A Note on the Additivity of Diffusional Resistances

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The additivity of resistances to mass transfer between phases, as postulated by the Whitman two-film theory of 1923, has become an accepted concept in chemical engineering. In an experimental test of this principle, the authors recently reported a study (*1*) of the rate of transfer of fifteen different solutes between liter portions of isobutanol and water in a moderately stirred vessel under conditions such that the interface was essentially flat and of known area.

The over-all resistance (reciprocal of over-all coefficient K_W) was found to be a linear function of the distribution coefficient $1/m$, as called for by the theory, and individual coefficients were obtained from the intercepts and slopes of plots of $1/K_W$ vs. $1/m$.

Individual coefficients k_{IW} for isobutanol into water and k_{WI} for water into isobutanol were also obtained experimentally in extraction tests using water and dry isobutanol, with no third solute present. The agreement between these measured values and those obtained from the analysis of the data on over-all coefficients was only fair for k_{IW} and was poor for k_{WI}.

In analysis of the data to make this comparison it was necessary to correct for variations in molecular diffusivities, and values of both D_{IW} and D_{WI} were taken to be 10.0×10^{-6} sq. cm./sec., based on the estimation from the Wilke correlation (*6*) and on experimental data for the diffusivity of *n*-butanol into water (*3*) and water into *n*-butanol (*5*) taken for a dilute solution. All these gave values in the region of the value used.

Two sets of experimental values of diffusivities have recently become available, and it is worth while to recompute the comparison of individual coefficients. Heertjes, Holve, and Talsma (*2*) report values for D_{IW} and D_{WI} at 20°C. of 6.0×10^{-6} and 2.0×10^{-6} sq.cm./sec., and Lewis (*4*) has obtained values of 8.4×10^{-6} and 3.6×10^{-6} at the same temperature.

On the basis of these new values of diffusivity (adjusted to 25°C.) the values of k_{IW} and k_{WI} obtained from the over-all coefficients for various solutes (from intercepts and slopes of the resistance plot) show much better agreement with the values obtained by direct experiment:

	From over-all coefficients, cm./hr., by use of diffusivities from			By direct experiment cm/hr.
k_{IW}....	8.0	9.4	9.6	8.36
k_{WI}....	5.4	7.2	11.0	5.9

The new values fall on both sides of those obtained by direct experiment. Evidently the poor comparison reported was due in large part to the use of incorrect values for D_{IW} and D_{WI}.

Figure 1 compares K_W as calculated from the two sources of values for the individual coefficients. Curves *A* and *B*, representing the comparison based on the new experimental values of diffusivities, straddle the solid line representing complete agreement, and both compare much better than curve *C*, previously presented on the basis of estimated values of D_{IW} and D_{WI}. As in the original paper, the transfer coefficients are assumed to be proportional to the square root of the molecular diffusivity.

The data on mass transfer of a number of solutes between stirred volumes of isobutanol and water not only support the additivity concept over a wide range of distribution coefficients, but now appear to agree with the data on individual coefficients.

LITERATURE CITED

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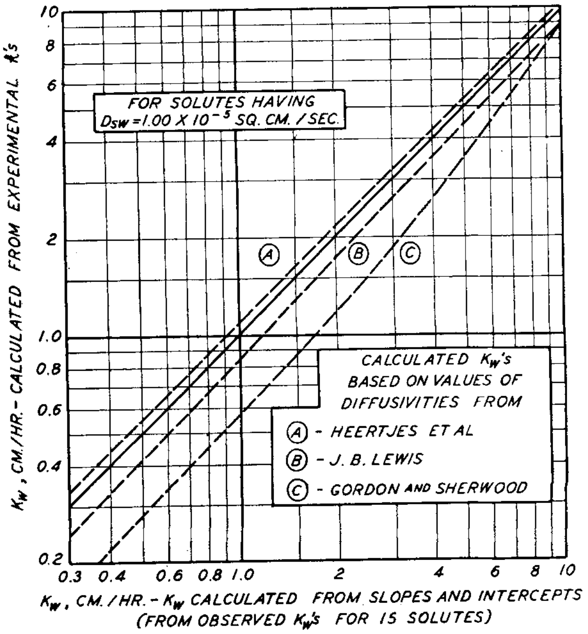

FIG. 1.