The preparation of crystalline *d*-threose triacetate (well-built prisms, m. p. 113–114°, $[\alpha]_D^{20}$ in $CHCl_3$ + 35.5°) by the degradation of strontium *d*-xylonate was described before the Division of Organic Chemistry of the American Chemical Society in Chicago, September, 1933, and with additional data will form the subject of an early communication.

NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.
RECEIVED MARCH 10, 1934

COMMUNICATIONS TO THE EDITOR

NON-ELECTROLYTE SOLUTIONS

Sir:

The author's equation for certain non-electrolyte solutions[1] has recently been seriously misinterpreted, doubtless because of the extremely brief form in which it was presented. For binary solutions the final equations may be expressed in the form

$$\Delta H = \Delta F - RT\,(n_1 \ln x_1 + n_2 \ln x_2) = \frac{A\,V_1 V_2 n_1 n_2}{n_1 V_1 + n_2 V_2}$$

$$\Delta\bar{F}_2 - RT \ln x_2 = \frac{A\,V_2 V_1^2 n_1^2}{(n_1 V_1 + n_2 V_2)^2}$$

where $\Delta\bar{F}_2$, ΔF and ΔH are the changes of the chemical potential per mole of the second component, of the free energy, and of the heat content of the system, respectively, n_1 and n_2 the mole numbers of the components, V_1 and V_2 their molal volumes and x_1 and x_2 their mole fractions. A is independent of the composition at constant temperature and pressure.

The relation of A to the temperature was not explicitly stated, but, recalling the Gibbs–Helmholtz relations, we see that, at constant composition, the second member of the first equation, and therefore the third, must be independent of the temperature. This can be true for all compositions only when the coefficient of expansion, α, is the same for the two components, and then only if $A\,V_1$ and $A\,V_2$ are independent of the temperature. Negishi, Donnally and Hildebrand[2] apparently failed to see this necessity, consider it "implied in Scatchard's treatment" that A is independent of the temperature, and discuss "the applicability of an equation derived by Scatchard" on this basis. The variation they find is very largely that of $1/V_2$.

When the two components do not have the same α and, as in the case discussed, the temperature and composition cannot be varied independently, the applicability of the equation as an approximation may be tested in either of two ways. The isothermal equation may be taken as exact and any change in $A\,V_2$ attributed to changing temperature by measuring the volumes at the temperatures in question; or the constant-composition equation taken as exact and any change in $A\,V_2$ attributed to changing composition by measuring all the volumes at some standard temperature. The author has used the second method.[1,3] The results of the two methods differ very little in the present case, and the mean deviation from the average varies only from 0.9 to 1.8% for the four solvents. The corresponding deviation of k in Hildebrand's equation is about the same in two cases, much better in the case of $TiCl_4$, which may be considered a coincidence, and very much poorer for $C_2H_4Br_2$, which is very likely not a fair test. These measurements add very little to the comparison of the two equations. There is no significant change in the relation of A to the value calculated from the energies of evaporation of the components.

Negishi, Donnally and Hildebrand state that "it would be preferable to substitute for" my expression of A an expression which seems to me ambiguous. If the a's in their equation (8) are the same as in the equation immediately preceding, the method they suggest is identical with mine; if the a's are the same as in equation (7), the substitution seems to me undesirable. A more detailed justification of the method I used is given by Hildebrand and Wood.[4]

These authors derive the second equation above and say, "The same equation has been given by Scatchard by the aid of some of the same assumptions as here employed, plus the arbitrary one

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(1) G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

(2) G. R. Negishi, L. H. Donnally and J. H. Hildebrand, THIS JOURNAL, **55**, 4793 (1933).

(3) G. Scatchard, *ibid.*, **53**, 3186 (1931).

(4) J. H. Hildebrand and S. E. Wood, *J. Chem. Physics*, **1**, 817 (1933).

that the cohesive energy of a mole of mixture is given by the expression...." In my original paper the justification of this expression was, "For non-ideal solutions also we shall neglect the change in volume, and we shall consider only the case in which the interaction between any pair of molecules is independent of the composition. We may then split the cohesive energy of a mole of the mixture in the following way...."[1] The second statement is, therefore, not arbitrary, but depends on the first, which still appears to me to contain all the necessary assumptions. The statement of them is, however, extremely brief and a fuller statement has been published only in a journal so inaccessible to American readers that it seems worth while to quote: "(1) *The volume change on mixing is zero.* (2) *The mutual energy of any two molecules depends only on the distance between them and their relative orientation, but not at all upon the kind of matter between or around them.* (3) *The distribution of the molecules in position and in orientation is random.*"[5] Except for the explicit statement of the second assumption, I can therefore find no difference between my assumptions and those of Hildebrand and Wood.

(5) G. Scatchard, *Kemisk Maanedsblad* (Copenhagen), **13**, 77 (1932).

CONTRIBUTION NO. 330 GEORGE SCATCHARD
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
RECEIVED JANUARY 24, 1934

Sir:

I am glad to acknowledge the above correction by Professor Scatchard concerning the variability with temperature of the constant "*A*" of his equation. I might attempt to give a justification of my interpretation of his language but that would have little point. The paper by Negishi, Donnally and Hildebrand, although published later than that of Hildebrand and Wood, was written much earlier, when Professor Scatchard's intentions were less clearly discernible from his very brief presentation than they became upon fuller examination.

I would like to emphasize that the slight temperature trends in the values of "*A*" shown by the solubility data we presented seem to me far less important than the remarkable agreement they show with the values calculated from the data for the pure components, which should be a source of satisfaction to Professor Scatchard. The constant "*k*" in my earlier equation is less significant theoretically than the "*A*" and is interesting now chiefly as a simple semi-empirical method practically applicable to many solutions.

The point made by Professor Scatchard concerning our Equation 8 is correct. We neglected to designate the "*a*" therein by type differentiating it from the "*a*" in Equation 7, which is his; if this is done it does not differ from 7.

In designating as an "arbitrary assumption" the particular equation referred to in the last paragraph of the above communication I did not intend to imply that it might not have a logical basis in Professor Scatchard's mind, but rather that the single sentence with which it was introduced could serve to a reader as but a slender basis for it, less convincing even than the derivation on the basis of the van der Waals equation, offered by van Laar in his prior publication of essentially the same equation. I have no quarrel with the equation itself, and I hope that this communication will remove any suspicion that Professor Scatchard and I differ in any important respects in our views regarding the validity of the methods we have both utilized.

DEPARTMENT OF CHEMISTRY J. H. HILDEBRAND
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
RECEIVED FEBRUARY 12, 1934

AN IRON COMPOUND OF GLUCONIC ACID

Sir:

In attempting to prepare a new iron compound, more suitable for the treatment of secondary anemia than the preparations now in use, we have been investigating the possibility of combining iron with certain polyhydroxy acids.

When 3 moles of calcium gluconate, dissolved in hot water, was treated with a solution of 1 mole of ferric sulfate, a reaction occurred with the formation of an almost quantitative amount of calcium sulfate. A normal salt, ferric gluconate, could have been expected, but, when the solution was filtered and the filtrate precipitated with four volumes of alcohol, the resultant compound was found to contain 19.6% of iron instead of the 8.7% calculated for the normal salt. Repeated experiments gave the same result. The reaction takes place quite as readily when both ingredients are suspended in water and the suspension is heated.