Fig. 1.

is saturated and there is formed the corresponding isopropyl grouping. It is of interest to see whether evidences of this chemical change can be observed in the infrared spectra.

In the 3.4-micron region (C–H vibrations) the hydrogenation results in a filling-in and general strengthening of the absorption envelope. The rock-salt prism resolution does not suffice to resolve any of the individual bands of the dihydrorotenone spectrum in this region, but the spectrum of rotenone does show a minimum at about 3.23 microns which is probably associated with the terminal methylene group.[6,7] An overtone which is shown by Colthup in the vicinity of 5.63 microns is not observed for rotenone, and there are no observed differences in the spectra in the 5.4–6.8 micron (double-bond) range, but differences in the latter region may well be obscured by overlapping C=O absorption or by the lessened accuracy caused by strong solvent absorption. Dihydrorotenone alone has a weak minimum at 7.21 microns which may be associated with the isopropyl group. The greatest differences in absorptivity appear in the 9.5 to 11.0 micron range. Rotenone has relatively strong absorption at about 11.0 microns, which falls within the range given by Colthup for a strong characteristic absorption of the vinyl group. Dihydrorotenone has relatively strong absorption at about 10.2 microns, at the short wave length end of the range given by Colthup for a weak characteristic absorption of the isopropyl group.

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(6) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

(7) E. L. Saier and N. D. Coggeshall, *Anal. Chem.*, **20**, 812 (1948).

The Hammett Acidity Function in 6 Formal Perchloric Acid–Sodium Perchlorate Mixtures

BY GARMAN HARBOTTLE[1]

Hammett[2] has defined an acidity function H_0 by the equation

$$H_0 = -\log (a_{H^+} f_B / f_{BH^+})$$

in which a_{H^+} is the activity of hydrogen ion and f_B and f_{BH^+} are the activity coefficients of a neutral base B and its conjugate acid BH^+, respectively. The quantity H_0 may be estimated, for a particular solution, by colorimetric measurements of the degree of conversion of certain indicator bases to their conjugate acids. The technique has been described by Hammett and Deyrup.[3]

The acidities H_0 of aqueous solutions of several acids have been reported in detail by Hammett and Paul[4] and Hammett and Deyrup.[3] In this note values of the acidity function in mixed perchloric acid–sodium perchlorate solutions of constant ionic strength 6.0 formal (moles solute per liter solution) are reported.

Experimental

Three indicators were used in these measurements. The compounds, and the logarithmic acidity constants of their conjugate acids, as reported by Hammett[3] were o-nitroaniline (pK_a −0.19), p-chloronitroaniline (pK_a −0.91) and 2,4-dichloro-6-nitroaniline (pK_a −3.18). The first two indicators were purchased from Eastman Kodak Co. while the third was prepared from the second by chlorination accord-

(1) Brookhaven National Laboratory, Upton, New York.

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 266–267.

(3) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

(4) L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

ing to the method of Witt.[5] The first indicator was recrystallized from alcohol, the second from water, and the third from mixed alcohol–acetone. Rough determinations of the melting points gave values in approximate agreement with those reported by Hammett and Deyrup.[3]

The source and purity of the sodium perchlorate and perchloric acid have been reported elsewhere.[6] The mixtures studied were prepared by the dilution of stock solutions of known concentration.

The colorimetric measurements were carried out with a Leitz photoelectric colorimeter: since the indicators had a yellow color in the basic form, and were colorless in the acidic form, a filter of blue tint was employed. A solution 6.0 formal in sodium perchlorate, in which the indicators were entirely converted to the basic form, was employed as a reference, and mixtures of perchloric acid and sodium perchlorate and the identical quantity of indicator were compared to this reference solution. All studies were made at room temperature (25 ± 2°).

Results

The results, calculated using the pK_a values given by Hammett[2] for the various indicators, are presented in the following table.

DETERMINATION OF H_0 FOR PERCHLORIC ACID–SODIUM PERCHLORATE MIXTURES OF CONSTANT IONIC STRENGTH 6.0 FORMAL

Perchloric acid, F	Sodium perchlorate, F	The quantity 2,4-Dichloro-6-nitro-aniline	$-H_0$ determined with p-Chloro-nitro-aniline	o-Nitro-aniline	$-H_0$, best value
6	0	2.91	2.93		2.92
5	1	2.66	2.63		2.64
4	2	2.37	2.32		2.34
3	3	(2.14)	2.01		2.0
2	4	(1.90)	1.72	1.73	1.72
1	5	(1.59)	1.31	1.39	1.35
0.5	5.5		0.98	1.02	1.00
0.3	5.7		0.72	0.76	0.74

Parentheses indicate determinations of $-H_0$ of lower accuracy resulting from the necessity of measuring a small difference when a large proportion of the indicator is in the basic form.

The results may be compared with those of Hammett and Deyrup[3] for pure perchloric acid 6.0 formal (about 8.4 molar) by interpolation from their data. The figure obtained, when corrected for a change in the zero-point of the H_0 scale[4] is -2.77, which is somewhat lower than the value of -2.92 reported above. The disagreement is not considered serious, since different lots of indicators, different instrumental techniques and reagents were employed.

The author wishes to thank Professor J. J. Beaver for the use of his photoelectric colorimeter, and Professor L. P. Hammett for discussions of the method.

(5) Witt, Ber., **8**, 820 (1875).

(6) G. Harbottle and R. W. Dodson, THIS JOURNAL, **73**, 2442 (1951).

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On the Freezing Point Diagram of the Germanium–Manganese System

BY JAMES H. DOWNING AND DANIEL CUBICCIOTTI

In the present attempt to determine the freezing point diagram of the germanium–manganese system no suitable thermocouple protection tube was found for melts containing more than 32 atom per cent. manganese. Therefore, the results are fragmentary.

The freezing points were determined with a chromel–alumel thermocouple in an Alundum protection tube. An alundum crucible was used to hold the melt. The entire system was contained in a porcelain tube filled with helium to prevent attack by air. The manganese had a tendency to attack the Alundum protection tube. The attack by mixtures containing more than 32 atom per cent. manganese was too great to consider the results reliable.

Germanium metal, C.P., and manganese metal, 99.9%, were obtained from the A. D. Mackay Co., New York. The freezing point observed for the germanium, 957°, agreed well with the value of 959° given by Kelley.[1]

The results obtained are given in Fig. 1. The curve indicates the temperatures, for each composition, at which a solid, almost pure germanium, began to precipitate. Since the eutectic halt was observed at 5% manganese, the solid precipitating was almost pure germanium, containing less than 5% manganese at 720°.
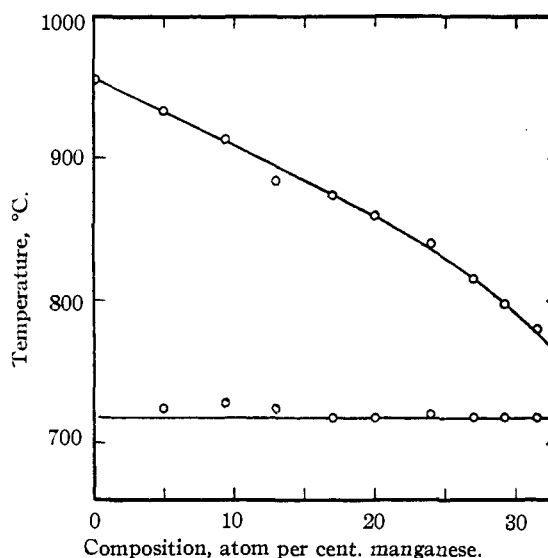

Fig. 1.—The freezing point diagram of the germanium–manganese system.

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(1) K. K. Kelley, Bur. Mines Bull. No. 393 (1936).

DEPARTMENT OF CHEMISTRY
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Optical Rotation of Peptides. III. Lysine Dipeptides[1]

BY BERNARD F. ERLANGER AND ERWIN BRAND

The first two papers in this series dealt with glycine and alanine dipeptides[2] and tripeptides.[3] In

(1) This report is part of a dissertation submitted by Bernard F. Erlanger in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. Presented in part before the Division of Biological Chemistry at the 118th Meeting of the A. C. S., Chicago, Ill., September, 1950.

(2) Erlanger and Brand, THIS JOURNAL, **73**, 3508 (1951).

(3) Brand, Erlanger, Sachs and Polatnick, ibid., **73**, 3510 (1951).