the organic acid was precipitated. The product was practically pure, but was further purified by reprecipitating it from dilute sodium hydroxide. The yield was 93%, m. p. 234–236°.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
MASSACHUSETTS STATE COLLEGE
AMHERST, MASSACHUSETTS

A. M. VANARENDONK
M. E. CUPERY

Correction. Para-Nitrophenyl Carbamyl Chloride and Para-Nitrophenyl Isocyanate.—In a recent paper it was stated that the product of the action of phosgene on p-nitraniline was p-nitrophenyl carbamyl chloride.[1] While this is the primary product of the reaction mixture, it has been found that after recrystallization from hot carbon tetrachloride as recommended in the procedure, the final purified product is then free from halogen and is p-nitrophenyl isocyanate, m. p. 57.° The analysis given is incorrect. Determination of the nitrogen by the micro Dumas method gave the following results.

Anal. Subs., 3.322 mg.: N_2 gas, 0.577 cc. at 31° and 744 mm. Calcd. for C_7H_4-O_3N_2: N, 17.07. Calcd. for $C_7H_5O_3N_2Cl$: N, 13.97. Found: N, 17.09.

The purified product with m. p. 57° is therefore p-nitrophenyl isocyanate[2] and is the reagent from which the urethans were prepared. It is evident that the p-nitrophenyl carbamyl chloride lost hydrogen chloride during the recrystallization from boiling carbon tetrachloride.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

W. H. HORNE
R. L. SHRINER

COMMUNICATIONS TO THE EDITOR

INTERATOMIC FORCES IN BINARY ALLOYS

Sir:

Under this title, N. W. Taylor has recently published [THIS JOURNAL, **53**, 2423 (1931)] a test of Langmuir's theory of non-electrolyte solutions which seems to me unfortunate in three respects. Following Hildebrand and Sharma [*ibid.*, **51**, 467 (1929)], he has confused Hildebrand's definition [*ibid.*, **51**, 66 (1929)] of a "regular solution," for which at constant composition $T \log a_1/N_1$ is independent of the temperature, with that of a "symmetrical system," for which at constant temperature $\log (a_1/N_1)/N_2^2$

[1] Shriner and Cox, THIS JOURNAL, **53**, 1601 (1931).

[2] This has also been noted by van Hoogstraten, Doctor's Dissertation Rijks University, Leiden, June 30, 1931.

is independent of the composition.   His method of comparison is to compare one quantity calculated by means of an extrapolation with another calculated by an integration from a few experimental points and involving the first extrapolation and also a second one.   He considers that the agreement with Langmuir's equation supports Langmuir's assumptions, but he does not give a comparison with the equations of Heitler and of Van Laar.

The test can be made directly with the experimental data, and the accompanying table shows the comparison for cadmium–lead alloys [Taylor, *ibid.*, 45, 28 (1923)].   The results for the other alloys, which are essentially the same, are omitted for the sake of brevity.   The solutions appear not to be "regular," but the values of $T \log a_1/N_1$ decrease with increasing temperature somewhat more than the irregularities of the individual measurements.   They are constant enough to make the use of their average in the comparison which follows preferable to the use of the measurements at any one temperature, even though the temperatures are not the same for all the compositions.

I have discussed elsewhere [*Chemical Reviews*, 8, 321 (1931)] the various theories as to the relation of the change in free energy to the composition. Heitler's theory gives "symmetrical systems" or $T \log a_1/N_1 = \alpha N_2^2$ (1); Langmuir's theory gives $T \log a_1/N_1 = \beta S_1 [N_2 S_2/(N_1 S_1 + N_2 S_2)]^2$ (2); Van Laar's theory and the more general theory I proposed give $T \log a_1/N_1 = \gamma V_1 [N_2 V_2/(N_1 V_1 + N_2 V_2)]^2$ (3).   The S's are the molecular (or molal) surfaces, and the V's the corresponding volumes, and α, β and γ are constants.   The comparison of these three equations is given in the last three rows of the table, with constants calculated for the most dilute

CADMIUM–LEAD ALLOYS

N_1	0.786	0.696	0.584	0.509	0.401	0.293	0.269	0.155	0.123
N_2^2	.046	.092	.173	.241	.359	.500	.534	.714	.709
$\left(\dfrac{N_2 S_2}{N_1 S_1 + N_2 S_2}\right)^2$	.064	.123	.220	.296	.421	.562	.594	.759	.806
$\left(\dfrac{N_2 V_2}{N_1 V_1 + N_2 V_2}\right)^2$	.074	.141	.246	.325	.453	.591	.623	.779	.823
$T \log a_1/N_1$									
427°		56		123			244		328
436°	31		92		172			298	
466°						222			
476°		58		122			245		325
484°	32		95		169				
544°		54		117		219	239		318
572°		54		115			237		317
Av.	31	55	93	119	170	220	241	298	322
Eq. 1	19	39	72	101	150	210	224	299	322
Eq. 2	26	49	88	118	168	225	238	304	322
Eq. 3	29	55	96	127	177	231	244	305	322

alloys. Although the physical theories are quite different, the resulting equations do not differ greatly for molecules so similar in size as these metals. The agreement of equation (1) with the experiments is distinctly poorer than that of the other two equations, but the difference between these two is too small to choose between them, and either one checks the measurements almost within the experimental error. The results with the other alloys are equally indecisive. In fact, I know of no measurements, in systems for which the agreement might be significant, which agree distinctly better with the equation of Langmuir than with that of Van Laar, or *vice versa*. The choice of theory must rest on a more fundamental analysis, a further contribution to which I hope to publish shortly.

CONTRIBUTION No. 266   GEORGE SCATCHARD
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE. MASSACHUSETTS
RECEIVED JULY 1, 1931
PUBLISHED AUGUST 5, 1931

THE FORMATION OF HYDROGEN PEROXIDE FROM HYDROGEN AND OXYGEN

Sir:

I have recently reported [THIS JOURNAL, **52**, 5106–5110 (1930)] that hydrogen peroxide is formed, along with water, when hydrogen–oxygen mixtures at atmospheric pressure are passed through a Pyrex reaction tube at 500–550°. Thermodynamic data [Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 496] indicate that the peroxide cannot have been formed via water

$$H_2 + 1/2\ O_2 \longrightarrow H_2O \tag{1}$$
$$H_2O + 1/2\ O_2 \longrightarrow H_2O_2 \tag{2}$$
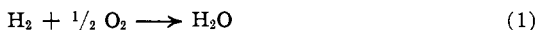
but must have been produced directly

$$H_2 + O_2 \longrightarrow H_2O_2 \tag{3}$$

Since hydrogen peroxide dissociates to give water, the question arises as to whether all the water formed passes through the peroxide stage, or whether a part comes direct from the elements.

An attempt was made to answer this by determining the ratio of peroxide to water formed under conditions leading to successively lower total conversions. If hydrogen peroxide were the only primary product, one should obtain something approaching pure peroxide in the limit. As the experimental results were on the whole inconclusive, it seems unnecessary to report them in full. However, a representative set of data may be of interest.

The data of the table refer to experiments in which $19H_2{:}1O_2$ mixtures were passed through a spherical Pyrex reaction vessel of 4.3 cm. diameter. The gases passed from flowmeters to traps cooled to $-79°$, then through

the reaction bulb and then through a weighing U-tube also cooled to $-79.^\circ$ Total product was determined by weighing; the peroxide was then titrated with 0.05 N potassium permanganate; and water was obtained by difference.

Temp., °C.	Approx. heating, sec.	Part press. in off-gas in 0.001 atm. H_2O_2	H_2O	Ratio H_2O_2/H_2O	H_2 re-acting, %
550	0.5	0.068	0.37	0.18	0.046
550	1	.21	1.7	.12	.20
540	1	.19	0.76	.25	.10
530	1	.056	0.21	.27	.028

In spite of the extremely small total conversions (less than 0.2% H_2), the best result obtained was one mole of peroxide to four moles of water. The possibility of independent, direct formation of water from the elements is thus by no means excluded.

DEPARTMENT OF CHEMISTRY   ROBERT N. PEASE
PRINCETON UNIVERSITY
PRINCETON, N. J.
RECEIVED JULY 10, 1931
PUBLISHED AUGUST 5, 1931

SURFACE REACTIONS OF ATOMS AND RADICALS

Sir:

Recently we[1] have found that water vapor, dissociated in a discharge tube, will oxidize carbon monoxide to carbon dioxide. Since atomic oxygen is not very effective in causing this oxidation we are led to believe that the carbon dioxide is formed as the result of a reaction involving the hydroxyl radical. Assuming that this is the case, we can use the oxidation of carbon monoxide as a test for OH and in this way determine whether it is affected by certain catalytic surfaces.

By observing the effect of different catalysts on the yield of carbon dioxide, we have found that a dehydrogenation catalyst is inefficient in causing the H + OH combination while a dehydration catalyst is quite efficient. This result is in accord with the work of Taylor and Lavin[2] and shows, as might be expected, that a strictly dehydrogenation catalyst is only effective in causing the recombination of hydrogen atoms.

In light of the fact that we are able to observe the oxidation of carbon monoxide after practically all of the hydrogen atoms have been removed (by the dehydrogenation catalyst) it seems that we have here a method for the separation of H and OH.

FRICK CHEMICAL LABORATORY   G. I. LAVIN
PRINCETON UNIVERSITY   W. F. JACKSON
PRINCETON, NEW JERSEY
RECEIVED JULY 16, 1931
PUBLISHED AUGUST 5, 1931

1 Lavin and Jackson, THIS JOURNAL, 53, 383 (1931).
2 Taylor and Lavin, *ibid.*, 52, 1910 (1930).

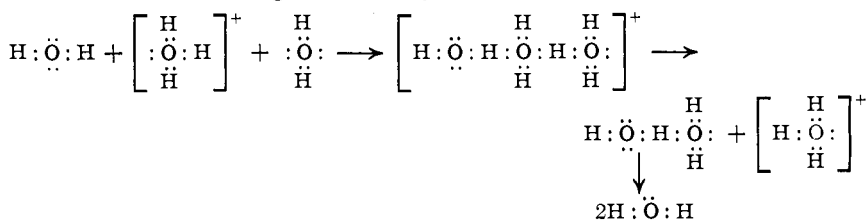## THE ROLE OF HYDROGEN BONDS IN CONDUCTION BY HYDROGEN AND HYDROXYL IONS

Sir:

The abnormally high conductance of hydrogen and hydroxyl ions in water solution is well known.[1] To account for this it has been proposed[2] that "an interchange takes place between the ions and the solvent molecules with the result that the mean path over which these ions travel is reduced in proportion to the effective diameter of the solvent molecules which are concerned in this interchange"—a modification of Grotthuss' chain theory of conduction.

Against this hypothesis it has been pointed out[1] that similar abnormally high conductances would be expected for solvent ions in solvents such as ammonia, whereas this is not the case. Recourse is then had to the assumption that the abnormal speeds of the solvent ions in water are due to their relatively low hydration.

I shall attempt to show now that the concept of "hydrogen bonds," first proposed by me in 1919 and shortly thereafter independently by Latimer and Rodebush, furnishes a satisfactory mechanism for chain conduction by the solvent ions in water but not in ammonia.

Let us assume, for simplicity, that hydrogen ions are $\left[\begin{array}{c} \text{H} \\ \text{H} : \ddot{\text{O}} : \text{H} \end{array} \right]^+$ in

water and $\left[\begin{array}{c} \text{H} \\ \text{H} : \ddot{\text{N}} : \text{H} \\ \text{H} \end{array} \right]^+$ in ammonia. The hydrogen kernels are held

quite tightly to the oxygen and even more tightly to the nitrogen. In the case of H_3O^+ the force holding each hydrogen will be greatly decreased if another hydrogen, say in an H_2O molecule, approaches the lone pair in the oxygen valence shell. If at the same time an oxygen lone pair in another water molecule should approach one of the H_3O^+ hydrogens, that hydrogen might well be transferred to this second water molecule, making it an H_3O^+ ion. Diagrammatically

$$\text{H} : \ddot{\text{O}} : \text{H} + \left[\begin{array}{c} \text{H} \\ : \ddot{\text{O}} : \text{H} \\ \ddot{\text{H}} \end{array} \right]^+ + \begin{array}{c} \text{H} \\ : \ddot{\text{O}} : \\ \ddot{\text{H}} \end{array} \longrightarrow \left[\begin{array}{c} \text{H} \quad\quad \text{H} \\ \text{H} : \ddot{\text{O}} : \text{H} : \ddot{\text{O}} : \text{H} : \ddot{\text{O}} : \\ \ddot{\text{H}} \quad\quad \ddot{\text{H}} \end{array} \right]^+ \longrightarrow$$

$$\text{H} : \ddot{\text{O}} : \text{H} : \ddot{\text{O}} : + \left[\begin{array}{c} \text{H} \\ \text{H} : \ddot{\text{O}} : \\ \ddot{\text{H}} \end{array} \right]^+$$

$$\downarrow$$

$$2\text{H} : \ddot{\text{O}} : \text{H}$$
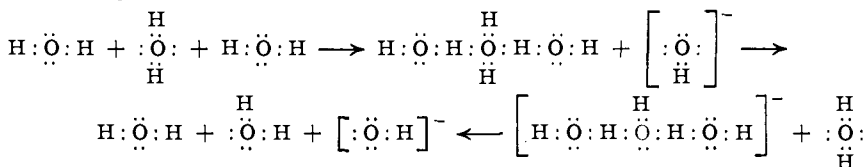
Such a mechanism is obviously impossible with NH_4^+ ions, for no lone pairs are available to aid in the "loosening" of the NH bonds.

[1] *Cf.* Kraus, "Properties of Electrically Conducting Systems," The Chemical Catalog Co., Inc., New York, 1922, p. 206.

[2] Lucasse, Thesis, Clark University, 1920.

Analogously, an OH⁻ ion can remove a hydrogen from a water molecule if the oxygen in the latter has around it three other hydrogens

$$\text{H} : \overset{..}{\underset{..}{O}} : \text{H} + : \overset{..}{\underset{..}{O}} : + \text{H} : \overset{..}{\underset{..}{O}} : \text{H} \longrightarrow \text{H} : \overset{\overset{\text{H}}{..}}{\underset{..}{O}} : \text{H} : \overset{..}{\underset{..}{O}} : \text{H} : \overset{..}{\underset{..}{O}} : \text{H} + \left[: \overset{\overset{\text{H}}{..}}{\underset{\text{H}}{O}} : \right]^- \longrightarrow$$

$$\text{H} : \overset{..}{\underset{..}{O}} : \text{H} + : \overset{..}{\underset{..}{O}} : \text{H} + \left[: \overset{..}{\underset{..}{O}} : \text{H} \right]^- \longleftarrow \left[\text{H} : \overset{\overset{\text{H}}{..}}{\underset{..}{O}} : \text{H} : \overset{..}{\underset{..}{O}} : \text{H} : \overset{..}{\underset{..}{O}} : \text{H} \right]^- + : \overset{\overset{\text{H}}{..}}{\underset{\text{H}}{O}} :$$

Although one might postulate hydrogen bonds between NH_3 molecules so as to produce nitrogen atoms surrounded by four hydrogens, these hydrogens would be more tightly held than each of four hydrogens surrounding an oxygen (NH_4^+ is more stable than OH_4^{++}) and apparently they cannot easily be removed by NH_2^- ions.

It seems likely, moreover, that $N : H : N$ bonds are not readily formed. $((: F : H : F :)^-$ is quite stable; $O : H : O$ bonds are weaker but common in crystals and probably in liquid water and temporarily during many reactions, whereas no examples whatever of $N : H : N$ or $C : H : C$ bonds are known to me.) If so, this in itself suffices to account for the lack of abnormally large conductances of NH_4^+ and NH_2^- in ammonia.

The conductance data for other solvents also seem to be in agreement with the ideas here expressed, but I shall not now take the space to discuss them.

DEPARTMENT OF CHEMISTRY   MAURICE L. HUGGINS
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIF.
RECEIVED JULY 15, 1931
PUBLISHED AUGUST 5, 1931

HEXAFLUORODISILANE

Sir:

Up to the time of the present writing the only binary fluoride of silicon that has been identified definitely is the tetrafluoride, SiF_4. Methods leading to the formation of so-called subfluorides, several of which have been reported, have failed when repeated by later experimenters. Nevertheless, the presumption remained that binary fluorides other than the tetrafluoride should be capable of existence, since certain of the corresponding compounds of carbon have been isolated.

We have now succeeded in preparing hexafluorodisilane, Si_2F_6, by gently warming hexachlorodisilane with anhydrous zinc fluoride, followed by condensation and fractionation of the products. The substance is gaseous under ordinary conditions of temperature and pressure, but may be condensed to a snow white solid, melting at $-18.5°$ under 780 mm. pressure.

The vapor pressure of the substance has been determined from -79 to $-4°$; the pressure becoming 760 mm. at $-19°$. Gas density determinations upon the same product lead to the molecular weight 173.8 (calcd. for Si_2F_6, 170.1). Inasmuch as the product has been shown to be quite pure,

not only by the rectilinear character of the vapor pressure curves when log p is plotted against $1/T$, but also by the observed sharpness of the melting point, and by the absence of any appreciable amounts of chloride, we feel that there can be little doubt concerning the actual composition of the substance.

When in contact with moist air or water, the substance is instantly hydrolyzed, the products formed including hydrogen, hydrofluoric acid, "silico-oxalic acid"—or 1,2-bis-(oxy-oxo)disilane—silicic and fluosilicic acids, the proportions of the several substances varying with experimental conditions. The quantitative study of this hydrolysis, which will also make possible the analysis of the original substance for silicon and fluorine, is now in progress, and will be described in the detailed account of this investigation in a later issue of THIS JOURNAL.

It may be added that the analogous preparation of hexafluoroethane, C_2F_6, by the interaction of zinc fluoride with hexachloroethane, has failed to give satisfactory results at ordinary pressure.

RESEARCH LABORATORY OF INORGANIC CHEMISTRY   WALTER C. SCHUMB
MASSACHUSETTS INSTITUTE OF TECHNOLOGY   E. LEE GAMBLE
CAMBRIDGE, MASSACHUSETTS
RECEIVED JULY 25, 1931
PUBLISHED AUGUST 5, 1931

THE DECOMPOSITION OF PYROSULFURYL CHLORIDE, A HOMOGENEOUS UNIMOLECULAR REACTION

Sir:

According to the literature, given to date in Mellor's "Treatise on Inorganic and Theoretical Chemistry," Vol. X, p. 683, pyrosulfuryl chloride, $S_2O_5Cl_2$, decomposes at its boiling point and above at a rate which should be convenient for study. The molecule is sufficiently large that one might expect, in accord with present theories, that the decomposition might be unimolecular. The vapor phase decomposition has been investigated, and found to be homogeneous and unimolecular.

The reaction has been followed by the pressure-increase method in a Pyrex bulb, both empty and when filled with glass tubing. The pressure approximately doubles during the reaction, which is considered to be one yielding SO_3 and SO_2Cl_2, and which, at 179° has a half-time of seven minutes in the empty bulb. When the surface is increased four times by packing, the half-time is approximately fifteen minutes.

Other temperatures are now being used, and the reality of the apparent decrease in rate with increased surface is being studied. The full report of the experiments will be submitted as soon as possible.

COBB CHEMICAL LABORATORY   DOUGLAS G. HILL
UNIVERSITY OF VIRGINIA
UNIVERSITY, VIRGINIA
RECEIVED JULY 27, 1931
PUBLISHED AUGUST 5, 1931