The preparation of crystalline *d*-threose triacetate (well-built prisms, m. p. 113–114°, $[\alpha]^{20}_{D}$ 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

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

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

where $\Delta\overline{F}_2$, 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.

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(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.

The purified compound was obtained in the form of light yellow amorphous powder, easily soluble in water, and stable in solution as well as in solid form. When it is exposed for a long time to the action of direct sunlight, it changes its color from yellow to greenish-gray. The solution is yellow in color when dilute, cherry-red when concentrated, and has a ferruginous taste. It is acid to litmus, and can be neutralized and even made distinctly alkaline to litmus by adding sodium carbonate or sodium hydroxide, without precipitating iron. When the solution was titrated with sodium hydroxide, using an external indicator, the amount of alkali closely correponded to the amount necessary for the formation of a sodium salt of basic ferri-gluconic acid, which can be isolated from a neutralized solution by precipitation with alcohol. The usual quantitative tests show that the iron in our compound is in ferric condition.

Elementary analysis and other experimental evidence suggests that the compound is a basic ferri-gluconic acid rather than one in which the iron is attached to the chain with all three valences, as in the complex iron and barium compounds of certain polyhydroxy alcohols and acids prepared by Traube, Kuhbier and Harting [*Ber.*, **66**, 1545 (1933)].

Anal. Calcd. for $C_6H_{13}O_9Fe$: C, 25.28; H, 4.60; Fe, 19.61. Found: C, 25.86; H, 4.61; Fe, 19.60.

The position of the iron in the chain is as yet not definitely determined. There is evidence of intermediate compounds containing sulfur being formed in the course of the reaction, the mechanism of which we continue to study.

Clinical tests of the compound have proved it to be of definite value in the treatment of secondary anemia.

RESEARCH LABORATORY A. PROSKOURIAKOFF
DEPARTMENT FOR DISEASES OF THE CHEST
JEFFERSON HOSPITAL R. J. TITHERINGTON
PHILADELPHIA, PENNSYLVANIA

RECEIVED FEBRUARY 19, 1934

THE VALIDITY OF FREUDENBERG'S DISPLACEMENT RULE

Sir:

The importance of Freudenberg's displacement rule, especially as it is founded on optical dispersion and absorption spectra, cannot be overemphasized; for it permits the determination of the optical configuration of such substances as α-chloropropionic acid [W. Kuhn, Freudenberg and Wolf, *Ber.*, **63**, 2367 (1930)] and methyl-tertiary-butylcarbinol [Stevens, THIS JOURNAL, **55**, 4237 (1933)] when direct chemical methods fail due either to Walden inversion or to rearrangement.

Recently Levene and Meyer [*ibid.*, **56**, 244 (1934)] reported to have found two legitimate exceptions to the displacement rule. Obviously, any such exceptions would throw doubt on the validity of the configurations of the substances mentioned above. For this reason the pertinent part of Levene and Meyer's work has been carefully repeated with the result that their first exception has been found to be incorrect.

TABLE I

$[M]^{25}_{D}$

	Free acid	Ethyl ester	*p*-Nitrophenyl ester	
1 $C_2H_5—CH[CH_3]—COOH$	−18.0	−22.9	−52.5	
2 $C_4H_9—CH[CH_3]—COOH$	−24.3	−30.7	−65.7	
3 $C_2H_5—CH[CH_3]—CH_2—COOH$	−10.4	−11.5	−20.0	
4 $C_3H_7—CH[CH_3]—CH_2—COOH$	+ 3.6	+ 0.7	+ 5.0	**−5.4**
5 $C_5H_{11}—CH[CH_3]—CH_2—COOH$	+ 8.1	+ 4.2	+11.2	

The table contains the values found by Levene and Meyer for the rotations of five configurationally related acids and esters. The corrected value as determined by the author for the rotation of the *p*-nitrophenyl ester of methylpropylpropionic acid [No. 4 in table] is in bold-faced type. According to this corrected value, the shift in rotation, as evidenced by the change in sign on passing from the ethyl to the *p*-nitrophenyl ester is in complete accord with the displacement rule.

An investigation of Levene and Meyer's second exception, that of methylamylpropionic acid and esters [No. 5 in table] is now in progress.

Levo β-Methyl-β-propylpropionic Acid.—The acid was prepared from 2-bromopentane and ethyl malonate and resolved with cinchonidine according to the directions of Levene and Marker [*J. Biol. Chem.*, **91**, 77 (1931)]. After resolution the acid was dissolved in aqueous sodium carbonate and washed with alcohol-free ether. The solution was then acidified, and the acid extracted with alcohol-free ether: b. p. (17 mm.) 113.5–114.5°, (bath 150°). This material was redistilled: b. p. (14 mm.) 109.0–109.5° (bath 142°), α^{25}_{D} −1.53°, $[M]^{25}_{D}$ −2.19°, d^{25}_{4} 0.9111, n^{25}_{D} 1.4190, *Molecular Refraction.* Calcd. 36.06; found 36.06.

Dextro *p*-Nitrophenyl Ester of Levo β-Methyl-β-propylpropionic Acid.—Ten grams of the acid [α^{25}_{D} −1.53°] was treated with 30 cc. of redistilled thionyl chloride. The mixture was boiled for two hours on the steam-bath, and then allowed to stand overnight. The next morning the excess thionyl chloride was removed *in vacuo.* Dry benzene was added and the material again boiled out *in vacuo*. This was done three times. The resulting colorless acid chloride was taken up in benzene and added to a benzene suspension of 12.3 g. of sodium *p*-nitrophenoxide. Considerable heat was evolved at the outset. The reaction was completed by boiling for two and one-half hours on the steam-bath. The mixture was then cooled, thoroughly extracted with water, aqueous sodium carbonate and water, dried over sodium sulfate and evaporated *in vacuo* at 95°. The crude phenolic ester, 15.5 g., yield 80%, was distilled in a Hickman molecular still at 0.001 mm. (bath 100°) taking two fractions, (A): α_D^{24} +1.51°, n_D^{25} 1.5106; (B) α_D^{24} +1.20°, n_D^{25} 1.5114. There was almost no residue. (A) and (B) were combined and redistilled in a Claisen flask yielding (C): b. p. (0.3 mm.) 128–135° (bath 176°), α_D^{23} +1.51°, d_4^{25} 1.1128, n_4^{25} 1.5109, and a residue (1 cc.) α_D^{23} +0.70°, n_D^{25} 1.5120. The former (C) was then separated into two fractions at 0.15 mm. (bath 160°), (E) b. p. 118–123°, $\alpha_D^{23.5}$ +1.52°, n_D^{25} 1.5114; (F) b. p. 124–125°, α_D^{23} +1.45°, $[M]_D^{25}$ +3.27°, $[M]_D^{25}$ max. +5.4°, d_4^{25} 1.1121, n_D^{25} 1.5113. Fractions (E) and (F) were light yellow and gave only a weak Beilstein test for halogen. The residue (0.5 cc.) was orange, dextrorotatory and gave a stronger Beilstein test for halogen.

Anal. (micro). Calcd. for $C_{13}H_{17}O_4N$: C, 62.12; H, 6.82; N, 5.58. Found: Fraction C: C, 62.00; H, 6.82; N, 5.52. Fraction F: C, 62.22; H, 6.66; N, 5.63.

Sodium *p*-Nitrophenoxide.—This salt was thrice recrystallized from water, dried at 120° *in vacuo* for twenty-four hours and allowed to cool *in vacuo* over phosphorus pentoxide. It was bright red and when hydrolyzed with dilute hydrochloric acid, formed *p*-nitrophenol, m. p. 110–112°.

THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CONTRIBUTION NO. 109 PHILIP G. STEVENS

RECEIVED MARCH 15, 1934

SOME PROPERTIES OF HEAVY WATER

Sir:

Experience gained in the production of comparatively large quantities of heavy water leads us to believe that the maximum density attainable by the electrolytic method is somewhat greater than that reported by Lewis and Macdonald [THIS JOURNAL, **55,** 3057 (1933)] for water containing less than 0.01% light hydrogen. Lewis and Luten [*ibid.*, **55,** 5061 (1933)] state the ratio of specific gravities of heavy and light waters at 25° to be 1.1056. We find d_{25}^{25} 1.1079. We also find the difference in refractive indices to be −0.00462 at 20° for the sodium D line.

Such water, of which we have prepared over 100 cc., has been subjected to prolonged electrolysis in order to determine whether any further increase in density takes place. For this purpose 25 cc. of maximum density water was placed in a carefully dried cell with 2% pure NaOD. The electrolytic gas was passed through a trap to remove spray and was ignited at a minute nozzle. The recovered water was not allowed to come into contact with the atmosphere. The density of the recovered water was taken at approximately 1-cc. intervals. The densities plotted against total weight recovered are shown in Fig. 1. Some time after constant density had been reached, the residual water in the cell was removed and repeatedly distilled. The density d_4^{20} was 1.1059. The fact that only 95% heavy water was obtained in the first 2 cc. illustrates the extreme readiness with which pure D_2O takes up moisture from the air and possibly from the glass walls of the apparatus. A cc. of water d_4^{20} 1.1038 was exposed to the atmosphere overnight and the density fell to 1.1016. Pure D_2O must be handled like any other anhydrous liquid.

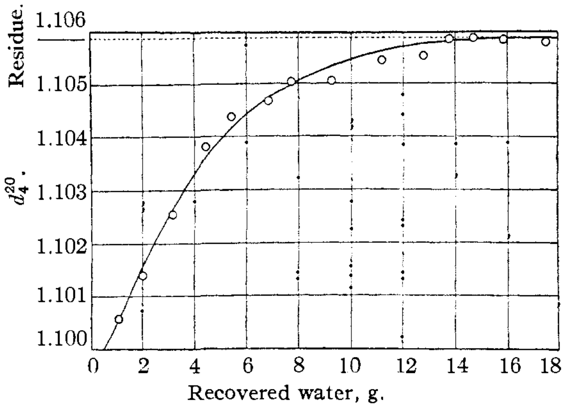

Fig. 1.—Density of recovered water in prolonged final electrolysis.

The ratio of the specific rates of discharge of light and heavy hydrogen at these high concentrations is about 6, which in view of the fairly large probable error cannot be considered as sensibly different from that obtaining throughout the more dilute stages of the process with either iron or nickel electrodes.

We find the freezing point of our maximum density water to be 3.82°, and the viscosity at 20°, 12.6 millipoises. An earlier report on the viscosity by Selwood and Frost [THIS JOURNAL, **55,** 4335 (1933)] was marred by an unfortunate error in calibration.

It may be of interest to add that prolonged fractional freezing of 90% D_2O has yielded no concentration. This is the result to be expected from the work of La Mer, Eichelberger and Urey [*ibid.*, **56**, 248 (1934)] on the freezing points of isotopic mixtures. Experience in the concentration of D_2O from tap water has shown that the ratio D_2O/H_2O in natural water is about 1 in 5 or 6 thousand, in agreement with the mass spectrographic study of Bleakney and Gould [*Phys. Rev.*, 41, 265 (1933)].

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
HUGH S. TAYLOR
P. W. SELWOOD

RECEIVED MARCH 21, 1934

THE NATURAL SEPARATION OF THE ISOTOPES OF HYDROGEN

Sir:

The densities of water obtained from the Atlantic Ocean,[1] from the Dead Sea and the Great Salt Lake and from the hydrated mineral rasorite are greater than that of fresh water by several parts per million, thus indicating a natural isotopic fractionation of water presumably by distillation.[2] The discoveries of Lewis and of Taylor, Swingle, Eyring and Frost[3] of the inability of living organisms to live or to grow in deuterium oxide have suggested the possibility of a natural selection of protium in preference to deuterium in the animal and vegetable kingdom. On the other hand, dilute solutions of deuterium oxide seem to stimulate physiological activity,[4] a fact which would lead one to predict that deuterium could possibly be concentrated physiologically. Washburn and Smith[5] have found that in the case of a growing willow tree an isotopic fractionation of hydrogen in the direction of a preferential selection of deuterium does occur.

Before this interesting work of Washburn and Smith was known to me, I had begun an investigation of the relative abundance of deuterium in organic compounds by burning the compounds in air or oxygen, condensing the resulting water vapor and measuring the density of the water after purification. Kerosene from the Oklahoma oil fields and Mallinckrodt thiophene-free benzene obtained in the destructive distillation of coal were separately burnt at the surface of a sintered glass wick in an atmosphere of dried air until 600 cc. of water had been condensed in each case. After careful purification the water from kerosene had a density seven parts per million greater than that of ordinary water while the benzene water was about eight parts per million heavier. Water obtained from the combustion of honey was four parts per million heavier than that of ordinary water. These data are comparable to the results of Washburn and Smith, who found that water from the combined hydrogen in the willow tree was between five and six parts per million more dense than ordinary water. I hope to investigate natural products of an animal origin in the near future.

The data for kerosene may shed some light on the origin of petroleum.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
MALCOLM DOLE

RECEIVED MARCH 21, 1934

ACCELERATED DIFFUSION IN DYE SOLUTIONS

Sir:

In a recent paper [THIS JOURNAL, **56**, 52 (1934)], McBain and Dawson give striking illustrations of accelerated diffusion, of electrolytes in aqueous solution, through a porous glass membrane. We wish to draw attention to another type of accelerated diffusion which has recently been observed in this Laboratory. Our observations are for the free diffusion of azo dyes in the presence of electrolytes as determined by the Fürth [*Kolloid-Z.*, **41**, 300 (1927)] micro-diffusion method. This method is particularly adaptable to observation of effects arising from rapid motion of color ions, and gives results with an average experimental variation of less than 5%.

When an aqueous solution of the sodium salt of *p* - sulfobenzene - azo - benzene - azo - 6 - benzoylamino-1-naphthol-3-sulfonic acid and sodium chloride is allowed to stand for a month at 25°, the rate of diffusion of the color ion is markedly affected by the presence of sodium chloride in the solution into which diffusion occurs. The results are summarized in Table I.

Numerous attempts were made to carry out diffusion from dye solutions containing 1.0 g./l. of sodium chloride, into sodium chloride solutions varying from 0.75–1.0 g./l. concentration. In every instance, measurement of the diffusion constant proved impossible owing to an accel-

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(1) E. S. Gilfillan, Jr., THIS JOURNAL, **56**, 406 (1934).

(2) Bur. Standards Tech. News Bull. 196, August, 1933.

(3) G. N. Lewis, THIS JOURNAL, **55**, 3503 (1933); H. S. Taylor, W. W. Swingle, Henry Eyring and A. A. Frost, *J. Chem. Physics*, **1**, 751 (1933).

(4) T. C. Barnes, THIS JOURNAL, **55**, 4332 (1933); *Am. J. Bot.*, **20**, 681 (1933); S. L. Meyer, *Science*, **79**, 210 (1934); O. W. Richards, *Am. J. Bot.*, **209**, 679 (1933).

(5) E. W. Washburn and E. R. Smith, *Science*, **79**, 188 (1934).

TABLE I

VARIABLE DIFFUSION OF *p*-SULFOBENZENE-AZO-BENZENE-AZO-6-BENZOYLAMINO-1-NAPHTHOL-3-SULFONIC ACID (SODIUM SALT)

Solution (g./l.) of		Age of dye solution	Diffusing into NaCl solution, g./l.	*T*, °C.	$D \times 10^{-6}$ sq. cm./sec.
Dye	+ NaCl				
1.0	1.0	90 hours	...	27	2.39
1.0	1.0	90 hours	0.5	27	2.47
1.0	1.0	90 hours	.75	27	Not measurable
1.0	1.0	4 weeks	...	29	2.14
1.0	1.0	4 weeks	.5	30	3.03
0.5	1.0	48 hours	...	29	3.13
.5	1.0	48 hours	.5	30	3.22
.5	1.0	3.5 weeks	...	25	2.12
.5	1.0	3.5 weeks	.5	26	3.18
.5	1.0	3.5 weeks	.125	25	2.58
After addition of 1.0 g./l. NaCl to preceding dye solution					
0.5	2.0		...	26	2.20
.5	2.0		1.0	26	2.08

erated diffusion which produced a marked distortion of the color boundary within two to three minutes. The distortion is best described as the formation of small spearheads of color projecting for a distance of 0.5–1.0 mm. into the salt solution. This breaking of the color boundary may result in diffusion of dye throughout the entire cell chamber within a few minutes.

Possibility that the accelerated diffusion is produced by density differences in the two solutions is ruled out by the fact that the more dense solution is in the lower part of the cell. It was shown in a number of tests that, when the solution in the upper half of the cell is of the greater density, a turbulent mixing occurs in which the dye is partially displaced from its original compartment within a few seconds. On reversing the positions of the solutions the diffusion occurs as originally described.

Measured increases of 20–50% in the diffusion constant of aged dye solutions into dilute sodium chloride solutions, as compared with diffusion into water, are given in Table I. The diffusion rate into more concentrated salt solutions is increased several fold. The motion of the color ions in the aged dye solution is markedly affected by the presence of sodium chloride in the solution into which diffusion occurs at a concentration as low as 0.125 g./l. With a fresh dye solution no effect on the motion of the color ions is observed until this concentration of sodium chloride is approximately 0.75 g./l. This difference in the sensitivity of the color ions toward salt indicates that, in the aged solution, the dye has adsorbed a large portion of the electrolyte originally added. This marked affinity for electrolytes may account for the accelerated diffusion observed in these experiments.

These observations were made in the course of another investigation, and since further study of the phenomena reported cannot be made by the authors, this brief report is given to draw attention to additional instances of accelerated diffusion.

TECHNICAL LABORATORY SAMUEL LENHER
ORGANIC CHEMICALS DEPARTMENT J. EDWARD SMITH
E. I. DU PONT DE NEMOURS & CO., INC.
WILMINGTON, DELAWARE

RECEIVED MARCH 22, 1934

THE VAPOR PRESSURE OF MIXTURES OF LIGHT AND HEAVY HYDROGEN

Sir:

Although our apparatus was not designed for the purpose, and the amount of gas available was insufficient for accurate work, we have made some preliminary study of the vapor pressures of various mixtures of H^2_2 and H^1_2. These mixtures approximate closely to Raoult's law, as shown in Fig. 1, where the total vapor pressure is plotted against the mole fraction of H^2_2 at 18.65°K.

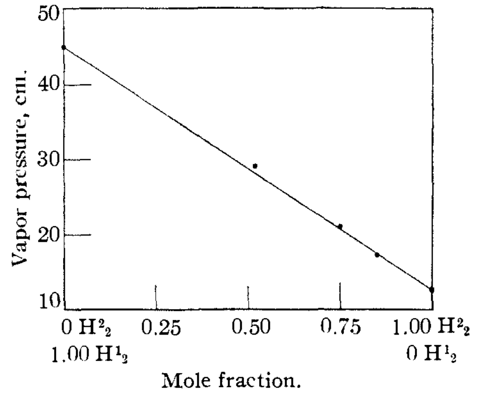

Fig. 1.

The temperature at which freezing begins also proved to be nearly linear with the mole fraction, as shown in Fig. 2, where the ordinate represents the temperature at which the first discontinuity in the vapor pressure curve occurs. In some cases a second discontinuity appeared, showing the final disappearance of the liquid phase. These observations indicate that while the solid phase contains a larger fraction of H^2_2 than the liquid phase, the difference is not great. We estimate that when the mole fraction of H^2_2 is 0.50 for the liquid, it is about 0.55 for the solid.

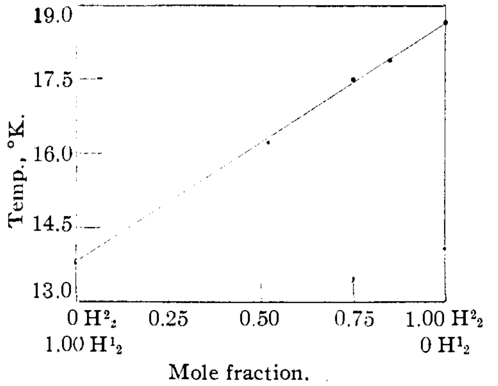

Fig. 2.

All these mixtures contained only the molecules H^1_2 and H^2_2. One mixture containing equal amounts of these two species was later kept for thirty hours in a bulb containing a hot platinum filament in order to produce the equilibrium amount of H^1H^2. The vapor pressure of this mixture was then studied. Unfortunately the amount of the mixture was too small for accurate measurements, but there appeared to be no great difference in vapor pressure before and after treatment with the hot wire.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

GILBERT N. LEWIS
W. T. HANSON, JR.

RECEIVED MARCH 22, 1934

THE VAPOR PRESSURE OF SOLID AND LIQUID HEAVY HYDROGEN

Sir:

In a series of investigations in which we have been aided by Dr. R. T. Macdonald and Dr. P. W. Schutz, to whom we wish to express our great obligation, we have studied the vapor pressure of pure H^2_2, and of mixtures of H^2_2 and H^1_2 (accompanying communication). The vapor pressures have been compared at each temperature with that of ordinary hydrogen in the para form, which has served as our thermometer. Our final measurements with pure H^2_2 are shown in the table and the figure. The ratio of p_2, the vapor pressure of H^2_2, to p_1, that of H^1_2(para), is plotted and tabulated as a function of p_1. The two large circles in the figure show for comparison provisional values which have just been announced by Brickwedde, Scott, Urey and Wahl [*Bulletin of the American Physical Society*, **9**, 16 (1934)].

The centigrade temperature corresponding to each value of p_1 may be obtained from the equation of Keeson, Bilj and van de Horst (Leiden Comm. 217a).

$$t = -260.937 + 1.0270 \log p + 1.7303 \log^2 p$$

Thence we find for $p_1 = 45.40$, corresponding to the triple point of H^2_2, 18.66°K.

TABLE I

p_1	p_2/p_1	p_1	p_2/p_1	p_1	p_2/p_1
77.00	0.3328	44.94	0.2824	41.01	0.2694
61.17	.3119	44.38	.2810	38.06	.2588
51.21	.2954	44.05	.2795	29.22	.2262
47.27	.2883	43.71	.2782	21.56	.1915
46.27	.2861	42.89	.2761	11.85	.1426
45.26	.2844	42.14	.2731		

The choice of an equation of state for heavy hydrogen, and its use in an exact calculation of the heats of vaporization and the heat of fusion from our data, will be discussed in a later publication, together with our apparatus and method.

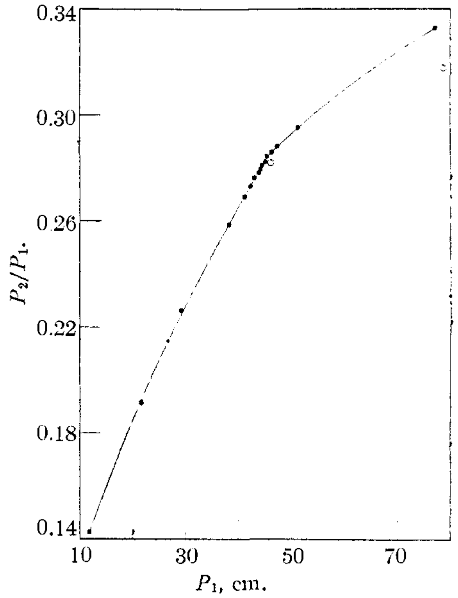

Fig. 1.

The measurements are extremely sensitive to an impurity of light hydrogen. In our first experiment, in which the hydrogen had been produced by the action of heavy water on a fresh sample of sodium, a considerable amount of H^1_2 was found to be present, which undoubtedly came from the sodium. The same sodium was treated again with H^2_2O and the gas still contained 1.5% of H^1. Finally the same sodium was treated with water in which every effort was made to exclude H^1. The impurity of 0.1–0.2% remaining in the gas thus produced was finally eliminated by fractionally distilling at 20°K. After one-half of the liquid had been removed the vapor pressure remained constant to 0.1% upon further fractionation.

After the vapor pressure of pure H^2_2 was measured it was transferred to another tube containing charcoal, with the expectation of finding a different vapor pressure through the establishment of equilibrium between ortho and para forms of heavy hydrogen. To our surprise the vapor pressure at several temperatures fell exactly upon the curve previously obtained. Whether this is due to failure of the charcoal to promote equilibrium or whether the equilibrium had already been established in the tube which contained no charcoal we cannot say. It is possible also that the difference in vapor pressure between the equilibrium H^2_2 at high temperatures and the low temperature form is too small to be observed.

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W. T. HANSON, JR.

RECEIVED MARCH 22, 1934

THE VAPOR PRESSURE OF LIQUID AND SOLID DEUTOCYANIC ACID

Sir:

In our communication on deutacetic acid [THIS JOURNAL, **56**, 493 (1934)] we mentioned the hypothesis that the large difference in vapor pressure between the hydro- and the deuto-forms of such substances as water and ammonia is almost entirely due to the greater strength of the H^2 bond as compared with the H^1 bond. This hypothesis had already been tested in our experiments on the vapor pressure of hydrochloric and deutochloric acids [Lewis, Macdonald and Schutz, THIS JOURNAL, **56**, 494 (1934)]. In that case there is little tendency to form the hydrogen bond and in spite of the low temperature, very little difference in vapor pressure was found.

To test this hypothesis we have chosen hydrocyanic acid, which is a highly abnormal liquid; this abnormality, however, is due not to the hydrogen bond formation but to a high dipole moment. Our measurements show a hardly perceptible difference between the vapor pressure of the two liquids, H^1CN and H^2CN, thus furnishing excellent confirmation of our hypothesis.

There is far more hope of securing a theoretical interpretation of the difference in vapor pressure between two isotopic solids than between two isotopic liquids. For this reason and because in this case the solids have measurable vapor pressures over a considerable range of temperature, we have also studied the two solids.

Our measurements of vapor pressure are given in the accompanying table and can be expressed by the four equations

$$H^1CN(l);\quad \log_{10} p = 7.795 - \frac{1467}{T} \qquad (1)$$

$$H^1CN(s);\quad \log_{10} p = 9.372 - \frac{1877}{T} \qquad (2)$$

$$H^2CN(l);\quad \log_{10} p = 7.695 - \frac{1440}{T} - \frac{175}{T^2} \qquad (3)$$

$$H^2CN(s);\quad \log_{10} p = 9.476 - \frac{1907}{T} \qquad (4)$$

TABLE I

H^1CN		H^2CN	
T, °K.	p, mm.	T, °K.	p, mm.
Solid		Solid	
236.2	27.0	235.3	22.5
241.1	38.5	240.2	34.5
246.7	58.0	245.2	49.0
251.6	82.0	250.5	73.0
256.6	114.0	255.3	101.5
258.4	128.5	260.4	142.5
Liquid		Liquid	
259.3	136.5	265.8	188.0
264.4	178.0	271.3	242.5
270.2	232.0	274.5	281.0
278.5	338.4	276.8	309.6
283.6	425.5	281.9	386.0
288.7	519.0	288.5	507.0
294.0	638.5	293.5	615.7

The measurements of Perry and Porter on liquid H^1CN [THIS JOURNAL, **48**, 299 (1926)] agree within less than 1% with equation (1). For solid H^1CN the agreement between their results and ours is less satisfactory.

The determination of freezing points from measurements of vapor pressure is not accurate. Our equations give 259°K. for the freezing point of hydrocyanic acid and 261°K. for that of deutocyanic acid.

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RECEIVED MARCH 22, 1934

THE IONIZATION CONSTANT OF DEUTACETIC ACID

Sir:

We have measured the conductivity of deutacetic acid in heavy water (97% H^2_2O) at 25° and at the concentrations 0.0722 *M* and 0.1444 *M*, in the same small cell used by Lewis and

Doody [THIS JOURNAL, **55**, 3504 (1933)]. The specific conductivities were respectively 1.83 and 2.59×10^{-4}, both giving for the ionization constant the value 0.59×10^{-5}. Unfortunately the heavy water used had a specific conductivity of 2.3×10^{-5} and in ignorance of the nature of its impurity it is difficult to apply the proper correction. If the whole conductivity of the water is subtracted from the conductivity of the acid the dissociation constant will be lowered by 20%. In any case we have the striking result that the ionization constant is less than one-third as great as that of acetic acid in common water, 1.84×10^{-5}. We hope to repeat this experiment with a purer solvent and also with a stronger acid (monochloroacetic) in order to obtain more accurate ionization constants.

This enormous shift of equilibrium in going from a hydro- to a deuto-compound shows again how much more tenaciously a deuton is held by a pair of electrons of another atom than is a proton. For although the ionization of an organic acid undoubtedly involves the addition of solvent molecules to the un-ionized acid and to the ions, still the main phenomenon is the separation of H^{1+} or H^{2+} from a pair of electrons of a carboxyl oxygen.

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RECEIVED MARCH 22, 1934

NEW BOOKS

Goethe als Chemiker und Techniker. (Goethe as Chemist and Technologist.) By PAUL WALDEN. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. 87 pp. 12 × 15.5 cm. Price, Mk. 2.

In the flood of books about Goethe which were published in 1932, occasioned by the centenary of his death, it is not surprising that there should have been one dealing with Goethe's relationship to chemistry—particularly when one recalls how many-sided was Goethe's genius.

The extent of Goethe's interests and activities in chemistry will, however, I think surprise most readers of this small volume. Joh. Philipp Fresenius, grandfather of Carl Remigius Fresenius, one of the great names in the history of our science, was Goethe's godfather; as an impressionable young man, Goethe's life was saved by the ministrations of an alchemical physician; the chemists Buchholz in Weimar, Göttling, Wackenroder and particularly Döbereiner in Jena, and later the great Berzelius, were Goethe's intimate friends.

At Ilmenau we find Goethe busied with the development of the reverberatory furnace for the better smelting of lead, with the reopening of the coal mines and with the various textile industries practised in that vicinity. In 1799, with Göttling, Goethe studied the extraction of sugar, and ten years later, with Döbereiner, the production of sugar and alcohol from beets.

In 1783–1784 we find Goethe deeply engrossed with the invention and perfection of the air balloon, only to be narrowly anticipated by Charles and Montgolfier in Paris.

Throughout his life, Goethe's notebooks are replete with descriptions and sketches of innumerable chemical and manufacturing establishments which he visited and inspected; the smelters at Rammelsberg, Clausthal, Andreasberg, etc., the porcelain and munition plants at Potsdam, the optical works at Stuttgart, the knife factory at Bad Pyrmont, the sulfur springs at Berka, the tanneries at Ingelheim, the jewelry and textile factories at Hanau and a host of others.

These and many other interesting facts and observations showing the important role that chemistry played in Goethe's life are skilfully told in this small brochure, which is a reprint of a lecture delivered by Professor Paul Walden before the Verein Deutscher Chemiker in Berlin in connection with the Goethe Memorial Celebration in that city on March the 14th, 1932.

Chemistry is scorned by some humanists as the preoccupation of lesser minds; here we find it a life-long interest and a continual inspiration to perhaps the greatest poet, writer and philosopher of modern times.

ARTHUR B. LAMB

Säure-Basen-Indicatoren, ihre Anwendung bei der colorimetrischen Bestimmung der Wasserstoffionenkonzentration. (Acid–Base Indicators, and their Application in the Colorimetric Determination of Hydrogen-Ion Concentration.) By DR. I. M. KOLTHOFF and DR. HARRY FISCHGOLD. Fourth edition of "Der Gebrauch von Farbindicatoren." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1932. xi + 416 pp. 26 figs. 14 × 22 cm. Price, RM. 18.60; bound, RM. 19.80.

This is a very complete survey of the theory and the practical use of acid–base indicators, especially valuable for its treatment of recent developments. Notable in this respect is the discussion of the use of indicators in non-aqueous solutions and in highly acid systems and of the so-called salt and alcohol errors in indicator measurements.

In an ideal educational world one would object to the devotion of more than one-quarter of a book on indicators to a perfectly general discussion of the modern theory of electrolyte solutions. This material ought to be so universally accepted a part of even an elementary chemical