdependence of α_A and α_W in Eq. (11) (*1*) makes the least squares analysis very sensitive to small errors in the data. Exact linear dependence would, of course, lead to a singular least squares matrix, and no solution could be obtained. Our least squares analysis indicates that the coefficient of α_W in Eq. (11) is not statistically

TABLE 1
LEAST SQUARES VALUES FOR k_3 AND K_W ($K_A = 1$)

	1.14 Meq catalyst, 75–125 μ size		4.44 Meq catalyst, 75–125 μ size		2.82 Meq catalyst 150–500 μ size		Combined data	
	Value	SD	Value	SD	Value	SD	Value	SD
k_3	120.1	5.7	95.3	13.6	89.6	9.7	104.5	7.8
K_W	18.6	1.3	17.7	3.1	14.8	2.4	17.7	1.9

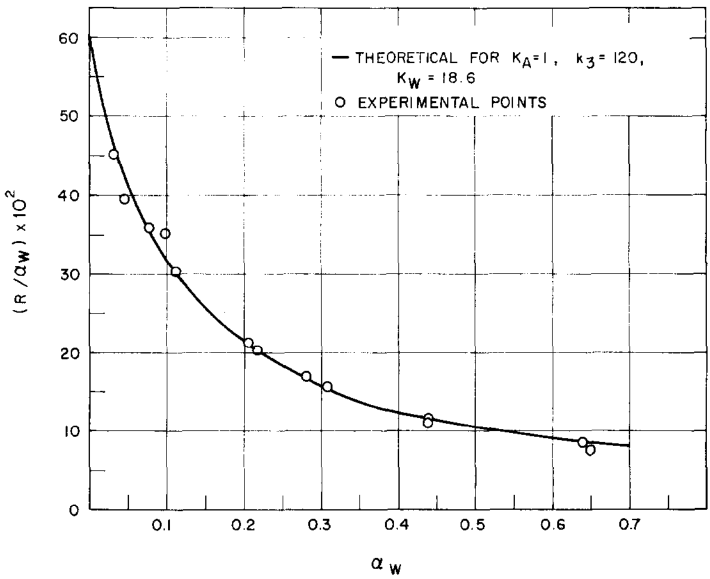

FIG. 1. Fit of experimental data with Yamanis' values for α_A and α_W.

significant ($t = 0.376$) and that α_A and α_W are highly correlated ($R = -0.9949$). Under these circumstances, the negative parameter could be simply a reflection of a minor systematic bias, such as the small temperature change; or the heavy weighting of errors for the low rates by the particular form of Eq. (11). Whatever its source, it is questionable that the least squares analysis as done by Yamanis, Vilenchich and Adelman is valid. Put another way, we have demonstrated that a negative parameter is not *required* by the data to give an acceptable fit, and that there is no cause to reject the model.

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