## COMMUNICATIONS TO THE EDITOR

#### THE ELECTRICAL CONDUCTIVITY OF SILICIC ACID GEL MIXTURES DURING GELATION

Sir:

A study has recently been made in this Laboratory of the electrical conductivity of various mixtures of aqueous solutions of sodium silicate and acetic acid. Measurements were obtained as soon as possible after mixing and were continued until some hours after the gel mixture had set. By this means it was hoped to present evidence in favor of either the fibrillar or the cellular theory for the structure of a silicic acid gel. Any considerable increase in electrical resistance would be considered to be strong evidence for the cellular theory.

In no case was a change of resistance obtained greater than the possible errors of measurement (< 0.4%) from the first reading after mixing until the gel was well set. Four sets of typical data are shown in Table I. Concentrations are expressed in gram moles per liter, the silicate being expressed in its equivalent of sodium hydroxide and silica.

|                | I. ELECTRICAL                | Resistance of S        | ilicic Acid Ge          | L MIXTURES          |                         |
|----------------|------------------------------|------------------------|-------------------------|---------------------|-------------------------|
| Conce:<br>SiO2 | ntrations, gram mole<br>NaOH | s per liter<br>CH3COOH | Time of set,<br>minutes | Resistance,<br>ohms | Change<br>in resistance |
| 1.452          | 0.876                        | 1.718                  | 35                      | 111                 | None                    |
| 0.970          | . 584                        | 1.140                  | 60                      | 136                 | None                    |
| .485           | .292                         | 0.570                  | 300                     | 213                 | None                    |
| .242           | . 146                        | .285                   | 1440                    | 450                 | None                    |

A more complete study of this problem is now under way, using a new type of cell and bridge and a 60-cycle alternating current galvanometer.

Department of Chemistry Union College Schenectady, N. Y. Charles B. Hurd Henry J. Swanker

RECEIVED MARCH 27, 1933 Pt

PUBLISHED JUNE 6, 1933

#### THE TRIMETHYLPENTANES

Sir:

The fact that the dehydration product of methylethyl-*tert*-butylcarbinol on hydrogenation apparently gives a single octane [private communication, P. L. Cramer, General Motors Research Laboratories] seemed to be contrary to our findings that the dehydration gives some rearranged product [THIS JOURNAL, **54**, 4011 (1932)]. Consequently we have prepared 2,2,3-trimethylpentane (corresponding to the normal dehydration product) and 2,3,3-trimethylpentane (corresponding to the rearranged product). Their properties are similar and their separation in small amounts would not be possible. Thus there is no discrepancy between our results and those of Cramer.

The pure olefins, 2,2,3-trimethylpentene-3, Cottrell b. p. 111.9° (760 mm.),  $n_D^{20}$  1.4232,  $d_4^{20}$  0.7395, and 2,3,3-trimethylpentene-1, Cottrell b. p. 108.2° (760 mm.),  $n_D^{20}$  1.4178,  $d_4^{20}$  0.7363, obtained by fractionation of the dehydration products of methylethyl-*tert*-butylcarbinol and dimethyl-*tert*-amylcarbinol, respectively, were hydrogenated at room temperature in a Burgess–Parr apparatus using the platinum oxide catalyst of Adams and methyl alcohol as a solvent (150 cc. per 0.25 mole). The products were precipitated by water, shaken with concentrated sulfuric acid to remove water, alcohol and unchanged olefin, and fractionated at a high reflux ratio through a 40 × 0.8 cm. packed column equivalent to 7.7 theoretical plates. The yields of octanes were 92 and 90%, respectively. The remaining isomer, 2,3,4-trimethylpentane, was made similarly from the dehydration products of 2,3,4-trimethylpentanol-3 [THIS JOURNAL, **54**, 4392 (1932)]. The properties of all the possible trimethylpentanes are

|   | Cottrell<br>b. p. (760 mm.)   | $n_{ m D}^{20}$ | $d_4^{20}$   |
|---|-------------------------------|-----------------|--------------|
| 2,2,3-Trimethylpentane                              | 110.2°                        | 1.4030          | 0.7173       |
| 2,2,4-Trimethylpentane                              | 99.3°°                        | 1.3916          | . 6918       |
| 2,3,3-Trimethylpentane                              | 113.6°                        | 1.4074          | . 7258       |
| 2,3,4-Trimethylpentane                              | $112.8^{\circ b}$             | 1.4045          | . 7197       |
| <sup>4</sup> This Journal, <b>51</b> , 1546 (1929). | <sup>b</sup> Corrected from h | o.p. 111.5°     | ' (732 mm.). |

The values for the first octane do not agree with those of Clarke and Jones [THIS JOURNAL, 34, 170 (1912)], who apparently had olefin in their product.

| PENNSYLVANIA STATE COLLEGE  | K. C. Laughlin         |
|-----------------------------|------------------------|
| STATE COLLEGE, PENNSYLVANIA | FRANK C. WHITMORE      |
| RECEIVED APRIL 1, 1933      | PUBLISHED JUNE 6, 1933 |

#### RAW RAMIE

#### Sir:

During some x-ray work on ramie fibers a property was noted which might prove of some interest to students of this material.

Untreated ramie (raw ramie) yields an insoluble lead compound when brought in contact with a solution containing lead salt (the chloride, acetate and nitrate were used). This lead compound has a characteristic x-ray powder diagram which is superimposed on the fiber diagram of the pure ramie. The diagram obtained is independent of the anion, so that the reaction product cannot be a double compound, but must be a salt. The original substance (presumably an acid, or salt of such acid) may be leached out with water from the raw fiber. When lead nitrate is added to such a solution a white precipitate settles out gradually. This precipitate yields an x-ray powder diagram identical with the one mentioned above and is therefore presumably identical with the lead salt deposited in the fiber. The precipitate chars when heated to about  $150^{\circ}$ , indicating the acid in question to be of organic nature.

Interplanar spacings (d) for some of the lines obtained in the x-ray patterns are given for comparison (intensity M = medium and W = weak).

| Lead s<br>precipit | alt<br>ated | Lead s<br>on fib |              |
|--------------------|-------------|------------------|--------------|
| 4.25               | М           | 4.25             | $\mathbf{M}$ |
| 3.29               | W           | 3.32             | W            |
| 3.16               | W           | 3.19             | W            |
| 2.97               | М           | 2.98             | $\mathbf{M}$ |
| 2.73               | W           | 2.75             | W            |
| 2.66               | W           | 2.69             | W            |

Various samples of refined ramie do not give any indication of forming a corresponding lead compound, which is in agreement with the water solubility of the acid in question.

The following salts of this acid are sufficiently water soluble to leach out of the fiber: Na, K,  $NH_4$ , Ca, Sr and Ba.

No attempts were made to establish the nature of the acid in question any further.

It is of interest to note that the lead salt precipitated in the fiber is entirely unoriented relative to the fiber.

DEPARTMENT OF CHEMISTRY THE JOHNS HOPKINS UNIVERSITY BALTIMORE, MARYLAND RECEIVED APRIL 28, 1933 PUBLISHED JUNE 6, 1933

### THE REACTION BETWEEN KETENE AND MERCURIALS

Sir:

Incidental to studies on the preparation of 3-aminofuran from 3-furyl methyl ketoxime, we have found that ketene reacts smoothly with organomercurials to give the corresponding methyl ketones. By this reaction, we have prepared 2-furyl methyl ketone, 3-furyl methyl ketone (b. p. 84° (21 mm.); m. p. of semicarbazone, 150°), 2,5-diacetylfuran (m. p. 94°; m. p. of dioxime, 187°) and acetophenone in 20–50% yields from the respective RHgCl and R<sub>2</sub>Hg compounds.

If reaction proceeds here in the manner of more reactive organometallic compounds, this is apparently the first case of addition of an organomercury compound to a carbonyl linkage. The carbonyl linkage in some reactive isocyanates may undergo a like reaction.

|                         | HENRY CHMAN            |
|-------------------------|------------------------|
| DEPARTMENT OF CHEMISTRY | DENKI OILMAN           |
| IOWA STATE COLLEGE      | BERNE L. WOOLLEY       |
| Ames, Iowa              | GEORGE F. WRIGHT       |
| RECEIVED APRIL 27, 1933 | Published June 6, 1933 |

#### THE ENTROPIES OF POLYATOMIC MOLECULES

Sir:

Very recently spectroscopic and specific heat data have been employed in the estimation of the entropies and symmetry numbers of polyatomic molecules in the vapor state.<sup>1</sup> We wish to point out that such calculations may be of uncertain value for molecules containing many atoms. To illustrate this for an apparently favorable case we have made entropy calculations for the tetrachlorides of carbon, silicon, titanium and tin. The Raman spectra of these substances<sup>2</sup> have been studied theoretically by a number of investigators and they are in substantial agreement regarding the interpretation of the experimental results. The molecular dimensions<sup>3</sup> have been determined by the electron diffraction method. Latimer,<sup>4</sup> by specific heat measurements from low temperatures (39°K. with CCl<sub>4</sub>), determined the entropies of the liquids at 25° and good vapor pressure data<sup>5</sup> are available for completing the calculation of the entropies of the gases at the customary standard state of one atmosphere and 25°. The results of the calculations together with the data used are presented in the table. The numbers in parentheses adjoining the symbol  $\omega$  are the multiplicities of the vibrational levels. To calculate " $S_{298}^{o}$  spectroscopic" it was assumed, in accordance with the results of electron diffraction experiments, that the symmetry number is 12, *i. e.*, that the chlorine atoms are at the corners of a regular tetrahedron.

| Substance         | $\omega_1(1)$ cm. <sup>-1</sup> | ω <sub>2</sub> (2)<br>cm. <sup>-1</sup> | ω3(3)<br>cm. <sup>-1</sup> | ω4(3)<br>cm. <sup>-1</sup> | $\Delta H$ Vap.<br>at 25°,<br>cal.     | V. p. at<br>25°, mm.                        | Cl–Cl<br>distance,<br>Å. |
|-------------------|---------------------------------|---|----------------------------|----------------------------|--|---|--------------------------|
| CCl₄              | 459                             | 217                                     | 775                        | 313                        | 7730                                   | 114.5                                       | 2.98                     |
| SiC1 <sub>4</sub> | 422                             | 148                                     | 608                        | 220                        | 7184                                   | 235   | 3.29                     |
| TiCl <sub>4</sub> | 386                             | 119                                     | 491                        | 139                        | 8960                                   | 13.38                                       | 3.61                     |
| $SnCl_4$          | 367                             | 104                                     | 401                        | 136                        | 9472                                   | 24.0  | 3.81                     |
| Substance         | S°<br>Trans.<br>cal./deg.       | R<br>cal.                               | ;•<br>ot.<br>/deg.         | S°<br>Vib.<br>cal./deg.    | S <sub>298</sub><br>Spec.<br>cal./deg. | S <sub>298</sub><br>Third law<br>cal. /deg. | Difference<br>cal./deg.  |
| CCl4              | 40.99                           | 28                                      | .78                        | 9.51                       | 74.3                                   | 71.2  | 3.1                      |
| SiCl <sub>4</sub> | 41.29                           | 29                                      | . 35                       | 13.53                      | 79.2                                   | 78.3  | 0.9                      |
| TiCl <sub>4</sub> | 41.62                           | 29                                      | . 90                       | 17.81                      | 84.4                                   | 81.5  | 2.9                      |
| SnCl <sub>4</sub> | 42.56                           | 30                                      | . 22                       | 19.37                      | 87.2                                   | 86.8  | 0.4                      |

The differences between the calculated entropies and those obtained from thermal measurements are, in at least two cases, larger than corresponds to the experimental error usually allowed to the measured quantities involved. The data for carbon tetrachloride are probably better than

- (2) Kohlrausch, "Der Smekal-Raman Effekt," J. Springer, Berlin, 1930, pp. 49, 215.
- (3) Wierl, Ann. Physik, 8, 521 (1931).
- (4) Latimer, THIS JOURNAL, 44, 90 (1922).

(5) "International Critical Tables," Vol. III, pp. 213, 214 (for CCl4 and SnCl4); Wintgen, Ber., 52, 724 (1919) (for SiCl4); Arii, Bull. Inst. Phys. Chem. Res. (Tokyo), 8, 714 (1929); cf. Chem, Abs., 24, 277 (1930) (for TiCl4).

<sup>(1)</sup> Dietz and Andrews, J. Chem. Phys., 1, 62 (1933); Mayer, Brunauer and Mayer, THIS JOURNAL, 55, 27 (1933).

June, 1933

those for the other three tetrachlorides, yet the difference is greatest for that substance. In all cases the symmetry number would turn out greater than 12 (59 for CCl<sub>4</sub>) if the results were used to calculate that quantity.

On the assumption that some more fundamental difficulty is not involved, it is possible that the differences found are to be ascribed to incomplete knowledge of the vibrational states of non-linear polyatomic molecules. Accordingly, great accuracy cannot, at present, be ascribed to the results of spectroscopic entropy calculations for polyatomic molecules in those cases where all of the necessary energy levels are not accurately known and correctly interpreted. For the approximate estimation of free energies<sup>6</sup> such entropies are, however, often of considerable value.

(6) Kassel, This Journal, **55**, 1351 (1933). Gates Chemical Laboratory Don M. Yost California Institute of Technology Charles Blair Pasadena, California Received May 1, 1933 Published June 6, 1933

#### THE METHYLENE DISULFONES<sup>1</sup>

Sir:

These substances are of considerable interest as cogeners of Sulphonal. The general methods of preparation, outlined as early as 1877,<sup>2</sup> are expressed

$$\begin{array}{c} CH_{2}I_{2} + 2HSR & -2HI \\ \hline \\ CH_{2}O + 2HSR & -H_{2}O \end{array} \longrightarrow CH_{2}(SR)_{2} \longrightarrow CH_{2}(SO_{2}R)_{2} \end{array}$$

In the past month a simple modification of the former scheme was described by Stutz and Shriner which, by obviating the isolation of mercaptan, greatly reduces the offensive odor of the process. Unfortunately, the yields were not very good, and the methylene disulfides, though less volatile, have persistent and unpleasant odors. These drawbacks can be avoided completely by an extension of the work of Brooker and Smiles.<sup>3</sup> They showed

 $\begin{array}{ccc} \text{RCOCHXCOR} & \xrightarrow{\text{RSO}_2 \text{SMe}} & \xrightarrow{\text{RCOCHXCOR}} \\ & & & & | \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array}$ 

By applying this to sulfonyl ketones I developed a process  $(1931)^4$ whereby disulfones were obtained with no obnoxious intermediate at all. RSO<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub> RSO<sub>2</sub>CHCOCH<sub>3</sub> Hydrolysis RSO<sub>2</sub>CH<sub>2</sub> R'SO<sub>2</sub>SR" SR" SR" SR" SR" SR"

<sup>(1)</sup> Stutz and Shriner, THIS JOURNAL, 55, 1242 (1933).

<sup>(2)</sup> Claesson, J. prakt. Chem., 15, 176 (1877).

<sup>(3)</sup> Brooker and Smiles, J. Chem. Soc., 1723 (1926).

<sup>(4)</sup> D. T. Gibson, ibid., 2637 (1931).

It is evident that this reaction possesses the additional advantage of applicability to the preparation of unsymmetrical<sup>5</sup> methylene disulfones, and in developing it to that end a most interesting type of radical exchange has been discovered<sup>6</sup>

(A) 
$$RSO_2CH_2COCH_3$$
 if (A) in excess  $RSO_2CHCOCH_3$   
+  $CE$  R''  $SO_2SCH_3$  if (E) in excess  $R''SO_2CHCOCH_3$   
SCH<sub>3</sub>  $CH_3$ 

Results already obtained indicate that the exchange is  $\mathbb{R}^{"}SO_2$  for  $\mathbb{R}SO_2$  (rather than  $\mathbb{R}^{"}$  for  $\mathbb{R}$ ). Further, where  $\mathbb{R}$  and  $\mathbb{R}^{"}$  are both aryl (or both alkyl), the exchange of radicals is a mass action effect, but while alkyl sulfonylacetones are readily converted to aryl derivatives, the reverse has not been observed.

Obviously, if  $\mathbf{R} = \mathbf{R}''_1$  the exchange phenomenon is not observed, and as methylene di-*n*-butyl disulfone now figures in the literature with two widely discrepant melting points,<sup>7</sup> I would suggest that the sulfonyl acetone route might be used to give an independent confirmation of one or the other value.

(5) Posner, Ber., 36, 200 (1903).
(6) J. Chem. Soc., 1819 (1932); 306 (1933).
(7) Stutz and Shriner, Ref. 1, m. p. 96°; Whitner and Reid, THIS JOURNAL. 43, 638 (1921), m. p. 182°.
UNIVERSITY OF GLASGOW DAVID T. GIBSON GLASGOW, SCOTLAND RECEIVED MAY 2, 1933 PUBLISHED JUNE 6, 1933

#### THE FRACTIONATION OF ISOTOPES BY ELECTROLYSIS

Sir:

In view of recent communications regarding the isotopic fractionation of the elements of water by electrolysis [Washburn and Urey, *Proc. Nat. Acad. Sci.*, 18, 496 (1932); Lewis, THIS JOURNAL, 55, 1297 (1933); Washburn, Smith and Frandsen, *J. Chem. Phys.*, 1, 288 (1933)] it is of interest to record that in 1923 Dr. Malcolm M. Haring, working under my direction at Columbia University, achieved a slight fractionation of mercury by the same method. Electrolysis of an acid solution of mercurous nitrate, using a low voltage and low current density, gave mercury with a density only 0.999981 that of ordinary mercury. This value was the average of fourteen different electrolyses. Parallel experiments in which a high voltage and high current density were employed gave mercury with density unchanged.

The reduction in density, it will be seen, was only 19 parts per million, which represented three times the average deviation of the individual results. The greatest difficulty encountered in the whole investigation was the exact setting of the mercury level in the pycnometers and, although the error involved thereby was minimized by repeating each setting five times and averaging the results of the five weighings, the probable error involved still amounted to 7.5 parts per million. This fact, together with the disappointingly small change (0.004 unit) in the average atomic weight of the electrolyzed mercury, discouraged us from proceeding further at the time. The results of the work were recorded by Dr. Haring in a Columbia University dissertation printed in 1924, but have not hitherto been given further publicity.

I have always been convinced, however, of the reality of the indicated fractionation and, in the expectation that more conclusive results would be obtained with a lighter element than mercury, Mr. James McLaren of Syracuse University began a systematic study of the electrolytic method of isotopic fractionation under the direction of myself and Dr. E. B. Ludlam at the University of Edinburgh in 1930. A considerable amount of work had been done on lithium, but no final results attained, when the discovery of the isotopic character of hydrogen turned our attention early in 1932 to that element, which obviously offered still greater chances of success. Spectrographic evidence suggesting that the proportion of the heavier hydrogen isotope in the first fraction of the electrolysis of water was less than in ordinary hydrogen was obtained, but while confirmatory experiments were in progress the more striking changes revealed in the last fractions, alluded to in the first paragraph of this letter, have been announced, and anything that we may now have to report regarding the other end of the process can only be of the nature of an anti-climax.

CHEMISTRY DEPARTMENT JAMES KENDALL THE UNIVERSITY KING'S BUILDINGS EDINBURGH, SCOTLAND RECEIVED MAY 8, 1933 PUBLISHED JUNE 6, 1933

# THE PARA-HYDROGEN CONVERSION AT PARAMAGNETIC SURFACES Sir:

In extending the investigations of Taylor and Sherman [THIS JOURNAL, 53, 1614 (1931); *Trans. Faraday Soc.*, 28, 247 (1932)] on the function of van der Waals and activated adsorption of hydrogen on the para-hydrogen conversion, we have found that, modifying the earlier results, there is a whole series of surfaces on which, at liquid air temperatures, the van der Waals adsorption of hydrogen is accompanied by extremely rapid conversions of ortho to para hydrogen. Chromium oxide gel was the first of these which we discovered with the assistance of Mr. J. Howard, who has been investigating the adsorption of hydrogen on this substance. More recently we have added to the list a crude cerium oxide, probably containing

neodymium, samples of pure neodymium oxide and gadolinium oxide. These were chosen because of their known paramagnetic properties and give very rapid conversions of the hydrogen at high space velocities. Zinc oxide, lanthanum oxide and vanadium pentoxide possessing low or negligible paramagnetism show low or negligible conversion efficiencies even with marked van der Waals adsorption at liquid air temperatures. The paramagnetic lower oxide of vanadium shows rapid conversions. The magnetic characteristics of the surface appear, therefore, to be a controlling factor. The magnetic properties may possibly account for our earlier positive results with metallic nickel and for the recent results of Harkness and Emmett (Washington Meeting, A. C. S., March, 1933) with van der Waals adsorption on iron synthetic ammonia catalysts. We understand that L. Farkas and H. Sachsse have similarly found that paramagnetic substances such as oxygen, nitric oxide, nitrogen dioxide and paramagnetic salt solutions effect the para-ortho conversion in homogeneous systems. We are extending our heterogeneous studies to obtain quantitative data on the relation between magnetic moment and surface efficiency.

PRINCETON UNIVERSITY FRICK CHEMICAL LABORATORY PRINCETON, NEW JERSEY RECEIVED MAY 11, 1933 Hugh S. Taylor H. Diamond

33 PUBLISHED JUNE 6, 1933

#### MAGNETO-OPTIC MINIMA OF ORGANIC COMPOUNDS

#### Sir:

We present below a table and graphs of readings of the minima obtained on the magneto-optic method of Allison with aqueous and ethereal solutions of four homologous series of organic compounds, namely, the normal, primary, aliphatic alcohols; the lower, normal, fatty acids; the alkyl acetates and the alkyl bromides. The concentrations in all cases were  $1 \times 10^{-8}$  by volume. Readings agreed to within one or two mm. and were the same within this limit irrespective of the solvent. Blanks were

MAGNETO-OPTIC MINIMA OF ORGANIC COMPOUNDS

|        | Alcohols | Acetates | Bromides | Acids |        |           |  |
|--------|----------|----------|----------|-------|--------|-----------|--|
|        |          |          |          | 12.08 | 12.26  | Formic    |  |
| Methyl | 5.56     | 12.00    | 13.89    | 11.80 | 11.88  | Acetic    |  |
| Ethyl  | 5.80     | 12.50    | 14.44    | 11.60 | 11.71  | Propionic |  |
| Propyl | 5.98     | 12.97    | 15.04    | 11.20 | 11.32  | Butyric   |  |
| Butyl  | 6.30     |          | 15.68    | 10.91 | 11.00  | Valeric   |  |
| Amyl   | 6.65     | 13.60    | 16.36    | 9.72  | . 9.80 | Caproic   |  |
| Hexyl  | 7.02     |          | 17.16    | 7.72  | 7.88   | Heptylic  |  |
| Heptyl | 7.37     | 14.11    | 18.10    | 4.90  | 5.02   | Caprylic  |  |
| Octyl  | 7.65     |          | 19.00    | 2.68  | 2.80   | Nonylic   |  |
| Nonyl  | 8.03     |          |          | 0.25  | 0.38   | Capric    |  |

run first in every case but no other minima were found in the region near those recorded which were not observed with the blanks.





It will be seen that in each homologous series scale readings for the minima increase with increasing weight of alkyl radical where the radicals are positive, and decrease where they are negative (acids). This is in general agreement with the results of Allison on inorganic compounds [THIS JOURNAL, **52**, 3796 (1930); J. Chem. Ed., **10**, Feb. (1933)].

DEPARTMENT OF BIOCHEMISTRY EMORY UNIVERSITY EMORY UNIVERSITY, GA. RECEIVED MAY 18, 1933 PUBLISHED JUNE 6, 1933

#### THE TEMPERATURE COEFFICIENT OF THE RECOMBINATION OF HYDROGEN ATOMS

Sir:

A study of the recombination of hydrogen atoms at  $25^{\circ}$  [I. Amdur with A. L. Robinson, THIS JOURNAL, **55**, 1395 (1933)] indicated that the most probable mechanism for the trimolecular gas reaction is the union of two hydrogen atoms with either a third hydrogen atom or a hydrogen molecule acting as the third body. Assuming no wall reaction the calculated reaction velocity constants showed a definite drift toward lower values at

higher total pressures, disagreeing with the results of Steiner and Wicke [Z. physik. Chem., Bodenstein Band, 817 (1931)], who concluded that the wall reaction is not very significant. Some preliminary measurements have been made at -79, 0 and 99° by surrounding 20-cm. lengths of the recombination tube with appropriate baths. The results indicate a small but seemingly definite positive temperature coefficient corresponding to an apparent energy of activation of about 900 calories.

There are several reasons for believing that this is further evidence for the existence of a wall reaction. Eyring's [THIS JOURNAL, **53**, 2537 (1931)] potential energy diagram for a three hydrogen atom system is to be interpreted as indicating a zero energy of activation for all possible gaseous trimolecular reactions involving hydrogen atoms and molecules. Reaction rates calculated with the use of kinetic theory diameters for the hydrogen atom and molecule, and assuming no energy of activation, yield reaction velocity constants that are only about half as large as the observed values and although the possibility of resonance interchange [Steiner, Z. physik. Chem., B15, 249 (1932)] could increase the effective collision diameters several fold, it seems doubtful that these diameters could be as large as would be demanded by the introduction of the activation factor  $e^{-900/RT}$ 

DEPARTMENT OF CHEMISTRY A. L. ROBINSON UNIVERSITY OF PITTSBURGH I. AMDUR\* PITTSBURGH, PENNSYLVANIA RECEIVED MAY 22, 1933 PUBLISHED JUNE 6, 1933 \* At present National Research Fellow in Chemistry at the Massachusetts Institute of Technology.

## SEPARATION OF THE ISOTOPIC FORMS OF WATER BY FRACTIONAL DISTILLATION

Sir:

With a twenty-foot fractionating column which has been shown to be equivalent to about forty theoretical plates [Henriques and Cornish, J. Phys. Chem., **37**, 397 (1933)], we have produced appreciable changes in the density of water by separation of the isotopes of hydrogen and oxygen. In our first experiment the ordinary isotopic composition was maintained at the bottom of the column. A stationary state was reached in two days, the water at the top showing a density diminished by 60 parts per million. In our second experiment the ordinary isotopic composition was maintained at the top of the column and samples were taken daily from the bottom. Conditions here were less satisfactory, owing to irregular flow. The density of the samples varied between 70 and 80 parts per million above ordinary water.

Even according to the first estimate [Lewis and Macdonald, J. Chem. *Phys.*, June (1933)] of the concentration of  $H^2$  in ordinary water, which we now believe to be altogether too high, the loss of all the  $H^2$  in the first experiment would cause a diminution in density of only 17 parts

#### New Books

per million. Assuming that the amount of  $O^{18}$  in ordinary water causes a density difference of 175 parts per million, these experiments indicate that the concentrations of  $O^{18}$  at the bottom and top of the column are nearly in the ratio 3 to 2, but do not show to what extent H<sup>2</sup> is concentrated. To answer this question Lewis and Macdonald are measuring the vapor pressure of water containing different amounts of H<sup>2</sup>. With water in which 66% of the hydrogen is H<sup>2</sup> the vapor pressure is below that of ordinary water by 3.5% at  $100^{\circ}$  and by 8.8% at  $25^{\circ}$ .

These large differences would at first sight indicate that large separation can be obtained by fractional distillation, but the system presents certain novel features. Consider the three species H<sup>1</sup>H<sup>1</sup>O, H<sup>1</sup>H<sup>2</sup>O and H<sup>2</sup>H<sup>2</sup>O. As a first approximation we assume that the three partial vapor pressures,  $p_{11}, p_{12}, p_{22}$ , are proportional to the mole fractions in the liquid,  $N_{11}, N_{12}, N_{22}$ , and further that there is a random distribution of the hydrogen atoms among the oxygen atoms so that  $p_{12}^2 = 4p_{11}p_{22}$  and  $N_{12}^2 = 4N_{11}N_{22}$ . It follows that if y is the atomic ratio of  $H^2$  to  $H^1$ , and the vapor pressures of pure H<sup>1</sup>H<sup>1</sup>O and H<sup>2</sup>H<sup>2</sup>O are  $a^2$  and  $b^2$ , then  $N_{11}: N_{12}: N_{22} = 1: 2y: y^2$  and  $p_{11}: p_{12}: p_{22} = a^2: 2aby: b^2y^2$ . Hence the equation for the total vapor pressure is  $P = (a + by)^2/(1 + y)^2$ . Or if x is the atomic fraction, y/(1 + y), then  $P^{1/2} = a - (a - b)x$ . It is not the vapor pressure, but its square root, that is a linear function of the atomic fraction. Similarly, if y' is the atomic ratio in the gas, y'/y = b/a (not  $b^2/a^2$ ). While, therefore, these calculations are not favorable to a large fractionation of the hydrogen isotopes at atmospheric pressure, it appears that fractional distillation under reduced pressure should be effective, and this experiment is now under way.

DEPARTMENT OF CHEMISTRY INSTITUTE OF EXPERIMENTAL BIOLOGY UNIVERSITY OF CALIFORNIA BERKELEY, CALIFORNIA RECEIVED MAY 22, 1933 PUBLISHED JUNE 6, 1933

### NEW BOOKS

Hommage a Henri Moissan, 4 Octobre 1931. Published by *Chimie et Industrie*, Société de Chimie Industrielle, 49 Rue des Mathurins, Paris VIII<sup>e</sup>, France, 1932. 93 pp. Illustrated.  $23 \times 28.5$  cm.

A monument and a plaque in memory of Henri Moissan were unveiled on October the 4th, 1931, at the Municipal College in Meaux. It was here that Moissan received his early education.

This volume contains an excellent account by Paul Lebeau of Moissan's life and scientific achievements, a bibliography of Moissan's publications, a description of the