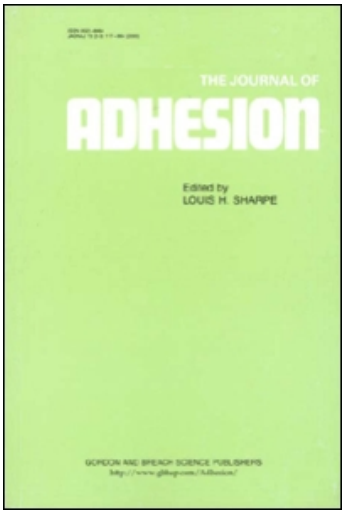

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Reply to A. W. Neumann

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To cite this Article Huntsberger, J. R.(1977) 'Reply to A. W. Neumann', The Journal of Adhesion, 9: 1, 93 — 94
To link to this Article: DOI: 10.1080/00218467708075103
URL: http://dx.doi.org/10.1080/00218467708075103

J. Adhesion, 1977, Vol. 9, pp. 93–94

Printed in Scotland

REPLY TO A. W. NEUMANN

Dear Sir,

A. W. Neumann's comments indicate to me that he has misinterpreted both the intent and some of the substance of my paper.

I wished to present a simple, coherent framework which would provide easy access to some of the important aspects of surface chemistry, their interactions, and relationships to adhesion.

To do so I used Good's parameter ϕ in the same sense in which it was first introduced by Girifalco and Good.[1] I elected to adopt the *premise* that ϕ made my Eq. (1) exact.

I thought I had made it clear that ϕ cannot now be calculated exactly and because of experimental difficulties cannot usually be measured accurately.

I do not recognize that the concept of exactness is restricted to differential equations.

I used several equations which were basic to my argument in which the frequently ignored spreading pressure π_e was included. These equations have been shown to be correct based on Gibbs' thermodynamics. I view the word fundamental as having meaning and validity outside of Gibbs' work and felt free to use it in the intended context.

I did, in fact, generate a series of figures using arbitrarily selected values for ϕ. Despite Dr. Neumann's views, I believe these allow considerable insight into the behavior of real materials since experimental data can be located on these coordinate systems to show approximate values of ϕ, and consequently provide reasonable estimates for W_{adh} using my Eq. (1).

I believe Dr. Neumann does both me and his readers a disservice by suggesting that I implied any "dogma" nor even any special significance to curves of constant ϕ. I did not; nor did I state that the N, G, H and S plots were in any way unsatisfactory because they are not curves of constant ϕ. I did imply that the pertinent information and desired inferences were more easily accessible and more readily interpreted in terms of these simple basic equations than from the N, G, H and S plots.

In Dr. Neumann's paper[2] the following statement appears: "The liquid surface tension $(\gamma_{LV})^*$—is the surface tension of the hypothetical liquid in a series for which the contact angle just equals zero."

Since that statement is virtually identical with Zisman's definition for γ_c it seems that equating the two is reasonable. Neither of these terms has any

fixed value without qualification. Within my premise of Eq. (1), γ_c is fixed as $\gamma_c = \phi^2\gamma_{SO}$.

Dr. Neumann is correct in saying he did not introduce the quantity $(\gamma_{SV})^*$ into his paper. I must confess that since all of the other related values $((\gamma_{SL})^*$, $(\gamma_{LV})^*$ and (ϕ^*) were so designated, I expected his Eq. (13):

$$\gamma_{SV} = (\gamma_{LV})^*$$

was intended to be also so qualified and the notation $(\gamma_{SV})^*$ was my own.

Dr. Neumann used Eq. (117) in the paper by Good and Elbing[3] to obtain his Eq. (11); in so doing he substituted $(\gamma_{LV})^*$ for γ_c, so while γ_c does not appear explicitly in the N, G, H and S paper it *is* there by virtue of that substitution.

Dr. Neumann in his comments again attributes to me statements which I not only did not make, but which I believe are wrong. I never used $\phi(\gamma_{SV})$. Good's ϕ is $\phi(\gamma_{SO}, \gamma_{LV}, \gamma_{SL})$.

Dr. Neumann, himself, on the other hand, elsewhere[4] used $\phi(\gamma_{LV})$ which is certainly not Good's ϕ.

Since the cases involved in this discussion are for given solid surfaces, the value for $d\phi/d\gamma_{SL}$ will be constant for a given γ_{LV} and consequently will be constant for either $(\gamma_{SO}\gamma_{LV})$ or $(\gamma_{LV}/\gamma_{SO})$. I simply expressed this in terms of the abscissas of my plots.

Dr. Neumann's differentiation of $d\phi/d\gamma_{SL}$ where $\gamma_{SL} = \gamma_{SL}\ (\gamma_{SV}, \gamma_{LV})$ includes in the second term a factor $\partial\gamma_{SV}/\partial\gamma_{SL}$. Since his equations are based on no adsorption it is evident that this term is zero. In the third term the factor $\partial\gamma_{LV}/\partial\gamma_{SL}$ is also zero since use of contact angles requires duplex films and by definition, for duplex films $d\gamma_{LV}/d\gamma_{SL} = 0$.

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(*Received May 20, 1977*)

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