

a negative carbon atom, with two unshared electrons, a condition similar to that supposed above for the aliphatic diazo compounds. Gibson suggests that ionization may have rendered the activity too fugitive to be observed. This indicates that active compounds of this type are difficult to isolate but, in the light of the evidence given above, is not conclusive against the possibility of such structures.

Summary

1. Amino-*d*-camphor, which had not previously been resolved, has been separated into two amines with specific rotations $[\alpha]_D$ 17.5 and 55.5°, respectively.

2. The diazocamphors prepared from the two amines were proved to be identical.

3. The theoretical aspect of this fact is discussed.

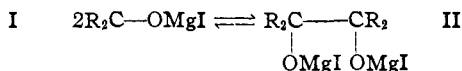
URBANA, ILLINOIS

COMMUNICATIONS TO THE EDITOR

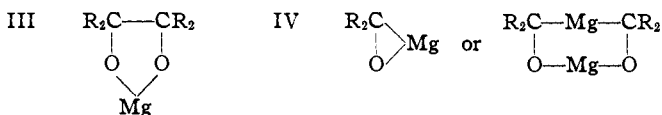
THE MECHANISM OF THE PINACOL SYNTHESIS BY THE SYSTEM $Mg + MgI_2$

Sir:

In a recent paper [THIS JOURNAL, **54**, 2112 (1932)] Bachmann criticizes adversely the arguments brought by Bergmann and Schuchardt [*Ann.*, **487**, 225 (1931)] in favor of their interpretation of the reduction of aromatic ketones by $Mg + MgI_2$. In the considerations advanced by Bachmann, there are two erroneous assumptions to which I intend to draw attention. In the first place, it is impossible to ascribe to the equation



more than only a formal meaning, because the ketyls—and the left-hand compound belongs, to all appearances, to the ketyls—are practically monomeric, as was pointed out by Schlenk and Thal [*Ber.*, **46**, 2840 (1913)]. In contrast to Bachmann's opinion, we are far from denying that the iodomagnesium pinacolate (II) is capable of dissociation into radicals, but we may almost deny that it is capable of existence in its dimeric form. It is very probable that molecules of the formula I can be formed, for instance by the action of a Grignard reagent on a pinacol, and come in equilibrium with the five-membered compound (III), but as it is impossible to obtain pinacols from the sodio-ketyls, we shall not make the "MgI-ketyls" responsible for the formation of the pinacols. In the paper criticized by Bachmann it was assumed, therefore, that the five-membered ring compound III is formed and, on hydrolysis, yields the pinacols.



Secondly, it is impossible to attribute the colors formed in the Gomberg-Bachmann reaction to the ketyl-like compound I. The colors observed are never those of the ketyls, but of the di-alkali or analogous compounds. In a great number of experiments we have verified this statement. When on addition of a Grignard reagent to the solution of a pinacol the color in question appears, we must conclude that by any means the compound IV is formed, for instance because it is very difficult to free a Grignard solution from finely divided magnesium. It is a well-known fact that not only the ketyls, but also the ketone disodium compounds, regenerate the ketones under the influence of oxygen in iodine. These reactions also, therefore, do not prove the formation of ketyls (I). I may believe that the mechanism proposed by Bergmann and Schuchardt for the excellent method of Gomberg and Bachmann is right.

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E. BERGMANN

RECEIVED JUNE 6, 1932
PUBLISHED SEPTEMBER 5, 1932

THE REDUCTION OF KETONES BY MAGNESIUM + MAGNESIUM IODIDE AND BY SODIUM

Sir:

In the preceding communication, E. Bergmann has presented a defense of his criticisms of the mechanism proposed by Gomberg and Bachmann, according to which reduction of ketones by $\text{Mg} + \text{MgI}_2$ to pinacols involves the intermediate formation of iodomagnesium ketyls, $\text{R}_2\text{C}-\text{OMgI}$. He insists that a vast difference exists between the sodium ketyls and our proposed equilibrium system, $2 \text{R}_2\text{C}-\text{OMgI} \rightleftharpoons \text{R}_2\text{C}(\text{OMgI})(\text{IMgO})\text{CR}_2$; and he concludes that we cannot be dealing with iodomagnesium pinacolates in equilibrium with a very small amount of iodomagnesium ketyls because ketyls are practically monomolecular.

I shall not stop now to point out why Professor Bergmann has arrived at erroneous conclusions, although the reasons are indicated partly in what follows. At this time I wish to say only that in a communication which will appear shortly in *THIS JOURNAL*, I shall present experimental evidence which will show definitely not only that our interpretation with respect to the magnesium compounds is correct, but also that the corresponding sodium compounds are like the magnesium derivatives. To be more specific, in the reaction between sodium and aromatic ketones, the sodium ketyl radicals persist as such *to a small extent only*, so that there

exists at the end of the reaction an equilibrium mixture of sodium ketyl and sodium pinacolate



in which the equilibrium is preponderantly in favor of the *right-hand* side of the formulation. In other words, the products obtained by addition of sodium to aromatic ketones are *not radicals existing in the monomolecular state, as has been commonly supposed for nearly twenty years*, but consist for the most part of the *dimolecular form*, namely, sodium pinacolate.

In addition, the forthcoming publication will point out the reason why Schlenk, E. Bergmann and others were misled in interpreting as they did the reaction and the structure of the compounds.

CHEMISTRY LABORATORY
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W. E. BACHMANN

RECEIVED JUNE 11, 1932
PUBLISHED SEPTEMBER 5, 1932

THE ELECTRODEPOSITION OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

Sir:

The possibility of the electrodeposition of molybdenum and tungsten from aqueous solutions is suggested by their position below hydrogen in the electromotive series. Acidic solutions of these elements in various valence states may be prepared with citric acid, glucose or other hydroxyl compounds. Since the procedure for the electrodeposition of molybdenum and tungsten should resemble to a certain extent the methods applicable to chromium, some studies were first made using solutions of trivalent chromium salts and citric acid.

Britton and Westcott [*Trans. Faraday Soc.*, **27**, 809 (1931)] have suggested, subsequent to the completion of these experiments, that chromium may be deposited from solutions containing chromium in the form of complexes with organic acids.

The following procedure was found to give bright, adherent deposits of chromium: 2 g. of hydrated chromic chloride and 4 cc. of 2.5 *M* monopotassium citrate solution are diluted in 20 cc., heated to boiling and cooled. A carbon anode is contained in a porous cup and a sheet of copper serves as cathode. Metal is deposited at a current density of 3 amp. per sq. dm. and a voltage drop of 4.5 to 7.5 volts. Too high current density and voltage will cause the deposition of black powder. Chromium was also deposited from a bath in which tartaric acid was employed.

Molybdenum may be deposited from an acid solution: 2 g. of molybdic acid and 15 cc. of 34% hydrobromic acid are evaporated almost to dryness. The dark red-brown residue is dissolved in 6 cc. of 2.5 *M* dipotassium citrate

and diluted to 20 cc. After neutralizing with potassium hydroxide, 1 cc. of 2.5 *M* citric acid is added. A current density three or four times greater than for chromium is used. Tartaric acid and glycerol were substituted for citric acid with less satisfactory results. Molybdenum has also been deposited from solutions of molybdic acid in citric and tartaric acids, but the results have also been less satisfactory.

Tungsten has been deposited from aqueous media [Fink and Jones, *Trans. Am. Electrochem. Soc.*, **59**, 461 (1931)] of alkaline nature. It may also be deposited from acid solutions in bright coherent form. Two grams of tungstic acid is dissolved in potassium hydroxide, 5 cc. of 2.5 *M* citric acid is added, then potassium hydroxide to neutrality and 1 cc. of 2.5 *M* citric acid. The solution is diluted to 20 cc. A platinum foil (5 sq. cm.) is the anode and a copper sheet is used as cathode. Similar results may be obtained if sodium hydroxide and tartaric acid are substituted for potassium hydroxide and citric acid, respectively. Tungsten may also be obtained from solutions containing acetic acid and glycerol or glucose.

Work now in progress has shown the possibility of the electrodeposition of columbium and tantalum by similar methods.

More complete data as to optimum conditions of procedure, current efficiencies and the properties of the deposits will be published at a later date.

DEPARTMENT OF CHEMISTRY
ST. LOUIS UNIVERSITY
ST. LOUIS, MISSOURI
RECEIVED JULY 5, 1932
PUBLISHED SEPTEMBER 5, 1932

L. F. YNTEMA

THE DISSOCIATION CONSTANT OF ACETIC ACID

Sir:

The new conductivity measurements on acetic acid of MacInnes and Shedlovsky [MacInnes and Shedlovsky, *THIS JOURNAL*, **54**, 1429 (1932)] lead to a dissociation constant that falls off rapidly at concentrations above 0.01 *N*, and the authors are inclined to attribute the effect to a change in the dielectric constant of the solvent. This seems unlikely, if only because such a change would affect both the mobilities and the activity coefficients of the ions, and the resultant effect upon *K* would be extremely small. On the other hand, there are good grounds for thinking that a viscosity correction of some sort should be applied to data such as these, and I have accordingly recalculated the degree of dissociation using the simple viscosity correction, *i. e.*, by employing in place of Λ the value $\Delta\eta/\eta_0$; values for the relative viscosity were taken from "International Critical Tables," Vol. V, p. 20. The results are reproduced in the figure, where the open circles represent the viscosity corrected values, the solid dots are

MacInnes and Shedlovsky's points, and the line e' is their "theoretical" line.

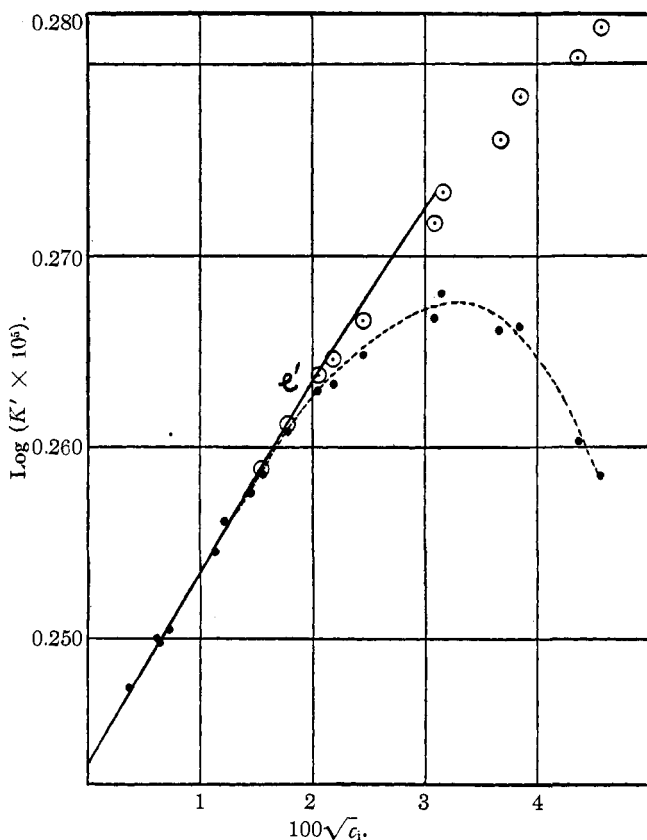


Fig. 1.—○, Viscosity-corrected value; ●, uncorrected values.

It appears that, at the concentrations considered, the mass action expression $f_{\pm}^2 \Lambda^2 c / f_{\pm} \Lambda_x (\Lambda_x - \Lambda)$ will give constant values, provided that Λ is a viscosity-corrected conductivity.

BATTERSEA POLYTECHNIC
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CECIL W. DAVIES

RECEIVED JULY 5, 1932
PUBLISHED SEPTEMBER 5, 1932

DERIVATIVES OF DIOXANE

Sir:

In view of the recent article by Butler and Cretcher [THIS JOURNAL, 54, 2987 (1932)] a brief preliminary report of work now completed in this Laboratory seems desirable. We have obtained the symmetrical tetra-

chlorodioxanes described by Butler and Cretcher and have confirmed their findings. In addition, we have obtained several new derivatives. The dichlorodioxane reacts with the Grignard reagent to produce disubstituted dioxanes. As an example, 2,3-diphenyldioxane (m. p. 49°) was prepared and its structure established. This reaction should be a general method of preparing the homologs of dioxane. We are now extending it to the symmetrical tetrachlorodioxanes. Catechol reacts with dichlorodioxane to give a derivative similar to 1,4,5,8-naphthodioxane [Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931)]. Only one isomer could be isolated. The evidence is inconclusive regarding the *cis-trans* isomers which Böeseken reported in this class of compounds. We expect to submit evidence in the near future on this point.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED JULY 14, 1932
PUBLISHED SEPTEMBER 5, 1932

ROBERT K. SUMMERBELL
ROBERT CHRIST

THE DECOMPOSITION OF DIETHYL ETHER AT LOW PRESSURES

Sir:

We have made experiments on the decomposition of diethyl ether at 525° with initial pressures ranging from about 0.15 mm. to 200 mm. and at 462° with initial pressures ranging from about 0.8 mm. to 450 mm. These experiments have been made in a Pyrex vessel immersed in a salt-bath the temperature of which can be controlled within 0.1°, using ether which had been dried over sodium and purified by distillation in vacuum. Runs have also been made with a bulb packed with Pyrex tubing in order to test the homogeneity of the reaction. At the lower pressures it is necessary to correct the runs with packed bulbs for gas, probably water vapor, which is continuously distilled out of the apparatus, whether the ether is there or not; when this is done it appears that the reaction is homogeneous throughout the pressure ranges reported. The results have been compared with the results previously obtained by Hinshelwood [*Proc. Roy. Soc. (London)*, **A114**, 84 (1927)] in the more limited range of pressures in which he worked. Our rates at 525° are somewhat faster, corresponding to a difference in the absolute temperature scale of about 7°; our activation energy is about 60,000 calories compared to Hinshelwood's 53,000; the cause of these discrepancies is not clear. It will be seen that this means that we agree, roughly, with Hinshelwood, and with Steacie [*J. Phys. Chem.*, **36**, 1562 (1932)] at the lower temperature.

When we plot the logarithm of the rate constant against the logarithm of the pressure, we get a curve which does not fall off nearly as fast in the lower pressure region as one would expect on the basis of the usual theory.

In fact, it appears to have a very slight concave upward curvature. This suggests, though we cannot be quite certain, that it is approaching a second unimolecular region at low pressures, a possibility previously discussed by one of us [*Z. physik. Chem.*, B7, 226 (1930)]. The temperature coefficient appears to be slightly greater at the lower pressures. We hope to be able to give a more thorough discussion of these phenomena at a later time, when the experimental results will also be presented in full.

It may be well to note that we have verified the effect of hydrogen in increasing the reaction rate. It appears to have the same effect within the limit of error—which is rather large in the presence of excess hydrogen—at the two temperatures, a point which is of some importance in connection with the question of whether hydrogen is really an inert gas, or whether its effect is due to reaction with the ether. We see no reason at present to believe that it is not inert, as far as the decomposition of the ether is concerned—it may, of course, react with the products of the decomposition.

CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

O. K. RICE
D. V. SICKMAN

RECEIVED JULY 12, 1932
PUBLISHED SEPTEMBER 5, 1932

ACTIVITY COEFFICIENTS OF BARIUM CHLORIDE

Sir:

In a communication from the Laboratory of Yale University [Harned and Nims, *THIS JOURNAL*, 54, 423 (1932)], it was presented that the evidence obtained indicates a maximum in the activity coefficient-temperature curve for sodium chloride. Direct confirmation of this phenomenon was lacking, however.

Studies in progress at this Laboratory on the activity coefficients of barium chloride from electromotive force data at different temperatures indicate that this phenomenon certainly exists for barium chloride.

Electromotive forces have been measured very satisfactorily using barium amalgam cells of special construction. Activity coefficients calculated from the data at 0 and 45° coincide fairly closely while those at 25° are appreciably higher for the same concentration.

With complete electromotive force data the heats of dilution may be calculated. When experimental work has been completed the data will be submitted for publication.

DEPARTMENT OF CHEMISTRY
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ROY F. NEWTON
EMERSON A. TIPPETTS

RECEIVED JULY 23, 1932
PUBLISHED SEPTEMBER 5, 1932

INFLUENCE OF GASEOUS THERMAL DIFFUSION ON EQUILIBRIUM MEASUREMENTS ON THE Fe-O-H SYSTEM

Sir:

In a previous publication [THIS JOURNAL, 52, 4268 (1930)] the authors have pointed out that equilibrium constants for the reaction $\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$ reported by various authors [see Eastman and Evans, THIS JOURNAL, 46, 888 (1924)] for static systems are about 40% higher than those obtained by a flow system. Furthermore, the flow system values are in good agreement with the constants calculated indirectly with the help of known Fe-C-O equilibrium data and equilibrium constants for the reaction $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$. Up to the present no conclusive explanation of the cause of the discrepancy has been presented. It is the purpose of the present letter to point out a source of error that seems to explain the high $\text{H}_2\text{O}-\text{H}_2$ ratio obtained in previous static experiments for both the Fe-H-O system and other metal-metallic oxide systems such as Sn-SnO₂.

It has long been recognized [S. Chapman, *Phil. Trans. Roy. Soc.*, 217A, 115-147 (1918)] that if a mixture of two gases of different molecular weights such as $\text{H}_2\text{O}-\text{H}_2$ or CO_2-H_2 is placed in a tube one end of which is hot and the other cold, the ratio of the heavy gas to the lighter gas will rapidly become and remain larger in the cold portion of the tube than in the hot portion because of thermal diffusion. The purely static experiments on Fe-H₂O-FeO-H₂, SnO₂-H₂-Sn-H₂O or similar equilibria permit this diffusion factor to come into play; the $\text{H}_2\text{O}-\text{H}_2$ ratios obtained in such experiments are always those existing in the part of the apparatus that is at about room temperature and not necessarily in the hot part of the reaction tube. Accordingly $\text{H}_2\text{O}-\text{H}_2$ ratios determined in static experiments for heterogeneous equilibria will in general be higher than the true steam-hydrogen ratios existing in the hot end of the reaction tube in contact with the metal-metal oxide sample, unless some continuous and rapid circulation of the gas mixture is effected.

Preliminary calculations of the maximum difference in the "hot end" and "cold end" $\text{H}_2\text{O}-\text{H}_2$ ratios for the temperature differences existing in the above equilibrium experiments have been made using formulas developed by Chapman (*loc. cit.*). The results indicate that the thermal diffusion factor may easily account for the observed high $\text{H}_2\text{O}-\text{H}_2$ values of the static experiments. To establish definitely that at least in the case of the Fe-H-O system thermal diffusion actually does account for the high $\text{H}_2\text{O}-\text{H}_2$ values, the authors have set up a standard Deville type static apparatus and arranged to analyze samples of the steam-hydrogen mixture taken by a quartz capillary from the hot part of the reaction tube adjacent to the Fe-FeO or FeO-Fe₃O₄ samples. Simultaneously the usual "cold end" steam-hydrogen ratios were determined by observing the total pressure in the system and the temperature of the water thermostat regulating the

vapor pressure of water in the cold part of the apparatus. The average results obtained for the Fe-H-O system may be summarized as follows:

Furnace temp., °C.	Solid phases	Steam-hydrogen ratio			
		In "cold end" (by pressure readings)	In "hot end" by analysis	In static expts. of Eastman and Evans	In flow expts. of Emmett and Shultz
700	Fe-FeO	0.57	0.41	0.584	0.422
800	Fe-FeO	.71	.48	.706	.499
900	Fe-FeO	.82	.55	.822	.594
1000	Fe-FeO	.97	.67	.937	.669
700	FeO-Fe ₃ O ₄	1.50	1.19	1.45	1.181
800	FeO-Fe ₃ O ₄	3.18	2.35	2.98	2.372

The obvious agreement between the "cold end" values (column 3) and the previous static results (column 5) on the one hand, and the "hot end" analysis (column 4) and the previous flow results (column 6) on the other, seems to show definitely that the principal cause of discrepancy between the various steam equilibrium constants for the Fe-H-O system is the factor of thermal diffusion. Since the magnitude of the steam-hydrogen ratios in the Sn-H₂O-H₂-SnO₂ system is about the same as for the Fe-FeO-H₂O-H₂ system, it is evident that the same diffusion factor will also account for the static experiments on the Sn-H-O system in which the steam-hydrogen equilibrium ratios are apparently about 40% high [THIS JOURNAL, 50, 1106 (1928)].

BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

P. H. EMMETT
J. F. SHULTZ

RECEIVED JULY 25, 1932
PUBLISHED SEPTEMBER 5, 1932

A FILM WHICH ADSORBS ATOMIC H AND DOES NOT ADSORB H₂

Sir:

We report the following brief study, which we shall discontinue for the present, because of its bearing on the subject of "activated adsorption."

A lamp had two pure tungsten filaments and one filament of Elinvar wire which contained 35% nickel and 12% chromium, the remainder being probably iron. The lamp was sealed to a vacuum system having liquid-air traps, and the Elinvar filament heated to a bright red heat in vacuum for fifteen minutes. The amount of metal thus evaporated was too small to be visible on the walls or to produce a change in resistance of the wire. Pure hydrogen was then admitted at a pressure of 0.250 mm. and one of the tungsten filaments was lighted at 2700°K., at which temperature 3.5% of the hydrogen molecules which strike a tungsten surface are dissociated. The hydrogen disappeared at an exponential rate, decreasing from 210 cu. mm. to 170 cu. mm. in 6.5 minutes.

The lamp was next evacuated and torched at about 450° for ten minutes,

during which time water vapor given off by the glass walls presumably oxidized the metallic deposit. A second clean-up run then showed a much more rapid disappearance from 210 cu. mm. to 35 cu. mm. in 2.5 minutes, with log pressure varying linearly with time. The evaporation of a fresh film from the Elinvar wire, covering up previous films, always reduced the rate of clean-up to a low value, and subsequent torching of the tube restored the high value. In one run enough hydrogen disappeared in the film to form a layer 20 atoms deep while the rate of clean-up remained undiminished.

When the tungsten filament was turned off the pressure started immediately to rise. In one experiment 10% of the adsorbed hydrogen reappeared in ten minutes at 25°, and 90% in two minutes at 450°. Owing to this tendency of the gas to leave the film at a slow rate, the net rate of disappearance diminished markedly as the pressure fell below 0.020 mm. If the lamp was cooled in liquid air, the clean-up stopped instantly, showing that the catalytic effect of the cold film caused recombination of all impinging atoms. If H was adsorbed at 25° and the lamp then cooled in liquid air, there was no escape of hydrogen on turning off the filament. It is known that hydrogen evaporates as atoms from glass surfaces at 25° but recombines on cold glass, so it probably diffused as atoms to the deeper layers of our film at 25°. The film never showed any tendency to adsorb molecular hydrogen.

The recombination of atomic hydrogen at a *tungsten* surface is promoted by cooling the lamp in liquid air, due probably to the removal of water vapor. The H generated by a filament at 2700°K. delivered 0.63 watt to a neighboring tungsten filament with the lamp at 25°, and 1.48 watts with the lamp in liquid air, although cold walls lower the concentration of H in the gas phase by catalyzing recombination.

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

RECEIVED AUGUST 10, 1932
PUBLISHED SEPTEMBER 5, 1932

KATHERINE B. BLODGETT
IRVING LANGMUIR

NEW BOOKS

The Life and Work of Charles James, 1880-1928. Edited by WALTER C. SCHUMB, HAROLD A. IDDLIS, LYMAN C. NEWELL and AVERY A. ASHDOWN. Published by the Northeastern Section of the American Chemical Society, A. A. Ashdown, Custodian, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1932. 26 pp. Illustrated. 15.5 × 23.5 cm. Price, \$0.50.

This memorial volume to Charles James contains, first, the Resolutions passed by the Northeastern Section on the occasion of his death; second, three essays, one on Charles James, the Man, by Melvin M. Smith, one on Charles James, the Teacher, by Lester A. Pratt, and one on Charles James,