suction, washed with water, and dried. In order to free the aminophthalhydrazide from sulfur, the crude mixture is stirred up with that amount of 5% sodium hydroxide solution which would just correspond to the assumption that the dry solid contained no sulfur. After stirring and very slight warming the solution is filtered from undissolved sulfur, cooled to 0°, and stirred and scratched. Presently precipitation of the monosodium salt[3] of 3-aminophthalhydrazide begins and increases for some time. Finally the solid is filtered with suction, pressed as dry as possible on the filter, then washed sparingly with absolute alcohol or ether. It may then be dried in the air if it is to be preserved as the sodium salt. If, however, it is desired to reconvert the substance to "Luminol," the original solid is not washed with alcohol but is redissolved in water and reprecipitated by adding a slight excess of glacial acetic acid. The voluminous flocculent precipitate is again filtered with suction, washed free from sodium acetate with water, and dried. The product so obtained is free from sulfur and melts at 319–320° uncorr. (using a 360° melting point thermometer in a Berl and Kuhlmann copper block). The color of the final 3-aminophthalhydrazide appears to vary according to the mode of precipitation from almost white to quite deep yellow.

Anal. Calcd. for $C_8H_7N_3O_2$: C, 54.22; H, 3.98; N, 23.73. Found: C, 54.20, 54.31; H, 4.48, 4.62; N, 24.20, 24.02. *Neut. equiv.* Calcd., 177. Found: 175.

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[3] Samples of the sodium salt (dried to constant weight at 105°) were analyzed by igniting in porcelain crucibles and converting the ash to sodium sulfate. Calcd. for $C_8H_6N_3O_2Na$: Na, 11.55. Found: Na, 11.77, 11.99.

CONTRIBUTION NO. 98 FROM THE
RESEARCH LAB. OF ORGANIC CHEM.
MASSACHUSETTS INST. OF TECH.
CAMBRIDGE, MASS. RECEIVED SEPTEMBER 13, 1933

COMMUNICATIONS TO THE EDITOR

AN INTERMEDIATE OXIDATION PRODUCT OF CYSTINE

Sir:

Previous work, reported at the April, 1933, Meeting of the American Society of Biological Chemists by Toennies and Lavine, but not completely included in the abstract [*J. Biol. Chem.*, **100,** XCI (1933)], has shown that the oxidation of cystine in non-aqueous solution by perbenzoic acid at low temperature consumed a maximum of four atoms of oxygen per molecule of cystine. The first two atoms of oxygen reacted more rapidly than the second two, and following the first stage and during the further oxidation there separated a precipitate whose composition accorded with that of the disulfone ($+{}^1/_2\,HClO_4$). This product, after hydrolysis by 95% methyl alcohol containing hydrogen chloride, and addition of chloroform, yielded a crystalline precipitate, whose properties and analytical values were those of a mixture of cysteic acid and the corresponding sulfinic acid. To permit step by step study of the course of the oxidation there was developed an analytical method involving rapid removal of perbenzoic acid from the reaction mixture, and application of a semi-quantitative form of the cyanide–nitroprusside test following acid–iodide treatment. It was observed that response to this test reached a maximum during the first stage of the oxidation (between one and two atoms of oxygen consumed), becoming negative toward the end, thus indicating the test to be associated with an oxide, or oxides, lower than the trioxide [*cf. J. Biol. Chem.*, **100,** 464 (1933)].

On the basis of these studies experiments aimed at the isolation of such intermediate oxidation products of cystine have been made. When cystine was oxidized to the stage at which somewhat more than two atoms of oxygen were consumed (with formation of only a little of the insoluble final oxidation product, and with only traces of unoxidized cystine left), immediate neutralization of the filtered liquid by addition of pyridine produced a precipitate. Sparing extraction of the filtered precipitate with water left a white residue which crystallized in the manner of an ampholyte, and which responded neither to the direct cyanide-nitroprusside test for —S—S—, nor to the nitroprusside test for —SH. After reduction of this substance with a large excess of 3 *N* hydriodic acid, the cyanide–nitroprusside test was as strong as for an equal amount of cystine. The amount of iodine liberated during the acid–iodide treatment corresponded to the requirements for reduction of the disulfoxide to cystine. The optical rotation of the reduced solution indicated an almost quantitative regeneration of cystine, and by neutralization of the solution cystine was precipitated.

The amount of iodine consumed upon oxidation of the new compound in dilute, faintly acid solution, by excess of 0.1 *N* iodine, was that required for conversion of the disulfoxide to cysteic acid. These facts, and the composition of the substance as shown by analysis, suggest that it is the disulfoxide corresponding to cystine. Further study of the compound is in progress.

DEPARTMENT OF CHEMISTRY T. F. LAVINE
UNIVERSITY OF PENNSYLVANIA G. TOENNIES
LANKENAU HOSPITAL RESEARCH INSTITUTE
PHILADELPHIA, PENNSYLVANIA E. C. WAGNER

RECEIVED NOVEMBER 9, 1933

THE PHOTOCHEMISTRY OF PHOSGENE[1]

Sir:

Montgomery and Rollefson[2] have proposed the following mechanism for the photochemical reduction of phosgene

$$COCl_2 + h\nu = COCl + Cl \qquad (1)$$
$$Cl + H_2 = HCl + H \qquad (2)$$
$$H + COCl_2 = CO + Cl + HCl \qquad (3)$$
$$CO + Cl + M = COCl + M \qquad (4)$$
$$2COCl = COCl_2 + CO \qquad (5)$$
$$d(CO)/dt = I_{abs}[1 + k_2(H_2)/k_4(CO)(M)] \qquad (1)$$

In their derivation of (1) the rate of production of carbon monoxide in (5) erroneously is taken equal to the rate of consumption of COCl in this step; when this is corrected the 1 within the bracket drops out, and agreement with experiment is lost. It does not help to replace (5) by (5a) below, which must be followed by either (7) below or

$$H + Cl_2 = HCl + Cl \qquad (6)$$

A number of other modifications have been examined; the most satisfactory consists of (1), (2), and (4), together with

$$H + COCl_2 = HCl + COCl \qquad (3a)$$
$$2COCl = 2CO + Cl_2 \qquad (5a)$$
$$COCl + Cl_2 = COCl_2 + Cl \qquad (7)$$
$$COCl + H_2 = CO + HCl + H \qquad (8)$$
$$d(CO)/dt = \frac{2I_{abs}k_2(H_2)}{k_2(H_2) + k_4(CO)(M)} + k_8\sqrt{I_{abs}/k_{6a}(H_2)} \qquad (2)$$

The second term here must be small, and the initial quantum yield accordingly cannot exceed 2.3–2.4, which is perhaps too low; the rate law is probably otherwise satisfactory.

The mechanism of Rollefson and Montgomery [Ref. 2, p. 4036] for the phosgene-sensitized oxidation of carbon monoxide, which is satisfactory only for low oxygen pressure, consists of (1) and (4) together with

$$COCl + O_2 = CO_3Cl \qquad (9)$$
$$CO_3Cl + CO = 2CO_2 + Cl \qquad (10)$$
$$CO_3Cl + COCl = 2CO_2 + Cl_2 \qquad (11)$$

By adding the further chain-breaking step

$$2CO_3Cl + CO = 3CO_2 + Cl_2O \qquad (12)$$

and making valid approximations one obtains the rate-law

$$d(CO)/dt = 2\sqrt{k_9k_{10}^2I_{abs}(CO)(O_2)/[k_{10}k_{11} + k_9k_{12}(O_2)]} \qquad (3)$$

which is in good agreement with experiment. The same result is obtained if CO_3Cl is replaced by $CO_2 + ClO$. It can be shown that (12) is the only step that will give this result. A similar law can be derived for a mechanism based on the chain $Cl + O_2 + M = ClO_2 + M$, $ClO_2 + CO = ClO + CO_2$, $ClO + CO = Cl + CO_2$; this chain, however, is less plausible chemically than that of Rollefson and Montgomery. It seems unlikely that there is any other possible mechanism.

PITTSBURGH, PA. LOUIS S. KASSEL[3]

RECEIVED NOVEMBER 13, 1933

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Montgomery and Rollefson, THIS JOURNAL, **55**, 4025 (1933).

[3] Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

THE STANDARD QUINHYDRONE ELECTRODE

Sir:

During an investigation into the effects of various electrolytes upon the potential of the cell Pt/H_2, electrolyte, quinhydrone/Au, we have had need for a standard electrode. Both the 0.1 *N* and saturated calomel electrodes were found to have too great a lag when subject to temperature change.

In view of the above it was decided to investigate the possibility of using the standard quinhydrone electrode, first studied by Viebel [*J. Chem. Soc.*, **123**, 2203 (1923)] and now frequently employed. This involved a redetermination of the reproducibility of the potential difference between the hydrogen and quinhydrone electrodes in standard acid mixture, namely, 0.01 *N* HCl + 0.09 *N* KCl. Experimental details will be described in a later paper, but it may be said that no liquid junction is involved and readings are significant to 0.00001 volt. Measurements were made with two series of acid mixtures prepared (a) by mixing 1 part of 0.1 *N* HCl and 9 parts of 0.1 *N* KCl, and (b) by weighing out appropriate quantities of KCl and constant boiling HCl and diluting at 25°. These might be expected to differ slightly in hydrogen-ion concentration. However, since the difference in potential between the hydrogen and quinhydrone electrodes in the same solution is not a function of the hydrogen-ion concentration but of the total electrolyte present, little difference between the values in the two series would be expected. This proved to be the case. The mean values at 25 ± 0.01° were: for (a) 0.69903 ± 0.00002 volt, for (b) 0.69898 ± 0.00002 volt. When the quinhydrone electrode is part of a cell involving liquid junction 0.6990 volt should be used for both (a) and (b). Due to its reproducibility and constancy we are convinced that in all around qualifications this standard quinhydrone electrode excels either the 0.1 N or saturated calomel electrode.

The above potentials differ appreciably from the ideal value for the cell Pt/H_2, electrolyte, quinhydrone/Au because of the salt error. This will be considered in a later report.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
FRANK HOVORKA
WM. C. DEARING

RECEIVED NOVEMBER 17, 1933

ADDITION OF HYDROGEN BROMIDE TO 4,4-DIMETHYLPENTENE-1

Sir:

The addition of halogen acids to substituted ethylenes has been under investigation in our laboratory for some time, particularly as regards the effects of peroxides and antioxidants on the direction of addition. For certain theoretical reasons these studies included the addition of halogen acids to 4,4-dimethylpentene-1.

In view of the recent publication of Whitmore and Homeyer [THIS JOURNAL, **55**, 4555 (1933)] it appears desirable to publish some of our pertinent findings.

Our results indicate that the direction of addition of hydrogen bromide to 4,4-dimethylpentene-1 is governed by the peroxide content of the material or reagents. From that standpoint the compound 1-bromo-4,4-dimethylpentane, the product first isolated by Whitmore and Homeyer, is what we define the "abnormal" product of the reaction. This product is formed whenever the addition of halogen acid is carried out in air, or when the mixture contains peroxides. On the other hand, if the addition of hydrogen bromide is carried out *in vacuo* in the presence of good antioxidants, the isomeric 2-bromo-4,4-dimethylpentane is obtained. It is this last product that we consider the "normal" product of the reaction.

In conformity with what we have just stated, we find that if the addition of hydrogen bromide to 4,4-dimethylpentene-1 is carried out *in vacuo* (instead of in air) 50% of the 2-bromo-4,4-dimethylpentane is obtained. The physical constants of the hitherto unknown 2-bromo-4,4-dimethylpentane are: b. p. 59.4° at 34 mm.; n^{20}_{D} 1.4463; while those of the 1-bromo-4,4-dimethylpentane under the same experimental conditions are: 68.8° and 1.4485. The table summarizes some of our results. The yields were excellent in all cases.

No.	Mole of olefin	Mole HBr	Reagent added, in mole
1	0.046	0.075	Ascaridole, 0.0012
2	.046	.075	None
3	.045	.079	Acetic acid, 0.075
4	.048	.077	*p*-Thiocresol, 0.0024
5	.049	.088	Diphenylamine, 0.0030

No.	Gas in bombs	n^{20}_{D}	2-Isomer, % ± 10%
1	Air (R. T.)	1.4483	0
2	Vac. (0°)	1.4474	50
3	Vac. (0°)	1.4479	27
4	Vac. (R. T.)	1.4469	73
5	Vac. (R. T.)	1.4463	100

JONES CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
M. S. KHARASCH
CHESTER HANNUM
M. GLADSTONE

RECEIVED NOVEMBER 20, 1933

THE RULE OF SHIFT (VERSCHIEBUNGSGESETZ)

Sir:

Efforts to discover an indirect method for the correlation of the configurations of structurally similar substances have led to the enunciation of several rules all of which may be classed under the general heading of the "Rules of Shift." The earliest of these is perhaps that of Tschugaeff[1] stating that in homologous series the rotations of individual members increase asymptotically to a maximum value. To the same group belong the "Lactone Rule" of Hudson,[2] the "Phenylhydrazide Rule" of Levene,[3] etc. In its most comprehensive form (presented by K. Freudenberg[4]) the rule states that in similar, configurationally-related substances an identical substitution on identical groups produces a shift of rotation in the

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[1] Tschugaeff, *Ber.*, **31**, 360 (1898); *Chem. Zentr.*, I, 93 (1905); *Trans. Faraday Soc.*, **10**, 70 (1914).

[2] Hudson, THIS JOURNAL, **40**, 813 (1918); **40**, 1141 (1919).

[3] Levene, *J. Biol. Chem.*, **23**, 145 (1915).

[4] Freudenberg, *Ber.*, **66**, 177 (1933).

same direction. Thus, in configurationally-related carboxylic acids or esters, identical substitution on the carboxyl groups should produce a shift of rotation in the same direction. Many of these rules were found very useful and results obtained by these methods were substantiated subsequently by direct chemical methods. On the other hand, there have accumulated in our laboratory a number of observations in which these rules, if used as the basis for establishing configurations, would have led to erroneous conclusions.

In order to show the possible error to which a "Rule of Shift" may lead, we present in the table the rotations of five acids and their esters. All the acids are configurationally related.

Table I

Maximum Molecular Rotations of Configurationally Related Acids and their Ethyl and (*p*-) Nitrophenyl Esters ($[M]^{25}_{D}$ (Homogeneous))

		Free acid	Ethyl ester	*p*-Nitrophenyl ester
	Acetic Acid Series			
(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
	Propionic Acid Series			
(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)	C_5H_{11}—CH(CH_3)—CH_2—COOH	+ 8.1	+ 4.2	+11.2

In the first three acids the substitution of the ethyl group by a *p*-nitrophenyl leads to a shift of the rotation to the left, and in the fourth and fifth, to the right.

In the first two acids, the contribution of the carboxyl is levorotatory and the increase of the rotation due to substitution of the ethyl group by a *p*-nitrophenyl is as expected. However, in the third, fourth and fifth, the contributions of the carboxyl groups are dextrorotatory and yet the fourth and fifth behave differently from the third on an identical substitution.

Thus, another case is presented in which the "Rule of Shift" fails.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH,
NEW YORK, N. Y.

P. A. LEVENE
G. M. MEYER

RECEIVED DECEMBER 11, 1933

THE ALCOHOLIC FERMENTATION OF *d*-GLUCOSE IN DEUTERIUM WATER

Sir:

The production of 100% deuterium water (D_2O) in this Laboratory has made it possible to study a natural process, the alcoholic fermentation of *d*-glucose by yeast, in this medium. Measurements of the rate of fermentation were made by determining the amount of carbon dioxide formed during the enzymatic reaction in a fermentation saccharimeter after various intervals of time. One half cc. of 100% deuterium water (d^{20}_4 1.105) containing 40 mg. of *d*-glucose and 18 mg. of yeast was employed in the first experiment. The changes in height of the glycerol column in the calibrated tube of the apparatus indicated the volumes (V_1) of carbon dioxide. A control experiment was run simultaneously with ordinary distilled water; in this case V indicates the volume of carbon dioxide evolved in the process. In a second experiment 0.4 cc. of D_2O containing 32 mg. of *d*-glucose and 18 mg. of yeast was used. This experiment, too, was at the same time duplicated with ordinary distilled water. No special care was exercised to keep the temperature constant; it varied between 21 and 25.5°, affecting the corresponding experiments with heavy and ordinary water equally. The results obtained are shown in Table I.

Table I

Expt.	Time, hours	V, vol. of CO_2 in cc. with H_2O	V_1, vol. of CO_2 in cc. with D_2O	V/V_1
1	..	..	..	...
	2	0.80	0.10	8.0
	12	4.40	.45	9.8
	15	5.50	.60	9.1
	18	6.50	.73	9.0
	21	7.25	.85	8.6
	24	7.65	1.00	7.6
	45	..	1.70	...
	85	..	2.63	...
	205	..	8.50	...
2	..	..	..	...
	2	0.90	0.10	9.0
	8	3.65	.40	9.1
	12	5.00	.50	10.0
	24	6.30	.70	9.0
	48	..	1.20	...
	73	..	1.80	...
	96	..	2.35	...

The values of the factor V/V_1 clearly indicate that the alcoholic fermentation of glucose in 100% deuterium water is about 9 times slower than in ordinary distilled water. In another set of experiments with 60% heavy water the values for V/V_1 were found to be about 1.6. When the fermenting sugar solution with D_2O, in the second experiment, became four days old, it was diluted with 0.5 cc. of ordinary distilled water. Subsequently, no significant increase in the daily rate of carbon dioxide formation was experienced.

This unexpected result seems to indicate that the retarding effect of the heavy water on the alcoholic fermentation might be due to a decreased activity of the zymase complex occasioned by an irreversible, partially destructive action of the heavy water on the enzymes. Further experiments with the object of studying the effect of D_2O on extracellular enzymatic reactions are in progress in this Laboratory.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
EUGENE PACSU

RECEIVED DECEMBER 14, 1933

SOME PHARMACOLOGICAL EXPERIMENTS WITH DEUTERIUM

Sir:

In consideration of the brief reports concerning physiological effects of deuterium, published by Lewis [THIS JOURNAL, **55,** 3502(1933)], who found it affected the germination of tobacco seeds, and Barnes [*ibid.*, **55,** 4332 (1933)], who noted an inhibitory effect of heavy water on spirogyra, we deemed it desirable to perform a series of pharmacological experiments with heavy water. Agreeing with Barnes that the most valuable practical information would be gleaned from experiments with weak solutions of deuterium, we employed a heavy water containing one part of deuterium to two thousand parts of protium, purchased from the Ohio Chemical and Manufacturing Company, which was of practically the same specific gravity (1.000060).

I. Germination of *Lupinus* seeds, soaked in this solution overnight, was studied by phytopharmacological methods described elsewhere [*Science*, **71,** 302 (1930); *J. Gen. Physiol.*, **4,** 573 (1922)]. It was found that the germination of seedlings in 1:2000 deuterium solution was slightly inhibited as compared with their growth in ordinary, glass-distilled water.

II. Growth of *Lupinus* seedlings in Shive's physiological saline [*Physiological Researches*, **1,** 327 (1915)], prepared with and without deuterium solution, respectively, revealed that the latter solution produced slight inhibition. Comparison of seedlings grown in deuterium saline with the controls showed that this difference, 5 to 10%, easily explainable by variations in the hydrogen-ion concentration, was insignificant.

III. Fermentation experiments with bakers' yeast and 4% cane sugar dissolved in ordinary and deuterium water, showed no difference in their activity.

IV. Mice injected with physiological and sodium chloride solutions, prepared with and without deuterium, respectively, exhibited no toxic action.

V. Goldfish, *Carassius Auratus*, behaved exactly alike when placed in ordinary and deuterium water, respectively.

VI. Surviving pieces of cats' intestines, suspended in oxygenated Locke's solution prepared with ordinary, distilled water and in deuterium water, showed no difference in normal rhythmic contractions of smooth muscle or response to pilocarpine and mono-brom saligenin [*Proc. Soc. Exptl. Biol. Med.*, **30,** 378 (1932)].

VII. Similar experiments with vasa deferentia of white rats showed no difference in contractions of such organs to epinephrine and corpus luteum.

VIII. Similar experiments with surviving segments of guinea pig uteri revealed no difference in the action of normal and deuterium Locke's solution.

IX. Intravenous injection into cats under ether of physiological saline itself, prepared with and without deuterium, revealed no difference in effect on blood pressure and respiration.

X. Identical results were obtained by assay of digitalis tincture on cats with ordinary and deuterium saline, respectively.

Our experiments indicate that when deuterium water is employed in concentrations of 1:2000, or less, no striking physiological or pharmacological effects are noted, except possibly a slight inhibitory influence on germination of some seeds. This does not preclude the possibility of more profound biological changes being produced by pure or very concentrated heavy water. Furthermore, since the plant-physiological preparations employed by us were not the same as those described by Lewis and Barnes, no factual contradiction between our experiments and theirs need be inferred. However, if a speculative *a priori* conjecture may be permitted, we doubt that weak concentrations of deuterium would produce remarkable biological effects, for we are probably all dealing with isotopes of many elements in our physiological, pharmacological and biochemical work.

PHARMACOLOGICAL RESEARCH LABORATORY
HYNSON, WESTCOTT & DUNNING, INC.
BALTIMORE, MD.
DAVID I. MACHT
MARY E. DAVIS

RECEIVED DECEMBER 18, 1933

HYDROGENATION OF AMIDES TO AMINES

Sir:

A useful process for the reduction of amides to amines has apparently not been described. Guerbet [*Chem. Zentr.*, II, 623 (1899)] reported the formation of ethylamine from acetamide (Na + ROH), but Bouveault and Blanc [*Compt. rend.*, **138,** 148 (1904)] obtained alcohols as the chief product from amides under similar conditions. Mailhe [*Bull. soc. chim.*, [3] **35,** 614 (1906)] reported the formation of ethyl and dimethyl amines from acetamide and of propyl and dipropylamines from propionamide in the vapor phase (Ni + H_2), but no details as to yields or purity of products were given.

The transformation $RCONH_2 + H_2 \longrightarrow RCH_2NH_2 + H_2O$ does not take place readily and is likely to go incompletely because the water formed in the reaction hydrolyzes unchanged amide with the formation of acid and ammonia, which may deactivate a catalyst. It has now been found possible to bring about this reaction over copper–chromium oxide under 100 to 300 atm. of hydrogen at 175 to 250°. It has been found advantageous to use dioxane as a reaction medium since thereby the water formed in the reaction is diluted and the hydrolysis of the amide is negligible. (Raney nickel should *not* be used with dioxane at 250°.)

Lauramide, heptamide, α-phenylbutyramide, furoamide and tetrahydrofuroamide have given yields of from 40 to 70% of the corresponding primary amines. The chief side reaction is the formation of secondary amines, which were isolated in yields of 25 to 50%. For example, 54 g. of α-phenylbutyramide in 125 ml. of dioxane with 10 g. of copper–chromium oxide under 250 atm. of hydrogen was hydrogenated in two hours at 250°, and 36 g. of 2-phenylbutylamine and 13 g. of di-2-phenylbutylamine obtained. The method has also been applied to the hydrogenation of substituted amides, *e. g.*, N-laurylpiperidine, N-sebacylpiperidine, mono- and di-N-β-phenylethyl lauramide, mono- and di-N-amyl lauramide, N-cyclohexyl lauramide, N-β-phenylethyl heptamide and N-phenyl lauramide. The yields of secondary or tertiary amines were from 70 to 95% except from the last mentioned compound [*cf.* Folkers and Adkins, THIS JOURNAL, **54,** 1152 (1932)]. The amides referred to above were prepared by the reaction of anhydrous ammonia or amines with an ester at 250°. The amide has also been prepared in place; *e. g.*, high yields of amines were obtained by the hydrogenation of ammonium laurate.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WIS.

HOMER ADKINS
BRUNO WOJCIK

RECEIVED DECEMBER 20, 1933

POSSIBILITY OF INTERCHANGE BETWEEN DEUTERIUM GAS AND HYDROGEN IN COMPOUNDS

Sir:

In some studies on the reaction between deuterium and hydrogen, it was necessary to determine if interchange took place between the deuterium in the gas phase and the hydrogen atoms in ordinary water when deuterium–hydrogen mixtures were stored over water and also if the concentration of deuterium in the gas phase was affected by the stopcock grease which was present in our apparatus. A 425-cc. Pyrex bulb was fitted with a three-way stopcock at the top and a stopcock at the bottom connecting with a leveling bulb. The bulb was filled with distilled water and then all but 35 cc. of the water displaced by adding, through one arm of the upper stopcock, a deuterium–hydrogen mixture obtained by electrolysis of heavy water. Both stopcocks were closed and the apparatus shaken for several minutes to saturate the water in the bulb with gas. The pressure in the bulb was about 1.1 atm. A sample of gas was then removed through the second arm of the upper stopcock leaving the gas in the bulb at atmospheric pressure. The bulb was kept at room temperature and shaken occasionally for nineteen days. At the end of this time, a second sample of gas was removed by displacement with water. Mass spectrographic analysis of the samples showed the first to contain 2.29% deuterium and the second 2.30%.

This result shows that the concentration of deuterium–hydrogen mixtures in contact with water in clean glass vessels remains constant if precautions are taken to avoid preferential solubility, diffusion and the presence of metallic surfaces [Horiuti and Polanyi, *Nature*, **132,** 819 (1933)], and that the result reported by Oliphant [*Nature*, **132,** 675 (1933)] cannot be interpreted as being an interchange between the deuterium in the gas phase and the hydrogen atoms in the water without the aid of a catalytic surface other than the glass wall of the containing vessel.

Two Pyrex tubes were evacuated and filled simultaneously from a reservoir containing a deuterium–hydrogen mixture. The first tube was fitted with a magnetic break at the lower end and, after filling, was sealed off at the upper end. The second tube was equipped with a stopcock and was coated on the inside with a layer of "Lubriseal." At the end of twenty-two days mass spectrographic analysis showed the gas in the first tube to contain 2.07% deuterium and that in the second 2.09%. It is evident, therefore, that an apparatus containing stopcocks may be used in the study of deuterium–hydrogen mixtures without fear of interchange between deuterium and hydrogen from the stopcock grease.

FRICK CHEMICAL LABORATORY
PALMER PHYSICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
AUSTIN J. GOULD
WALKER BLEAKNEY

RECEIVED DECEMBER 22, 1933

THE SYNTHESIS OF POLYNUCLEAR HYDROCARBONS BY THE CYCLODEHYDRATION OF AROMATIC ALCOHOLS

Sir:

Since our preliminary publications in this field,[1] a number of articles have been published abroad[2] which show that these communications of ours have escaped notice there and which make it seem desirable to us to report the following additional results which have been obtained in our laboratories. This is done in the hope that it will save our fellow investigators the time and money which might otherwise be spent in the duplication of experiments.

Our studies in the tetralin field, for example, already have shown that 1-methyltetralin can be obtained by the action of sulfuric acid upon any one of the following: $PhCH_2CH_2CH_2CH(OH)Me$, $PhCH_2CH_2CH_2CH{=}CH_2$, $PhCH_2CH_2CH(OH)CH_2Me$, or $PhCH_2CH{=}CHCH_2Me$.

1-Ethyltetralin has been prepared similarly from both $Ph(CH_2)_4CH(OH)Me$ and $Ph(CH_2)_4CH{=}CH_2$.

In two of the above compounds, a shift in the location of the double bond is indicated in connection with the cyclization.

In the case of $Ph(CH_2)_2CMe(OH)CH_2Me$, both 1,2-dimethyltetralin and 1-methyl-1-ethylindane appear to be formed.

As stated in our initial announcements,[1] these studies are being pursued in various directions, especially with the object in view of preparing synthetically compounds of biological interest.

LABORATORIES OF ORGANIC
CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
MARSTON TAYLOR BOGERT
DAVID DAVIDSON
RICHARD O. ROBLIN, JR.

RECEIVED DECEMBER 21, 1933

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[1] (a) Bogert, *Science*, [N. S.] **76**, 475 (1932); (b) **77**, 197 (1933); (c) **77**, 289 (1933).

[2] (a) Schlenk and Bergmann, *Chemistry & Industry*, **52**, 207 (1933); (b) Cook, Hewett, Haslewood, *et al.*, *ibid.*, **52**, 949 (1933); (c) Ruzicka, Ehmann, Goldberg and Hösli, *Helv. Chim. Acta*, **16**, 833 (1933); (d) Kon, *J. Chem. Soc.*, 1081 (1933); (e) Cook and Hewett, *ibid.*, 1098 (1933); (f) Fulton and Robinson, *ibid.*, 1463 (1933).

FREEZING POINTS OF MIXTURES OF THE WATERS, $H^1{}_2O$ AND $H^2{}_2O$

Sir:

We have determined the freezing points and specific gravities at 25° on 15-cc. portions of mixtures of $H^2{}_2O$ and $H^1{}_2O$ using a Beckmann thermometer calibrated by the Bureau of Standards, and standard technique. The samples were prepared by electrolysis of potash solutions using nickel electrodes, followed by repeated distillations from alkaline permanganate to remove carbon dioxide and other impurities which would lower the freezing point. The freezing points were independent of the supercooling (1 to 2.8°) and were constant to within 0.001° for periods of at least ten minutes. The zero point of the thermometer was determined repeatedly against the freezing point of ordinary distilled water using precisely the same technique. Slow freezing of the 39.9% sample over a period of three hours with continuous stirring, until one-third had separated as ice, produced no change in equilibrium temperature greater than the experimental error of 0.002°. The specific gravities of the melted ice and unfrozen liquid, using a 1.3-cc. pycnometer, checked to 0.02%.

These observations indicate that the solid

Approx. % heavy component 100% = sp. g. 1.11165	F. p., °C.	Sp. gr. 25/25°	$\frac{\text{F. P.}}{(\text{sp. g. }-1)}$	Observer
1.23	0.053	1.001376	38.5	Washburn, Smith and Frandsen, *B. S. J. Res.*, **11**, 453 (1933)
14.7	.632	1.01644	38.5	This investigation
19.1	.824	1.02135	38.6	This investigation
39.9	1.679	1.04456	37.7	This investigation
39.5	1.670	1.04411	37.9	This investigation; redistilled *in vacuo*
94.6?	3.8	1.1056[a]	36.	Lewis and Macdonald

[a] The terms specific gravity and density are used interchangeably for this value [Lewis and Macdonald, THIS JOURNAL, **55**, 3058 (1933)].

phase is a solid solution of the two components and that on freezing the mixtures behave as though they were pure substances. The values in column 4 of the table show that the freezing point is a linear function of the specific gravity to 20% (H^2_2O) but a deviation outside our experimental error is perceptible at 40%. The experiments are being extended to more concentrated mixtures.

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RECEIVED DECEMBER 26, 1933

NEW BOOKS

Great Men of Science. A History of Scientific Progress. By PHILIPP LENARD. Translated from the German by H. Stafford Hatfield. The Macmillan Company, 60 Fifth Avenue, New York. 389 pp. Price, $3.00.

This volume presents brief and sympathetic accounts of the lives and contributions of sixty-six great figures in the history of Science. It starts with Pythagoras, Euclid, Archimedes and Hipparchus, and concludes with Stefan, Boltzmann, Hertz and Hasenöhrl. As Professor Andrade points out in the Introduction—"It is not often that one who, like Professor Lenard, has won for himself an assured place in the history of science, undertakes a systematic appreciation of the work of his predecessors, of the kind which we have before us in this book.... In these studies of great men by Professor Lenard the reader will find a vivid sympathy, a generous enthusiasm and an illuminating criticism which bring out in lively fashion both the personality and the secret of the scientific greatness of the subject."

Out of the sixty-six scientists there are fourteen who can be reasonably classified as chemists—namely, Boyle, Black, Scheele, Priestley, Cavendish, Klaproth, Dalton, Gay-Lussac, Davy, Berzelius, Faraday, Bunsen, Hittorf and Crookes. It is of particular interest to the chemists of today to have the achievements of these men measured against the background of Science as a whole.

The portraits that accompany the biographies are arresting. The author's remark in the Preface is no overstatement—"Let anyone who has a sense for portraits examine the plates of this volume...he will find from this examination a spiritual profit, an introduction to a world of clearer and more natural thinking."

We must be grateful to the translator for making this inspiring book more easily accessible to English readers. Unfortunately, while the meaning is in general clear, the diction is frequently awkward and laborious.

ARTHUR B. LAMB

Modern Alchemy. By WILLIAM ALBERT NOYES, University of Illinois, and W. ALBERT NOYES, JR., Brown University. Charles C. Thomas, 220 East Monroe Street, Springfield, Illinois, 1932. ix + 207 pp. 15 × 23 cm. Price, $3.00.

Under the picturesque title of Modern Alchemy the authors, father and son, have given us an excellent philosophical survey of the more important modern theories of the structures of atoms and their relations to chemical activity. Modern transmutations of elements and typical instances of advances in industry and medicine under the influence of chemistry are presented in an interesting way. The latter are the modern equivalents of the twin objectives of the alchemist of old, wealth and health.

In the chapter on valence the reviewer believes that a valuable opportunity has been missed by the insistence on "potential polar" valences as opposed to actual polarity. Two different electrical systems of different positive kernel charge and different space relations can have the same attraction for pairs of negative electrons holding them in chemical union only in the rare cases where the sizes of charges and distances compensate each other. For the majority of combinations, this is not so. Surely, the structures $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}:(\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:)_3$ and $:P(:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:)_3$ for the trichlorides of nitrogen and phosphorus give a summary of the striking chemical differences between these two substances, which neither the old structures NCl_3 and PCl_3, nor those used on pages 107 and 108 of the present text, do. In the opinion of the reviewer, the general application of this rational type of partial polarity as distinguished from ionic polarity, will ultimately play the same leading role in elucidating the chemical behavior of non-electrolytes in the organic and the inorganic fields, as the theory of ionization has accomplished for electrolytes.

The chapter on the effect of radiation on chemical systems is particularly timely and is an excellent presentation of a subject that has become of such moment in the intimate study of atoms and molecules.

The volume should prove of great value to advanced students in the sciences. General readers with a thoroughly good foundation in physics and chemistry would find it extremely interesting.

JULIUS STIEGLITZ

Physico-Chemical Methods. By JOSEPH REILLY, Professor of Chemistry, National University of Ireland, and WILLIAM NORMAN RAE, Professor of Chemistry, University College, Colombo; with a foreword by F. G. Donnan. Second edition, revised. D. van Nostrand Company, Inc., 250 Fourth Ave., New York, 1933. xv + 822 pp. 586 figs. 16.5 × 23.5 cm. Price, $8.00.

The second edition of this well-known standard work on physico-chemical methods seems to the reviewer a very