lowed by acetylation and treatment with sodium bicarbonate then gives D-*erythro*-triacetoxy-1-nitropentene-1, the key compound for the desose synthesis, in 45% yield.

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RECEIVED APRIL 4, 1949

REVISION OF THE PARACHOR

Sir:

The author[1] has recently advanced an interpretation of Sugden's parachor. In view of the observation of Ferguson and Kennedy[2] that the index of Macleod's equation[3] is sensibly different from 4, the need for a revision of the parachor[4] arises.

Sugden's method of testing Macleod's equation is misleading as large variations in C appear small by comparing the fourth roots of C. In attempting to show that $C^{1/4}$ is nearly constant over wide temperature intervals, Sugden[5] attributes deviations to experimental errors. A graphical or algebraic test would have shown that the experimental results are satisfactory, justifying the modification of Macleod's equation as suggested by Ferguson and Kennedy which is observed by the present author to be applicable right up to the critical temperature. Carbon dioxide, for instance, obeys it up to even 1° below the critical temperature. Further, the so-called associated liquids, methyl, ethyl and *n*-propyl alcohols and acetic acid obey this modified equation remarkably well at all temperatures. The substances ordinarily occurring as gases cited in Table I serve to supplement the observations of Ferguson and Kennedy, the data being taken from the "Int. Crit. Tables."[6]

Since p is not the same for all substances, $MC^{1/4} = P$ has no natural significance. Hence, Ferguson and Kennedy[2] proposed to express the parachor in the revised form $P_r = MC^{1/p}$. But, unfortunately, their paper has not attracted the attention which it deserves. Sugden[5] has stated that the parachors of lower alcohols and acids steadily increase with temperature. This anomaly disappears on taking the revised parachors. The theory postulated by Sidgwick[7] to account for the so-called parachor anomaly of associated liquids is, therefore, unnecessary.

TABLE I

Substance	C	p
Acetic acid	23.28	3.716
Carbon dioxide	9.736	3.857
Carbon monoxide	24.85	4.343
Ethyl alcohol	55.69	3.774
Methyl alcohol	54.91	3.792
Nitrogen	20.31	3.887
Oxygen	7.683	4.053
n-Propyl alcohol	50.84	3.465

Further work on the investigation whether or not the revised parachor can eliminate the parachor anomalies is desirable, but it is too laborious and time-consuming for any individual worker. It would be a good idea to have a group of experts working on a coöperative basis and as such the forthcoming meeting of the International Union of Pure and Applied Chemistry should provide the necessary opportunity for taking up this work.

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RECEIVED APRIL 13, 1949

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(1) M. S. Telang, THIS JOURNAL, **71**, 1883 (1949).

(2) A. Ferguson and S. J. Kennedy, *Trans. Faraday Soc.*, **32**, 1474 (1936).

(3) D. B. Macleod, *ibid.*, **19**, 38 (1923).

(4) S. Sugden, "The Parachor and Valency," Routledge, London, 1930, p. 30.

(5) S. Sugden, *J. Chem. Soc.*, **125**, 32 (1924); "The Parachor and Valency," p. 26.

(6) In Sugden's paper,[5] for benzene at 280°, $(D - d)$ has been wrongly taken as 0.2305 instead of 0.2854; consequently, $C^{1/4}$ has suddenly shot up.

(7) N. V. Sidgwick and N. S. Bayliss, *J. Chem. Soc.*, 2033 (1930).

INHIBITION OF UREASE

Sir:

In a recent publication Niemann and Harmon[1] showed that the enzyme urease is inhibited by phosphate ions, this inhibition being competitive with the substrate, urea. Following upon the finding of Lumry[2] that sulfite inhibits urease and that this inhibition is responsible for the "abnormal" temperature dependence of reaction rates in the urea-urease systems,[3] we have studied the inhibition by sulfite in detail.

Working with high concentrations of urea, at which the rate is zero order in urea, we find that this inhibition is first order in sulfite and in enzyme. It appears that both the sulfite and bisulfite ions are equally effective in causing inhibition, the equilibrium constant being inversely proportional, however, to hydrogen ion concentration. The data definitely do not fit the hypothesis that bisulfite ions alone are the cause of inhibition, as evidenced by Table I. The heat

TABLE I

Temperature 8.5°

pH	A_0 (original activity)	A (inhibited activity)	K $\frac{(A_0 - A)}{(A)(HSO_3^-)}$	K' $\frac{(A_0 - A)}{(A)\text{ (total sulfite)}(H^+)}$
6.20	3.5	0.77	63	10.4×10^7
6.50	4.8	1.3	38	8.9×10^7
6.93	6.5	2.9	23	10.5×10^7
7.12	7.4	3.4	14	8.4×10^7
7.55	7.2	3.8	10	7.9×10^7
			Av.	9.2×10^7

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(1) Niemann and Harmon, *J. Biol. Chem.*, **177**, 601 (1949).

(2) Kistiakowsky and Lumry, THIS JOURNAL, **71**, in press (1949).

(3) Sizer, *J. Biol. Chem.*, **132**, 209 (1940).

of this reaction is 11,000 cal./mole of active centers of the enzyme and is independent of the *p*H. This value differs considerably from that estimated by Kistiakowsky and Lumry, and is more accurate because of a more direct method of determination and a greatly improved reproducibility of measurements. The inhibition by sulfite, similarly to the inhibition by phosphate ions described by Niemann and Harmon, has been found to be competitive with urea.

We also find that certain organic sulfur compounds, such as sodium benzene sulfinate, inhibit the enzyme in the same manner as sulfite ions, and our experiments in this direction are continuing.

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RECEIVED APRIL 21, 1949

MANGANESE CARBONYL

Sir:

The synthesis of volatile manganese compounds, believed to be carbonyls of manganese, has been accomplished by reducing manganese iodide with Grignard reagent under pressure of carbon monoxide. The general reaction technique has been that described for the preparation of chromium carbonyl by Owen, English, Cassidy and Dundon.[1]

Identification of the volatile manganese compounds as carbonyls has been made by the observation that they behave chemically as would be predicted from a consideration of their relation to the carbonyls of iron and cobalt, and by mass spectrometric analyses which show characteristic peaks predicted for manganese carbonyl.

Qualitative tests for manganese in distillation fractions, etc., have been made by decomposing the samples with nitric acid and developing the permanganate color with the highly specific persulfate test.

The ethereal solutions from the synthesis reactions have been subjected to repeated washings with dilute hydrochloric acid and distilled water to remove manganese halide, and unreacted manganese iodide, and to destroy any organomanganese compounds possibly formed in the reaction. Tests for halogen in these washed solutions have been negative. The solutions then have been dried, and the solvent ether removed by evaporation at low temperatures on a vacuum line. Some volatile manganese generally distills with the ether and may be collected in a trap at −80°. Less volatile ether-soluble manganese compounds remain in the residue. The compounds also are soluble in *n*-pentane.

Manganese is extracted from an ether solution of manganese carbonyl by aqueous alkali. Acidification of the resulting solution in a stream of carbon monoxide releases a volatile manganese compound which can be collected in a subsequent trap at −80°. This may be the $Mn(CO)_4H_3$ which has been predicted.[2]

The addition of mercuric chloride to an ethereal solution of manganese carbonyl results in a slow evolution of gas and a precipitate containing manganese and mercury. Heating the dried precipitate liberates free mercury, leaving a residue containing manganese. This behavior is consistent for a mercuric salt of manganese carbonyl hydride.

The peaks observed for manganese carbonyl in the mass spectrometer are strong, occur at regular intervals following a pattern similar to that of other metal carbonyls, and do not correspond to any of the predictable impurities The observation of the fragments $Mn_2(CO)_5^+$, $Mn_2(CO)_6^+$ and $Mn_2(CO)_7^+$, formed in the spectrometer by electron bombardment, indicates the existence of a dimeric manganese carbonyl but does not define the formula since it is not uncommon for the parent peak to be absent in a mass spectrometric analysis. Peaks corresponding to Mn^+, MnC^+, $MnCO^+$, $MnC(CO)^+$, $Mn(CO)_2^+$, $MnC(CO)_2^+$, $Mn(CO)_3^+$, and $MnC(CO)_3^+$ also have been observed. The appearance of the intermediate fragments containing C atoms is typical of the mass spectra of all metal carbonyls investigated so far and will be reported later.

Transparent crystals (containing manganese) have been isolated by subliming solvent-free material in a stream of carbon monoxide. The quantity of material has been small and no pure compounds have been identified as yet.

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RECEIVED APRIL 22, 1949

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(1) B. B. Owen, *et al.*, THIS JOURNAL, **69**, 1723 (1947).

(2) Blanchard. *Chem. Rev.*, **21**, 35 (1937).